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GEL FRACTURE AT HIGH STRESSES: THE EFFECTS OF SOL FRACTION

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Introduction

The fracture behavior of polymer gels and soft materials has not been fully explored. Most studies in fracture mechanics thus far have been focused on metals, ceramics, and rigid polymers, where high values of strength are desired. However, the fracture behavior of low-modulus elastomers and polymer gels are often important as well. In order to understand the fracture behavior of these materials, experimental and analytical methods are needed that account for the ability of these materials to be elastically deformed to very high strains.

Most previous work on the fracture and failure of soft materials has focused on the cohesive failure of polymer networks. Gent et al. [1-2] and Lake and Thomas [3] have investigated the fracture energy, threshold strength, and fracture processes in elastomeric materials. Such studies often involve destructive methods where an incision is made in the sample, and only a limited range of data can be gathered from each sample. Experimental geometries include trouser tests or edge-crack tests. Other experiments have focused on adhesion of elastomers using peel tests [4-5], adhering spheres [4], indenters [4], and dual cantilever beams [6]. Few studies thus far have used indentation to study the fracture behavior of elastomers in compression. Shergold and Fleck and Nguyen and Vu-Khanh used indentation to research the puncture of silicone as a model system for skin wounds and latex gloves [7-9].

Our experiments have focused on developing an efficient technique for measuring the mechanical properties of soft materials. We use indentation geometry on thick polymer layers supported by a rigid substrate. This geometry allows us to perform multiple tests on a single sample, improving the statistical reliability of our results. Since the gel is supported by a rigid substrate, many types of samples can be used, including sol-gels and other soft materials. Another advantage of this geometry is that the stress can be applied for an extended period of time, allowing for examination of relaxation behavior of polymer systems under compression. Specifically, we investigate the relaxation and fracture behavior of cross-linked polymer gels with varying levels of added sol fraction.

By varying of sol fraction, sol weight, network fraction, and molecular weight between cross-links, a broad spectrum of viscoelastic and fracture behavior can be obtained.

Experimental

Poly(dimethyl siloxane) (PDMS) was chosen as a model system because its elastic behavior has been well characterized and it is used in a variety of applications. The silicone gel networks were formed from vinyl-terminated PDMS prepolymers, as described previously [10]. Three molecular weights were used: 500 g/mol (V05), 28,000 g/mol (V31), and 117,000 g/mol (V46). Trimethyl terminated PDMS prepolymers of varying molecular weights were then added in weight fractions of 0.20, 0.40, and 0.50 of the solution. The naming convention for the sol is as follows: T11 is 1560 g/mol, T31 is 28,000 g/mol, and T51 is 139,000 g/mol. Gels with no added sol fraction will be referred to as 'neat.'

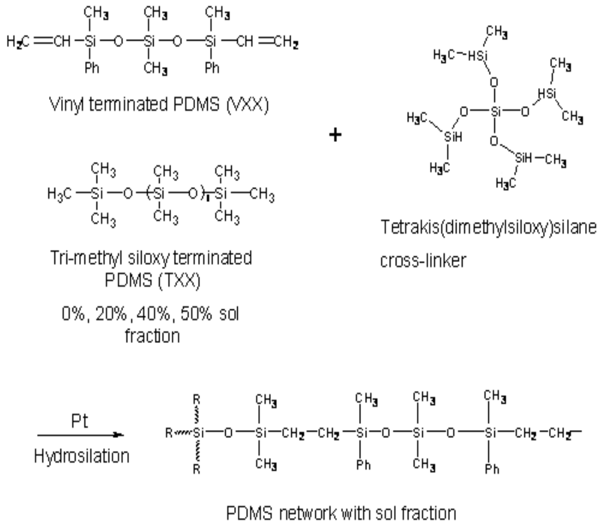

Figure 1. Vinyl-terminated PDMS is hydrosilated with a cross-linker, resulting in a branched PDMS network. A gel is formed by the addition of sol fraction (TXX).

Indentation tests were performed using a flat punch probe apparatus, as described previously [11-12]. The apparatus consists of an inchworm motor attached to a 50 g (Lucas Schaevitz) or 1 kg (Sensotec) load cell. An indenter and optical displacement sensor (Philtec) are attached beneath the load cell. For our experiments, a punch radius of 0.39 mm was used. The instrument is connected to a computer and the loading rate, maximum load, and experiment duration are controlled via LabView. A side view camera allows for imaging during the experiment. A schematic of the apparatus is shown in figure 2.

