

## Finite shear strain behavior of a crosslinking polydimethylsiloxane near its gel point

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**Abstract:** A power law distribution of relaxation times, large normal stress differences, and physical rupture of molecular network strands dominate the shear behavior of polymers at the gel point (critical gels). This is shown in a series of well-defined experiments with increasing magnitude of shear on a model-network polymer system consisting of a linear, telechelic, vinyl-terminated polydimethylsiloxane (PDMS) and a four-functional siloxane crosslinker. Stable samples were prepared by stopping the crosslinking reaction at different extents of reaction in the vicinity of the gel point (GP). The Gel Equation has been shown to be valid up to strains of about 2 when using a finite strain tensor. Larger strains have been found to disrupt the network structure of the crosslinking polymer, and introduce a mechanical delay to the gel point. A sample that was crosslinked beyond the gel point ( $p > p_c$ ) can be reduced from the solid state to a critical gel, or even to a viscoelastic liquid, depending on the magnitude of shear strain. As a consequence, the relaxation exponent of a critical gel created under the influence of shear is less than that of a quiescently crosslinked critical gel.

**Key words:** Gel point, gel equation, polydimethylsiloxane, shear modification

### 1. Introduction

Gelation is the phenomenon by which a crosslinking polymeric material undergoes a phase transition from the liquid to the solid state. A thermosetting polymer system is transformed from a viscoelastic liquid to a viscoelastic solid by the introduction of chemical crosslinks, thereby creating a three-dimensional network. The sol-gel phase transition, known as the gel point, occurs at some critical extent  $p_c$  of the crosslinking reaction. The polymer at the gel point is in a critical state, and is therefore referred to as a critical gel, to distinguish it from various other materials commonly known as gels.

The linear viscoelastic material functions at the gel point are fully described by a simple rheological constitutive equation known as the Gel Equation [1, 2]. This can be written as

$$\tau(t) = S \int_{-\infty}^t (t-t')^{-n} \dot{\gamma}(t') dt' \quad (1)$$

where  $\tau$  = stress tensor,  $S$  = material constant called the gel strength,  $\dot{\gamma}$  = rate of strain tensor, and  $n$  = network specific relaxation exponent.

The significance of the Gel Equation lies in the simplicity of the rheological behavior of a critical gel (polymer at the gel point). The Gel Equation predicts the classical attributes of a critical gel, namely, infinite zero-shear viscosity  $\eta_0$  and zero equilibrium modulus  $G_\infty$ . The more readily measureable quantities are the relaxation modulus

$$G(t) = S t^{-n} \quad (2)$$

and the complex moduli in an oscillatory shear experiment, related by:

$$\tan \delta = G''(\omega)/G'(\omega) = \tan(n\pi/2) \quad (3)$$

At the gel point, the complex moduli  $G'$  and  $G''$  show a power-law dependence on the frequency of oscillation  $\omega$  and the loss tangent  $\tan \delta$  is independent of  $\omega$ . Holly et al. [3] have utilized this phenomenon to

devise a new rheological technique to determine the gel point of crosslinking polymers. It is well known that the relaxation exponent adopts a value of  $n = 0.5$  in the case of several stoichiometrically balanced systems, but a wide range of exponents between 0.18 and 0.92 have been shown possible [4–8] on several different chemical and physical crosslinking systems.

While all the previous work on the rheological behavior of polymers near the gel point has concentrated on the linear viscoelastic region, an extension into the non-linear region is required for the understanding of reactive processing and gel processing flows. The main objectives of this work have, therefore, been to develop a constitutive equation to describe the rheological properties of a crosslinking polymer network near the gel point and to measure the effect of large shear strains on the rheology.

## 2. The gel equation for intermediate shear strains

An infinitesimal strain measure was sufficient for describing the linear viscoelastic behavior of a critical gel [1]. To satisfy continuum-mechanics principles, the infinitesimal strain measure in the gel equation must be replaced by a finite strain measure. The volume changes are assumed to be negligible. Assuming that the linear relaxation modulus  $G(t)$  also applies in the region of intermediate strain, Winter and Chambon [1] proposed that the constitutive equation for the stress can then be rewritten as

$$\tau(t) = -S \int_{-\infty}^t (t-t')^{-n} \frac{\partial}{\partial t'} [C_t^{-1}(t')] dt', \quad (4)$$

which can then be transformed by partial integration to

$$\tau(t) = nS \int_{-\infty}^t (t-t')^{-n-1} [C_t^{-1}(t') - 1] dt', \quad (5)$$

where  $C_t^{-1}(t')$  = Finger strain tensor and  $\mathbf{1}$  = unit tensor.

This is the most simple extension of the Gel Equation. It should be noted that the linear viscoelastic constitutive equation, Eq. (1), is recovered intact in the limit of small strains. The Finger strain tensor has been used here due to the success of the Lodge rubber-like liquid model [9] in predicting viscoelastic liquid

behavior. Other strain measures or a combination of strain tensors, as discussed in detail in [10], might also be appropriate, and will be considered in future studies. A combination of Finger and Cauchy strain tensors might be appropriate for describing the second normal stress difference and the extensional behavior of critical gels. A possible formulation for the stress is

$$\tau(t) = nS \int_{-\infty}^t (t-t')^{-n-1} ((1-\varepsilon)[C_t^{-1}(t') - 1] + \varepsilon[1 - C_t(t')]) dt' \quad (6)$$

for  $0 < \varepsilon < 1$ .

