

Rheology, Adhesion, and Debonding Mechanisms in Fluorosilicone Polymer Gels

Nicholas B. Wyatt,¹ Anne M. Grillet²

¹Materials Science and Engineering Division, Sandia National Laboratories, P.O. Box 5800, MS - 0958, Albuquerque, New Mexico 87185

²Engineering Sciences Division, Sandia National Laboratories, P.O. Box 5800, MS - 0346, Albuquerque, New Mexico 87185

Correspondence to: N. B. Wyatt (E-mail: nbwyatt@sandia.gov)

ABSTRACT: Polymer gels are complex materials used in myriad applications and industries including foods, consumer products, and adhesives. We examine the rheology and adhesion characteristics of three fluorosilicone gels of varying equilibrium modulus. Adhesion is studied in terms of confinement and separation velocity or initial strain rate. Further, the role of debonding mechanism on the adhesion properties is also elucidated. At low initial strain rates or low degrees of confinement, interfacial failure dominates while at high initial strain rates or high degrees of confinement bulk cavitation is the dominant debonding mechanism. We also report for the first time a transition region where both interfacial failure and bulk cavitation are observed. The adhesion results are explained in light of the rheological properties of the gels examined. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40034.

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INTRODUCTION

Polymer gels are physically or chemically crosslinked networks of polymers which are swollen in a liquid.¹ The network structure is formed by the polymer chains that are bound together either chemically (covalent bonds) or physically (entanglements). The resulting structure of the gel network is dictated by the composition as well as the kinetics of the reactions that form it.² The material properties of a polymer gel are determined, in large part, by the structure of the gel network. The swelling liquid (or sol) is composed of other molecules (e.g., solvent, short chain polymers, entangled polymer chains, etc.) that are not bound into the network. The contribution of the sol to the polymer gel material properties varies depending on the nature of the sol. For example, a sol comprised of a low viscosity Newtonian liquid will have a very different contribution to material properties than a sol comprised of an entangled polymer solution. By manipulating the microstructure and composition of a polymer gel, a wide variety of material properties ranging from hard rubbery plastics to soft hydrogels can be obtained.

The wide range of material properties accessible through manipulation of the gel microstructure and composition has resulted in polymer gels being employed in diverse applications ranging from food^{3,4} and drug delivery⁵ to adhesives⁶ and consumer products.⁷ Silicone-based polymer gels have found wide application in consumer products ranging from medical implants and

treatments^{8,9} to cooking utensils. Polymer gels have also found application as adhesives in sophisticated technologies such as nanotechnology, microelectronics, and biotechnology.¹⁰ Given the myriad applications and uses for polymer gels, a sound understanding of polymer gel material properties and behaviors under various conditions is essential to their continued effective use.

For adhesive applications, an understanding of how the material properties of the gel affect the adhesive performance is critical. Further, the effect of material properties and use conditions on the debonding behavior and mechanisms is also important. Generally, the debonding mechanism observed is dependent on such factors as gel modulus, gel rheology, confinement (the combination of adhesive layer thickness and contact force), and the velocity at which the probe and adhesive are separated.^{11–15} The most common debonding mechanisms observed can be categorized as interfacial failures which include surface cavitation and edge crack propagation and bulk failures where cavitation occurs in the bulk of the material. Understanding the relevant debonding mechanisms, the factors that influence which mechanisms are observed, and how the debonding mechanism affects overall adhesive properties is a key research challenge.

In this article, we examine the rheology and adhesion properties of three fluorosilicone polymer gels of varying equilibrium

modulus. First, the rheology of the gels is characterized over five decades of frequency to give a basis for interpreting the subsequent adhesion measurements. Then adhesion is examined in terms of the gel confinement and separation velocity. Finally, we examine the mechanisms of debonding and their effect on measured adhesion properties including practical work of adhesion, peak adhesive force, and strain to failure.

EXPERIMENTAL

The polymer gel used in the present studies is a commercially available, heat cured, platinum catalyzed fluorosilicone gel (DC4-8022) obtained from Dow Corning (Midland, MI). The gel is characterized by Dow Corning according to its hardness, which correlates with equilibrium modulus, at 25°C. Three samples of the fluorosilicone gel were obtained ranging in hardness from very soft (30 g) to hard (110 g). The gel samples used here are cured at 82°C for a period of 24 h.

During and after cure, rheological tests were performed using a TA Instruments (New Castle, DE) AR-G2 stress controlled rheometer with a 40-mm diameter parallel plate geometry and a Peltier plate for temperature control. Sol content of the cured gel was determined via Soxhlet extraction in methyl ethyl ketone (MEK) as described in detail elsewhere.¹⁶ For each of the gels studied here, the gel contains $46 \pm 2.5\%$ by weight unreacted sol.

Tack adhesion measurements were performed using a TA Instruments (New Castle, DE) ARES G2 strain controlled rheometer. Tack samples were prepared by casting a 2-mm thick layer of fluorosilicone gel onto a 50-mm diameter aluminum plate then curing as stated above. This process resulted in a cured gel layer approximately 0.9-mm thick. All tack samples were tested at room temperature (22°C). For tack measurements, an 8-mm diameter stainless steel probe with a flat surface was brought into contact with the gel layer and a given force applied for a controlled period of time. The probe was then separated from the gel surface at a controlled rate while measuring the force exerted by the gel as a function of time. Specific values of the experimental variables used (contact force, separation velocity, etc.) are given with the results of the measurements.