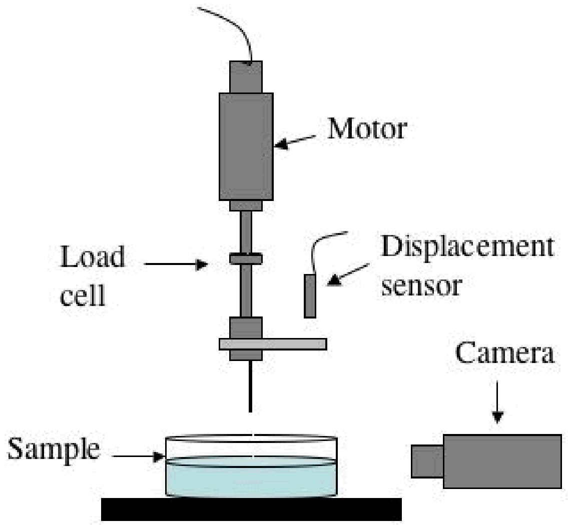

Figure 2. The microindentation apparatus.

This instrument was used to determine the mechanical properties of our silicone gels, including the small strain modulus and the large strain fracture behavior. The indenter was brought into contact with the gel, loaded to a specified compressive force, held at constant displacement for up to 1000 sec, and then retracted from the gel. The loading and unloading rates were 10 μm/sec.

Results and Discussion

The elastic modulus was determined from the slope of the small strain region of the loading portion of the stress-strain curve, where linear elasticity theory is still valid. To calculate the modulus, the slope is multiplied by a factor of 1.17, which accounts for the relationship between compliance and the modulus:

$$E = \frac{3P}{8a\delta} = \frac{3\pi a^2 \sigma_{av}}{8a^2 (\delta/a)} = \frac{3\pi\sigma_{av}}{8(\delta/a)} \cong 1.17 \frac{\sigma_{av}}{\delta/a} \quad \text{(Eq. 1)}$$

In this equation, a is the punch radius, δ is the measured displacement, and σ_{av} is the average stress (given by the measured load, P, divided by πa^2) [13]. In a cross-linked polymer, the elastic modulus, E, is inversely proportional to the molecular weight between cross-links, M_x:

$$E = \frac{3RT\rho\phi_{network}}{M_x} \quad \text{(Eq. 2)}$$

where ρ is the polymer density, $\phi_{network}$ is the volume fraction of polymer network, R is the universal gas constant, and T is the absolute temperature. Moduli for the V05 samples, which have the lowest weight between cross-links (500 g/mol), range from 0.2 and 1 MPa. These values decrease for the V31 and V46 samples, which range from 50 to 200 kPa and 1 to 10 kPa, respectively. Thus, our results are consistent with behavior predicted by equation 2.

The addition of sol fraction to the system lowers the modulus as compared to the neat gel. In this case, the system can be modeled as an interpenetrating network, in which the tri-methyl terminated PDMS chains entangle and interpenetrate the vinyl-terminated PDMS network. Figure 3 plots the average modulus for increasing sol fraction in the T31-V31 system.

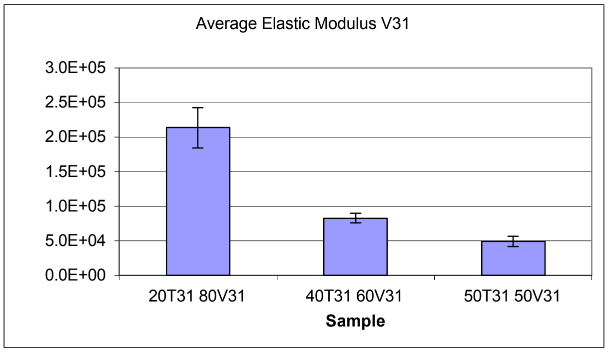

Figure 3. Elastic modulus values with increasing sol fraction in the V31 (28,000 g/mol) system.

As shown in equation 2, the addition of sol decreases the overall volume fraction of cross-linked polymer chains ($\phi_{network}$), thus decreasing the elastic modulus.

The fracture behavior of the gels is also affected by the presence of the sol fraction. During our experiments, the gels were loaded to a maximum stress and held for 1000 sec at constant displacement. Some gels fractured upon loading to high loads, as chains in the base network were stretched to the point of rupture. Delayed fracture also occurred in samples after the maximum load was reached because the network was unable to fully relax. The presence of sol provides an additional mechanism for viscoelastic relaxation at high stresses, thus toughening the network. Figure 4 shows typical crack shapes for different molecular weight systems. The gel in figure 4a is the V31 base network with 50% T31 sol added and figure 4b is the neat V05 gel. Fracture occurred at 12 MPa in the higher molecular weight system (V31), as opposed to 2.2 MPa in the more highly cross-linked system (V05).