RESULTS AND DISCUSSION

Gel Rheology

Gel rheology was measured by curing a sample of the gel at 82°C in a 40-mm stainless steel parallel plate fixture of the controlled stress rheometer with a gap (sample thickness) of 1 mm. The kinetics of the cure process were monitored over the course of the 24 h cure time via small amplitude oscillatory shear measurements (Figure 1). Initially, the uncured gel, which is a viscous liquid, has a viscous modulus (G'') that is more than an order of magnitude higher than the elastic modulus (G'). During the cure period the elastic modulus quickly grows as the gel network is formed. Eventually, the magnitude of the elastic modulus surpasses that of the viscous modulus indicating that the material behavior changes from being more viscous to more like an elastic solid. The elastic behavior of the cured gel is due mainly to the formation of the chemically crosslinked gel net-

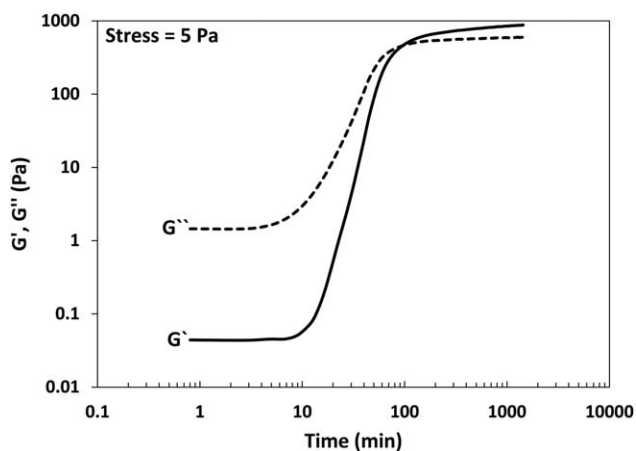


Figure 1. Evolution of the dynamic moduli at a frequency of 1 Hz and stress of 5 Pa as a medium modulus fluorosilicone polymer gel undergoes the curing reaction at 82°C.

work while the viscous contribution can be attributed mainly to the unreacted polymer sol.

The critical gel point is determined from the oscillatory measurements at several different frequencies during the curing reaction. The critical gel point is defined by the point where a percolated polymer network is first formed. Physically, it is the point at which the viscosity of the reacting material diverges to infinity as a space filling three-dimensional network is formed.¹⁷ Beyond the gel point, the material is a viscoelastic solid for which the crosslink density increases as the reaction proceeds.¹⁸ The critical gel point is quantified by the time at which $\tan(\delta)$, which is the ratio of the viscous and elastic moduli, measured at different frequencies is the same (Figure 2).¹⁹ For the medium modulus gel (shown in Figure 2), the critical gel point is reached at a reaction time of 71 ± 8 min, based on three independent gel cure measurements. The low and high modulus gels reach the critical gel point in 83 ± 8 min and 59 ± 3 min, respectively (also based on three independent measurements).

Following the 24 h cure period, the cured gel sample was cooled to 25°C and allowed to equilibrate for at least 20 min. The

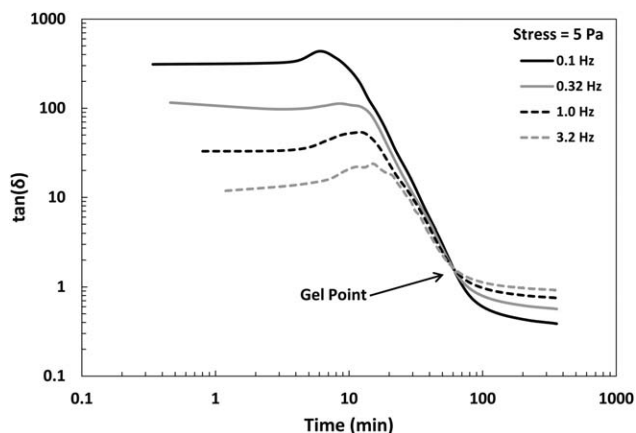


Figure 2. Evolution of $\tan(\delta)$ over time as the fluorosilicone gel cures. The gel point is determined from the point where $\tan(\delta)$ is independent of frequency.

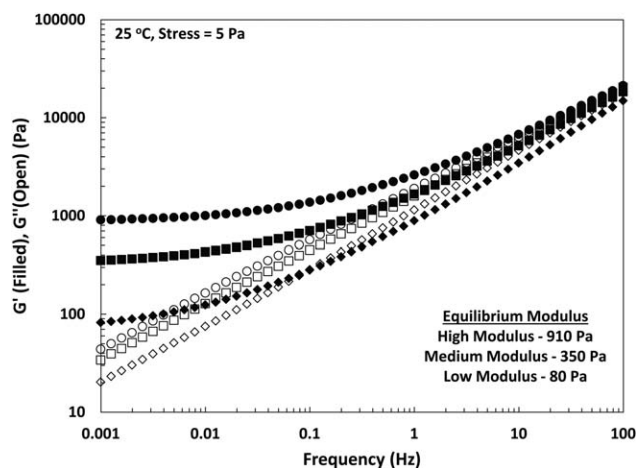


Figure 3. Frequency dependence of the dynamic moduli for three fluorosilicone polymer gels [(♦) low modulus, (■) medium modulus, (●) high modulus] in the linear viscoelastic regime with a stress of 5 Pa at 25°C.

rheology of the cured gel was then measured over five decades of frequency using small angle oscillatory shear measurements (Figure 3). For each of the gels tested, the elastic modulus is independent of frequency at the lowest frequencies. This frequency independence at low frequencies is used to determine the equilibrium modulus of the material. The strength of a gel, quantified by the equilibrium modulus, is generally proportional to the density of crosslinks (either chemical or physical) in the gel network.²⁰ In the limit of low frequency, the elastic modulus for each gel is considerably larger than the viscous modulus with the highest modulus gel having the greatest difference in magnitude between G' and G'' . The dominance of the elastic modulus at low frequency indicates that the material response is dominated by the elastic gel network. The frequency of the oscillation is slow enough that the viscous polymer sol has sufficient time to relax under the applied stress and, thus does not contribute significantly to the material response. Similar results for the relative contributions of the elastic gel network and viscous sol have been reported for silicone gels with various solvents.²¹ Further, the dependence of G' on frequency observed here (specifically the significant increase in G' at higher frequencies) is characteristic of a gel containing and entangled sol.²¹ The increase in both G' and G'' is due to the effect of physical entanglements increasing the effective crosslink density and contributing to the material response via viscous dissipation. This increase is not observed (or not as strong) when the sol is not an entangled polymer.

As the oscillation frequency is increased, the viscous modulus for each gel increases in a power law fashion. For the low and medium modulus gels, the viscous modulus becomes greater than the elastic modulus at a frequency of about 0.1 Hz and 1.5 Hz, respectively. The high modulus gel does not exhibit a similar crossover in the range of frequency studied here, but the crossover frequency is estimated to be 120 Hz based on the slopes of the associated curves. This crossover in moduli has also been reported for other adhesive gel materials.¹² At the highest measured frequencies, the magnitude of the viscous modulus is very close to the magnitude of the elastic modulus

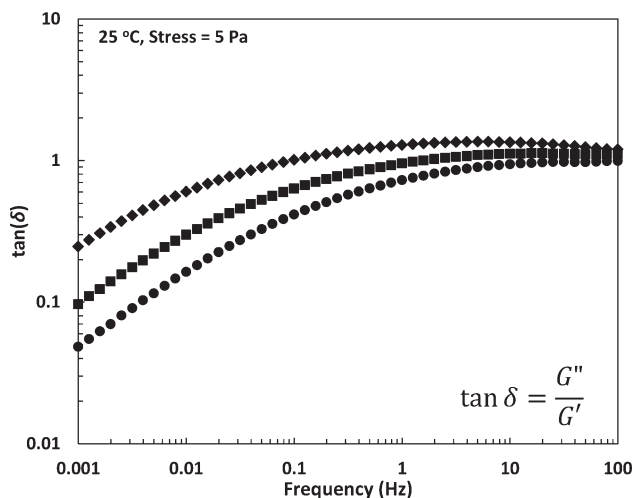


Figure 4. Frequency dependence of $\tan(\delta)$ for three fluorosilicone polymer gels [(♦) low modulus, (■) medium modulus, (●) high modulus] in the linear viscoelastic regime at a stress of 5 Pa and 25°C.

for each gel suggesting that the overall material response is significantly impacted by contributions from both the elastic gel network and the viscous polymer sol (i.e., the response is viscoelastic). The time scale of the deformation at high frequencies is such that the polymer sol does not have sufficient time to relax under the applied stress and, thus contributes more significantly to the material response than at lower frequencies.

The relative contribution of the elastic gel network and viscous polymer sol to the overall material response is further emphasized by examining the behavior of $\tan(\delta)$ over the range of frequencies studied (Figure 4). At low frequencies, $\tan(\delta)$ has values much less than 1 for each gel indicating that the elastic contributions dominate the material response. However, as the frequency is increased, $\tan(\delta)$ approaches and plateaus at a value near 1 indicating that the elastic and viscous contributions become equally significant in the material response. Further, the value of $\tan(\delta)$ for each gel converges to the same value at high frequencies. This convergence indicates that, for the fluorosilicone gels studied here, the behavior of the gel at short time scales is similar. Further, it suggests that, regardless of the equilibrium modulus of the gel, at short time scales the gels become indistinguishable in their material response.

Gel Adhesion and Debonding

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.²² 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.²³ Soft polymer gels can have excellent adhesive properties due to their combination of viscous and elastic properties.^{5,24,25} As surfaces bonded with a polymer gel are peeled apart, the gel deforms, but only a fraction of the applied energy is stored as elastic energy in the gel network. The ability of the bulk polymer gel to dissipate energy effectively determines, in large part, its

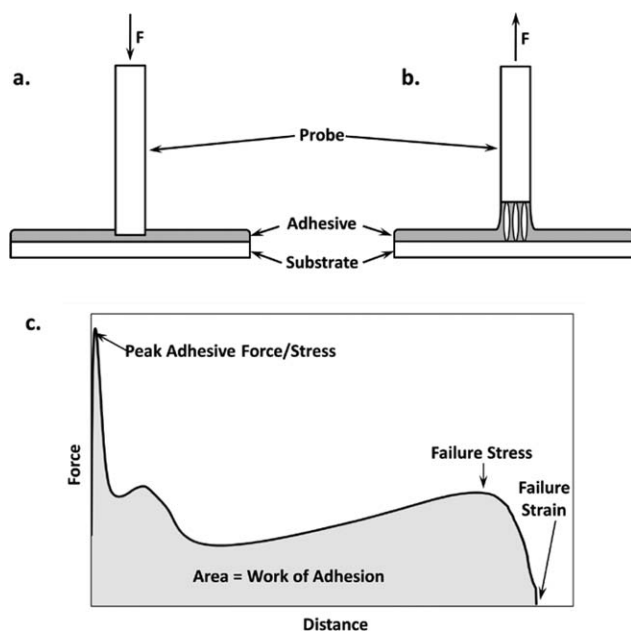


Figure 5. Schematic representation of an adhesion experiment (a and b) and a representation of the associated data (c).

effectiveness as an adhesive. During the separation phase, the adhesive must be able to accommodate large deformations to store and dissipate a large amount of energy before fracture occurs.^{24,26,27} The energy dissipating ability of the material is directly related to its viscoelastic properties (i.e., rheology).