In the higher molecular weight networks (V31), the indenter is very close to the substrate when fracture occurs. Although the substrate effects have not yet been fully investigated, the cracks can be classified into two general modes. When the indenter is further from the substrate, a surface flaw initiates Hertzian cone cracks (Fig. 4a). Near the substrate, the gel fails at the corners of the indenter, where the highest tensile stresses are located. A ring crack is formed and it propagates up the shaft to relieve stress. The V46 gels did not fracture within the limits of our load cell. In these gels, the chain relaxation at such high loads is still sufficient to prevent fracture. Initial attempts at using an indenter with a smaller radius were unsuccessful, as the indenter bent under high loads. In contrast to the V31 gels, fracture in the V05 gels cannot be easily categorized. A crack initiates when the indenter is close to the sample surface, and the geometry varies between highly defined planes and disordered, asymmetric cracks (Fig. 4b). Further experiments are needed to better understand how the formation and geometry of these cracks depend on the sol fraction and molecular weight.

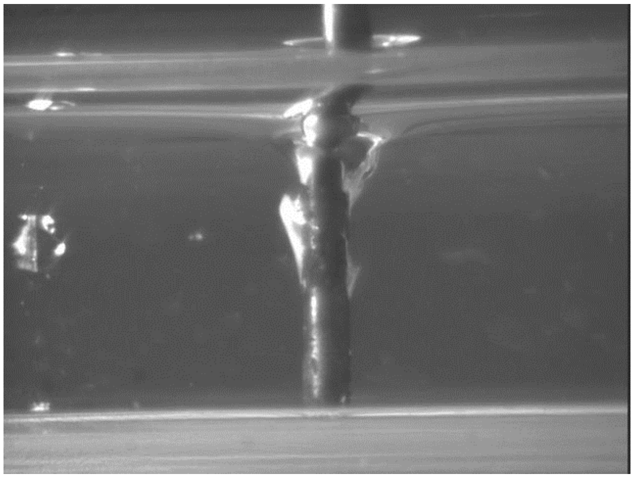

Fig. 4a – 50T31 50V31

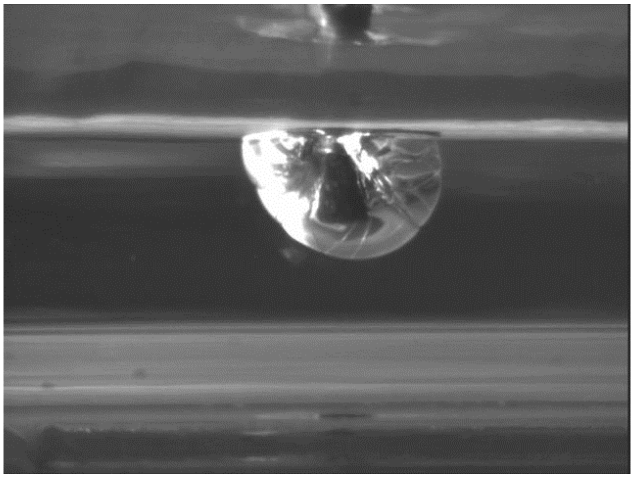

Fig. 4b - 100V05

Figure 4. Typical crack patterns for high (a) and low (b) molecular weight systems. 4a illustrates a typical cone-like shape seen in systems of higher molecular weight and with sol added. 4b contains no sol and has a much lower weight between cross-links, resulting in a more typical, asymmetric crack shape.

Conclusions

An axisymmetric flat punch probe apparatus was used to observe compressive fracture in silicone gels under high strain conditions. As expected, increasing the molecular weight between cross-links in the PDMS network decreases the elastic modulus. The incorporation of sol into the network also decreases the modulus by diluting the number of load bearing chains. Furthermore, the addition of sol fraction toughens the base network and results in an increase in the load required for fracture. This toughening most likely comes from the ability of the chains to redistribute the large stresses that are near the corners of the indenter.

The mode of fracture depends on the location of the indenter with respect to the substrate. Far from the substrate, cracks are initiated by a surface flaw and are highly irregular in shape. In the mid-region of the gel, cracks are also initiated by surface flaws, but result in more defined Hertzian cone cracks. Near the substrate, ring cracks are initiated by failure at the corners of the indenter.

We will continue to test our samples to more fully develop an understanding of the silicone gel behavior. A smaller indenter will be useful for inducing fracture in the loosely cross-linked system (V46) at high loads. We have also begun to study silica gels as a compliment to our current silicone gel system. These systems are more highly cross-linked, and are a useful complement to the materials studied here.

Acknowledgements

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