Adhesive bond formation also requires sufficiently high polymer segmental mobility to obtain contact in molecular dimensions between the adhesive and solid substrate during the possibly very short contact time. Contact formation is an important factor in determining the strength of an adhesive joint²⁸ and can be highly dependent on the time of the contact. If the gel material is cured on the substrate, then intimate contact is determined by the ability of the uncured material to wet the substrate surface.²⁵ 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 (or confinement), contact time, and rheology of the gel. Increasing the contact force generally results in better contact and, thus, better adhesive strength.²⁸ Obtaining intimate molecular contact between the gel and the substrate greatly determines the strength of the adhesive joint.²⁸

Here, the effects of confinement and separation velocity on the adhesive properties of fluorosilicone gels are examined. Adhesion is measured by bringing an 8-mm diameter cylindrical probe into contact with a 0.9-mm thick layer of cured fluorosilicone gel at a controlled force for a controlled period of time [Figure 5(a)]. The probe and gel are then separated at a specified velocity [Figure 5(b)] while recording the force required to maintain that velocity as a function of distance. The resulting force-displacement curve is then used to determine the work of adhesion and peak adhesive force (or peak adhesive stress) for the given conditions [Figure 5(c)]. In every case reported here, bond failure occurred between the gel and the probe in an adhesive manner meaning that the gel cleanly

separated from the probe surface without leaving any visually observable residue behind.

Debonding Mechanisms

From the force data measured during separation, a stress versus strain curve can be generated for each experiment. The shape of the stress versus strain curve gives insight into the mechanisms of bond failure that are relevant at each experimental condition.^{11–13,15} To correctly interpret the mechanical results and to support the discussion of our results, we will briefly discuss the types of stress–strain curves observed in this work and their interpretation. For this discussion, we use data for the low modulus gel taken at varying separation velocities (Figure 6). At the lowest separation velocity, the stress reaches a maximum (peak adhesive stress) at small strain values followed by a reduction in stress as the strain is increased [Figure 6(a)]. The downturn of the stress here is caused by the initiation of the bond failure. This failure can be attributed to propagation of an edge crack or surface cavitation around a defect (e.g., an air bubble trapped at the probe surface).^{12,13} In the remaining discussion, this type of bond failure will be referred to as interfacial failure and we will not distinguish between surface cavitation and crack propagation. As the strain is increased further, the stress may monotonically decrease or there may be another increase in the measured stress as shown in Figure 6(a). This increase in stress is attributed to strain hardening in the adhesive film during fibril formation.

At high values of separation velocity, the stress–strain curve indicates that a different failure mechanism is at play [Figure 6(c)]. Like the low separation velocity case, when the probe and gel are separated quickly the stress reaches a maximum at small strain values. However, in the case of high separation velocities, the magnitude of the peak adhesive stress is much greater (about two orders of magnitude greater in this case) than in the low separation velocity case. Here, the decrease in stress following the maximum is caused by cavitation within the bulk of the adhesive film.^{12,13,15} The sudden decrease in load bearing area caused by the appearance of bulk cavities results in a drop in the measured tensile force. As the strain increases further, the stress also increases as the adhesive strain hardens and eventually separates from the probe surface. Following bulk cavitation, the cavities collapse and remain in the film after separation—a feature that distinguishes bulk cavitation from surface cavitation.¹³

At intermediate separation velocities, the stress–strain curve suggests a bond failure behavior that is a hybrid of the low and high separation velocity cases [Figure 6(b)]. To our knowledge, this is the first report of this transition behavior. At low strain values, the behavior mimics the case where bulk cavitation occurs. The stress rises rapidly and to much higher values than are achieved when interfacial failure occurs. However, following the peak adhesive force, there appears another peak. The shape of this peak, the peak stress, and the strain at the peak stress are all consistent with what is observed for purely interfacial failures. Thus, following the cavitation in the bulk of the adhesive layer interfacial failure (by either surface cavitation or edge crack propagation) significantly contributes to the failure

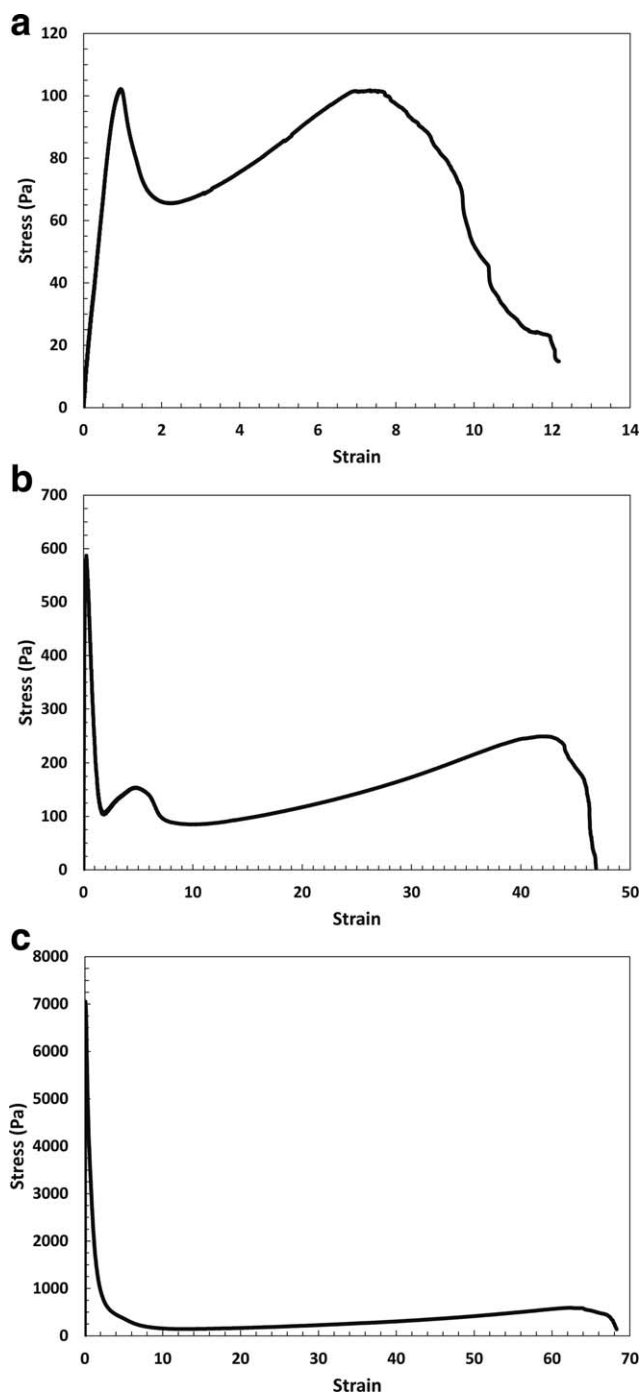


Figure 6. Stress versus strain curves for the low modulus gel at probe separation velocities of 0.001 mm/s (a), 0.01 mm/s (b), and 0.1 mm/s (c).

behavior. Finally, as strain is increased further strain hardening is observed until separation is achieved.

In summary, the character of the stress–strain curves gives insight into the adhesive bond failure mechanisms pertinent to the given experimental conditions. We have shown three representative curves that indicate the predominant failure mechanism of interfacial failure [Figure 6(a)], a blend of bulk cavitation and interfacial failure [Figure 6(b)], and bulk cavitation [Figure 6(c)]. We now examine the influence of the adhesive properties of several gels on

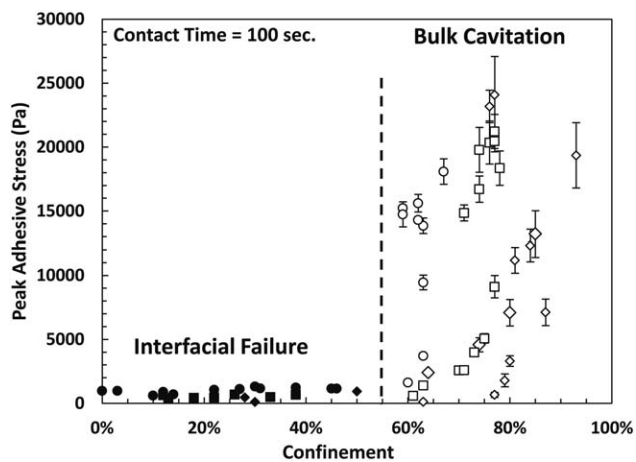


Figure 7. Dependence of the peak adhesive stress on film confinement for three fluorosilicone polymer gels [(♦) low modulus, (■) medium modulus, (●) high modulus]. Open points represent cases where bulk cavitation is observed while filled points show cases where interfacial failure is observed. Error bars represent one standard deviation from three independent measurements.

the adhesion failure mechanism in light of the variables of confinement, and initial strain rate.

Confinement Effects

First, the effects of confinement were examined by varying the contact force from 10 g to 1000 g. For contact forces of 500 g, the separation velocity was varied over five orders of magnitude from 0.001 mm/s to 100 mm/s. For this discussion, confinement is defined as follows

$$\text{Confinement} = \left(1 - \left(\frac{h}{h_0}\right)\right) \times 100$$

where h is the film thickness at the point where the measured force changes sign and h_0 is the original film thickness. Using this definition, a confinement of 60% means that the film has been compressed to 40% of its original thickness. For degrees of confinement below 50%, the peak adhesive stress is independent of both confinement and separation velocity (Figure 7). In this region interfacial failure dominates. When the confinement is increased above about 60%, the failure mechanism transitions to bulk cavitation and the peak adhesive stress increases dramatically with confinement (Figure 7). Even though the lower modulus gel is able to reach much higher values of confinement (maximum of about 93% as opposed to about 67% for the high modulus gel) due to its compliant nature, the transition between interfacial failure and bulk cavitation occurs in the same region (50–60%) for each of the gels regardless of modulus. These results are consistent with work by Crosby et al.¹² who reported that the bond failure mechanism can be changed simply by changing the confinement of the adhesive layer.

Separation Velocity/Initial Strain Rate

The adhesion properties of fluorosilicone gels were also found to depend strongly on the speed at which the probe and gel were separated from one another (separation velocity). For these tests, the contact force and contact time were 500 g and 100 s, respectively, which is sufficient to ensure good contact. For low and moderate separation velocities, the work of adhesion

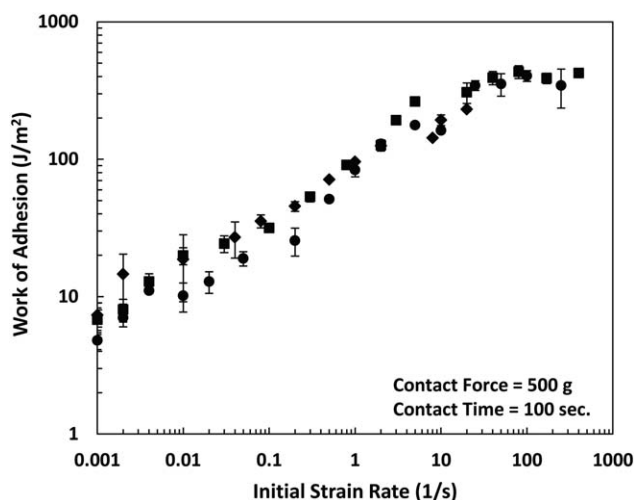


Figure 8. Dependence of the work of adhesion on the initial strain rate for three fluorosilicone polymer gels [(♦) low modulus, (■) medium modulus, (●) high modulus]. Error bars represent one standard deviation from three independent measurements.

exhibited a power law dependence on the separation velocity (Figure 8). The power law relationship breaks down at high separation velocities as the work of adhesion becomes independent of the separation velocity. Further, for high separation velocities, the work of adhesion for the three different modulus gels converges to a similar value. This convergence is congruent to the convergence in viscous and elastic moduli observed at high oscillation frequency (Figure 3) and is further supported by the same behavior observed in the high frequency dependence of $\tan(\delta)$ (Figure 5). At high separation velocities, the three gels become indistinguishable as the measurement is too fast to allow for the relaxation of the polymer sol. When the polymer sol is unable to relax under the applied stress, the contributions from physical entanglements in the polymer sol to the gel response become significant.

The peak adhesive stress also depends strongly on separation velocity [Figure 9(a)]. For moderate separation velocities, a power law relationship is observed. However, at both high and low separation velocities, the peak adhesive stress is independent of the separation velocity. At high velocities, all three gels show similar values of peak adhesive stress. This similarity in behavior at high velocities is also observed in the work of adhesion (Figure 8) and is attributed to the similarity of the gel material response at short time scales or high frequencies. However, at low separation velocity, the high modulus gel exhibits the highest peak adhesive stress while the low modulus gel exhibits the lowest peak adhesive stress. This can be understood by examining the low frequency rheology of both of these gels. The magnitudes of the viscous modulus for the high and low modulus gels are comparable at low frequencies (Figure 3). For small values of separation velocity, the polymer sol has sufficient time to relax under the applied stress. Therefore, viscous contributions to the material response are negligible in this regime. However, there is a large difference in the magnitude of the elastic modulus for these gels. Since the elastic network is mainly responsible for the material response at low measurement speeds, it follows

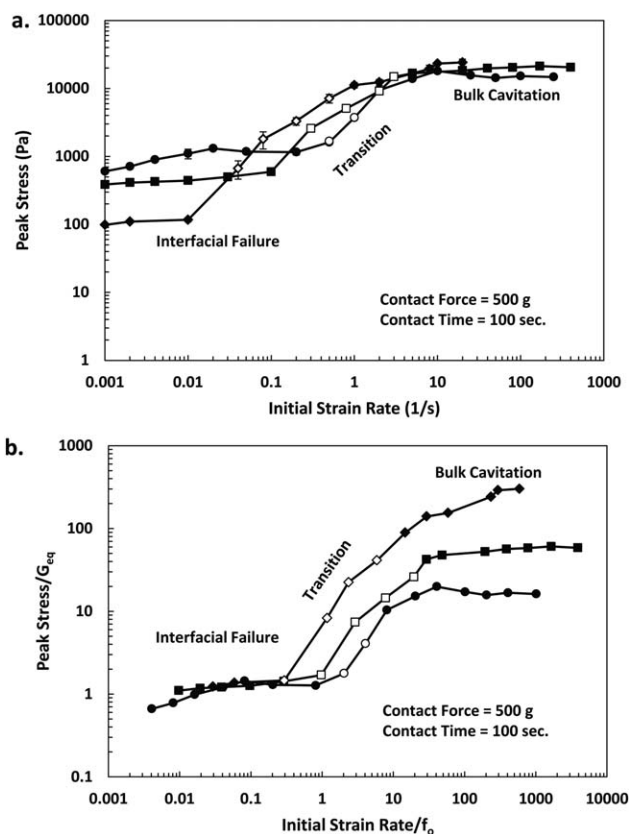


Figure 9. Dependence of the peak adhesive stress (a) on the initial strain rate for three fluorosilicone polymer gels [(♦) low modulus, (■) medium modulus, (●) high modulus]. In (b) the peak adhesive stress is normalized by the equilibrium modulus and the initial strain rate is normalized by a characteristic frequency. Open points represent experiments where transition from interfacial failure and bulk cavitation was observed. Error bars represent one standard deviation from three independent measurements.

that a more elastic network will exhibit a higher peak adhesive stress than a less elastic network.

Further insight into the adhesion properties of these gels may be gained by examining the peak adhesive stress normalized by the equilibrium modulus of each gel as a function of the initial strain rate normalized by a characteristic frequency for each gel [Figure 9(b)]. The characteristic frequency used was determined by the intersections of straight lines fitting the plateau of $\tan\delta$ at high frequencies and $\tan\delta$ at low frequencies. The resulting frequency is the frequency at which viscous effects become significant in the material response. When the data are reduced in this manner, the curves for each gel converge to a single value at low initial strain rates. Thus, in the regime where interfacial failure dominates, the peak adhesive stress generated is proportional to the equilibrium modulus of the gel. This proportionality suggests that the peak adhesive stress for a material in this region is a property of the material rather than a product of the experimental conditions. At high initial strain rates where bulk cavitation dominates, no such similarity in peak stress values is observed. This is not unexpected since the raw values of peak adhesive stress [not normalized, Figure 9(a)] are very similar

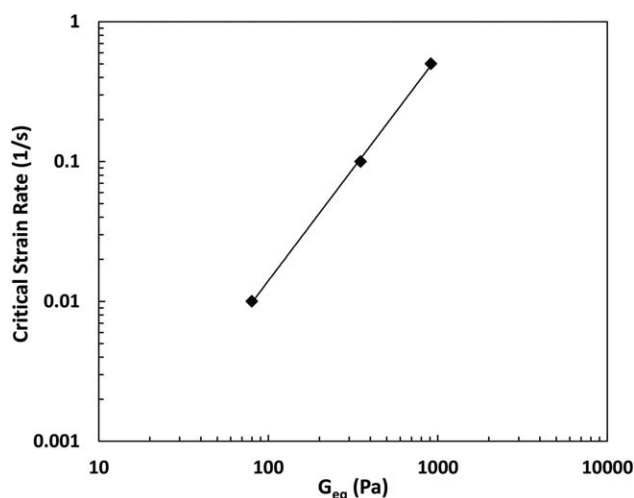


Figure 10. Critical strain rate for the onset of bulk cavitation as a function of equilibrium modulus for fluorosilicone polymer gels.

for each gel in the bulk cavitation regime due to their similarity in rheological response at short time scales (i.e., at short time scales, the gel material response is independent of G_{eq}).

From the data presented in Figure 9(a), we can extract a critical initial strain rate where the debonding mechanism transitions from interfacial failure to bulk cavitation (Figure 10). The critical initial strain rate is found to depend on the equilibrium modulus of the gel in a power law fashion. Thus, softer gels (lower equilibrium modulus) transition to bulk cavitation at much lower initial strain rates than stiffer gels. One possible explanation for this trend can be made by examining the effects of confinement and rheology. Each of the gels was treated with the same contact force. However, due to the varying rheology of the gels, each experiences a different confinement with the softest gel experiencing the highest degree of confinement. If the confinement is determined from the height of the gel sample at the point that the measured force changes sign, higher degrees of confinement will also be experienced at higher initial strain rates. Thus, at a given initial strain rate, the low modulus gel experiences more confinement than the high modulus gel simply due to differences in rheology. This higher degree of confinement leads to bulk cavitation appearing sooner with the softer gels.

Next we examine the strain to failure for the fluorosilicone gels as a function of the initial strain rate (Figure 11). At high initial strain rates, the strain to failure is independent of the initial strain rate. In this region, bulk cavitation is also the dominant debonding mechanism [Figure 11(a)]. In the lower initial strain rate regimes where interfacial failure occurs and through the transition to bulk cavitation, the failure strain depends on the initial strain rate in a power law fashion.

More insight into the failure strain behavior for fluorosilicone gels may be gained when the failure strain is multiplied by the equilibrium modulus for each gel studied [Figure 11(b)]. This normalization results in the three distinct curves from Figure 11(a) to collapse to a single curve. As such, strain to failure appears to be an intrinsic material property across all initial strain rates studied.

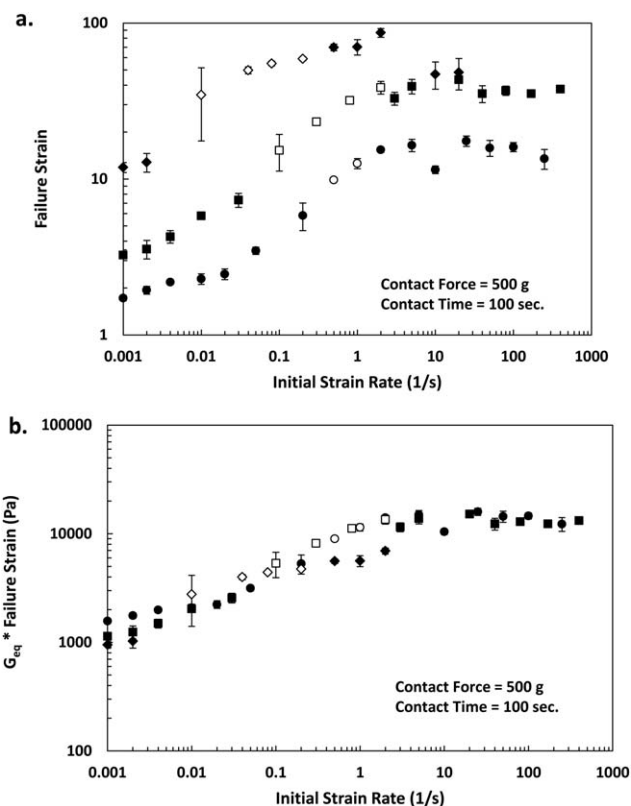


Figure 11. Strain to failure (a) and failure strain multiplied by the equilibrium modulus (b) as a function of initial strain rate for three fluorosilicone polymer gels [(\blacklozenge) low modulus, (\blacksquare) medium modulus, (\bullet) high modulus]. Open points indicate the transition region between interfacial failure and bulk cavitation. Error bars represent one standard deviation from three independent measurements.

The three gels share a power law dependence of the failure strain on initial strain rate for low and moderate initial strain rates. At high initial strain rates, the failure strain reaches a plateau and is independent of the initial strain rate. This behavior mimics the data for the work of adhesion as a function of initial strain rate shown in Figure 8. However, failure strain reaches the plateau value at an initial strain rate that is about an order of magnitude lower than the initial strain rate at which the work of adhesion plateaus (3 s^{-1} vs. 30 s^{-1}). This difference can be explained by the fact that even though the materials fail at the same strain, the work of adhesion continues to increase over the range of 3 s^{-1} to 30 s^{-1} because the peak adhesive force also continues to rise over this range of initial strain rate [Figure 9(a)].

Generally speaking, the modulus of a material is given by the quotient of the stress and strain imposed on the material. Thus, multiplying a material modulus by a strain results in a stress. As such, the data presented in Figure 11(b) suggest that, for a given initial strain rate, each of the gels fails at common stress stored in the elastic gel network. Indeed, when the failure stress is examined, it is found to have the same qualitative dependence on initial strain rate as does the product of the equilibrium modulus and failure strain (Figure 12). At low and moderate values of initial strain rate, the failure stress exhibits a power law dependence on initial strain rate while at high initial strain

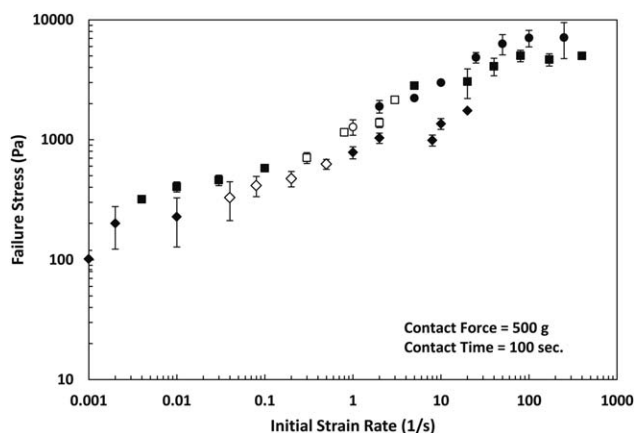


Figure 12. Failure stress as a function of initial strain rate for three fluorosilicone polymer gels [(◆) low modulus, (■) medium modulus, (●) high modulus]. Open points indicate the transition region between interfacial failure and bulk cavitation. Error bars represent one standard deviation from three independent measurements.

rates the failure stress is independent of initial strain rate. These dependencies are similar to those observed in the dependence of work of adhesion on initial strain rate and also in the dependence of $\tan \delta$ on frequency.

CONCLUSIONS

The adhesive properties and debonding mechanisms of fluorosilicone polymer gels are sensitive to the confinement and separation velocity the gels experience. For low degrees of confinement, debonding is dominated by interfacial failure, regardless of the gel equilibrium modulus. As the degree of confinement is increased the debonding mechanism shifts to being dominated by bulk cavitation. Further, at low initial strain rates debonding is dominated by interfacial failure. In this region, the work of adhesion and failure strain exhibit similar power law dependencies on the initial strain rate. As the initial strain rate is increased a transition in debonding mechanisms is observed where both interfacial failure and bulk cavitation are present. To our knowledge, this is the first report of this transition behavior and its impact on adhesion properties as well as the qualitative shape of the associated stress–strain curve. At high values of initial strain rate, the work of adhesion, peak adhesive stress, failure strain and failure stress are all independent of the initial strain rate. Debonding in this regime is dominated by bulk cavitation.

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REFERENCES

- Osada, Y. *Polymer Gels and Networks*; Marcel Dekker, Inc.: New York, **2001**.
- Yoldas, B. E. *J. Non-Cryst. Solids* **1984**, *63*, 145.
- Ross-Murphy, S. B. *J. Rheol.* **1995**, *39*, 1451.
- Tunick, M. H. *J. Agric. Food Chem.* **2010**, *59*, 1481.
- Andrews, G. P.; Jones, D. S. *Biomacromolecules* **2006**, *7*, 899.
- Creton, C. *MRS Bulletin* **2003**, *28*, 434.
- Solomon, M. J.; Spicer, P. T. *Soft Matter* **2010**, *6*, 1391.
- Perkins, K.; Davey, R. B.; Wallis, K.A. *Burns* **1983**, *9*, 201.
- Sproat, J. E.; Dalcin, A.; Weitauer, N.; Roberts, R. S. *Plast. Reconstr. Surg.* **1992**, *90*, 988.
- Moon, S.; Swearingen, S.; Foster, M. D. *Polymer* **2004**, *45*, 5951.
- Lindner, A.; Lestriez, B.; Mariot, S.; Creton, C.; Maevius, T.; Luhmann, B.; Brummer, R. *J. Adhes.* **2006**, *82*, 267.
- Crosby, A. J.; Shull, K. R.; Lakrout, H.; Creton, C. *J. Appl. Phys.* **2000**, *88*, 2956.
- Brown, K.; Hooker, J. C.; Creton, C. *Macromol. Mater. Eng.* **2002**, *287*, 163.
- Creton, C.; Hooker, J.; Shull, K. R. *Langmuir* **2001**, *17*, 4948.
- Shull, K. R.; Creton, C. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 4023.
- Grillet, A. M.; Wyatt, N. B.; Gloe, L. M. In *Rheology*; De Vincente, J., Ed.; InTech, Rijeka, Croatia, **2012**, Chapter 3, p 59.
- Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, Inc.: New Jersey, **2006**.
- Gupta, R. K. *Polymer and Composite Rheology*, 2nd ed.; Marcel Dekker, Inc.: New York, **2000**.
- Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
- Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039.
- Mrozek, R. A.; Cole, P. J.; Otim, K. J.; Shull, K. R.; Lenhart, J. L. *Polymer* **2011**, *52*, 3422.
- Jones, D. S.; Woolfson, A. D.; Brown, A. F. *Pharm. Res.* **1997**, *14*, 450.
- El-Gibaly, I. *Int. J. Pharm.* **2002**, *232*, 199.
- Gay, C. *Integ. Comp. Biol.* **2002**, *42*, 1123.
- Hurler, J.; Engesland, A.; Kermany, B. P.; Skalko-Basnet, N. *J. Appl. Polym. Sci.* **2012**, *125*, 180.
- Zosel, A. *Int. J. Adhes. Adhes.* **1998**, *18*, 265.
- Zosel, A. *J. Adhesion* **1991**, *34*, 201.
- Zosel, A. *J. Adhesion Sci. Technol.* **1997**, *11*, 147.