Here, the simplest model, given in Eqs. (4) and (5), will be applied to predict the material response of a critical gel to two different, well-defined shear flows.

*a) Startup of shear flow:* An experiment is considered in which the material is initially kept at rest  $\dot{\gamma} = 0$  until at time  $t = 0$  a constant shear rate  $\dot{\gamma}_0$  is imposed. The specific shear history is therefore:

$$\begin{aligned} \gamma &= \dot{\gamma}_0 t & \text{for } -\infty < t' < 0 \text{ and} \\ \gamma &= (t-t')\dot{\gamma}_0 & \text{for } 0 < t' < t. \end{aligned}$$

The resulting shear stress and first normal stress difference depend on the time of shearing. The shear stress  $\tau_{12}(t)$  response is predicted from Eq. (4) as

$$\tau_{12}(t) = S \int_0^t (t-t')^{-n} \dot{\gamma}_0 dt' = \frac{S\dot{\gamma}_0}{1-n} t^{1-n}. \quad (7)$$

Similarly, the first normal stress difference  $N_1(t) = \tau_{11}(t) - \tau_{22}(t)$  is predicted from Eq. (5) as:

$$N_1(t) = nS \int_{-\infty}^t (t-t')^{-n-1} \gamma^2 dt' = \frac{2S\dot{\gamma}_0^2}{2-n} t^{2-n}. \quad (8)$$

The ratio of the first normal stress difference to the product of the shear stress and the shear rate is then calculated to be

$$\frac{N_1}{\dot{\gamma}\tau_{12}} = 2 \frac{1-n}{2-n} t. \quad (9)$$

This function grows linearly with time for any critical gel, and the relaxation exponent  $n$  solely determines the slope. The linear growth can be used as a convenient reference for finding the limits of linear response in this transient shear experiment.

b) *Creep and recovery behavior*: Similarly, the analytical expressions for the shear strain during creep under a constant shear stress  $\tau_0$  and the viscoelastic recovery after the cessation of shear can be derived from the Gel Equation [11]. The shear stress in a creep-recovery experiment is prescribed as a pulse function

$$\tau(t) = \tau_0 [1 - H(t - t_0)] , \quad (10)$$

where  $\tau_0$  = applied shear stress,  $H(t - t_0)$  = Heaviside function, and  $t_0$  = creep time.

The strain response for a material that exhibits power-law relaxation behavior, like a critical gel, can be calculated quite simply from the linear viscoelastic constitutive equation for the shear strain:

$$\gamma(t) = \int_{-\infty}^t J(t-t') \dot{\tau}(t') dt' , \quad (11)$$

where  $J(t-t')$  = creep compliance. With the creep compliance of a critical gel given by

$$J(t) = \frac{(1-n)}{S\Gamma(2-n)\Gamma(1+n)} t^n , \quad (12)$$

the strain response reduces to

$$\gamma(t) = \tau_0 \frac{(1-n)}{S\Gamma(2-n)\Gamma(1+n)} \times (t^n - H(t-t_0)(t-t_0)^n) . \quad (13)$$

It can be seen that the creep strain should not reach a steady value in finite times. Also, a complete recovery ( $\gamma_\infty = 0$ ) is predicted for infinite times. Thereby, the critical gel exhibits material behavior between that of a liquid and a solid.

### 3. Experimental

#### Materials

For an experimental test of the predictions of the Gel Equation for finite strains, we need to prepare chemically stable samples near the gel point. An ideal candidate for these purposes is the well-characterized network polymer system [12] consisting of a linear, telechelic, vinyl-terminated polydimethylsiloxane (PDMS) and a four-functional crosslinker, tetrakis (dimethylsiloxy) silane. Both components were obtained from Petrarch Systems. The hydrosilation reaction [13] was first catalyzed by dichlorobis (diethylsulfide) platinum (II), and then stopped by poisoning the catalyst. Details of the chemistry are given by Chambon [14], and are summarized here. The PDMS

prepolymer was first heated to 140°C for 14 h under vacuum to remove about 0.6 wt.% of low molecular weight impurities. The PDMS had a number average molecular weight  $\bar{M}_n$  of 10000, as reported by Venkataraman et al. [12], and a polydispersity of about 2.9. The silane crosslinker had an effective functionality of  $3.99 \pm 0.02$  [4]. The catalyst was used as a solution in toluene at concentrations of  $8 \times 10^{-5}$  mol platinum/mol vinyl. The catalyst poison used was tetramethylethylenediamine (TMEDA) [14] in the form of a 0.6 molar solution in toluene.

This particular system was chosen for a number of reasons: a) the individual components are well characterized, b) the kinetics of the catalyzed reaction can be controlled easily at room temperature, c) the crosslinking reaction can be stopped at any intermediate extent of reaction, d) side reactions are negligible at low temperatures, and e) there are no competing effects of phase transitions or vitrification throughout the reaction. In short, this can be considered to be a model network polymer system.

To understand more about the effect of large deformations on the properties of a critical gel, dynamic and steady shear experiments have been conducted on a set of stable samples, in which the crosslinking reaction has been stopped close to the gel point. By using chemically stable samples, we avoid the possible competing effect of flow on the reaction kinetics. A set of removable fixtures was designed and built to enable rheological experiments directly on the cast samples. This is described in greater detail in the next section.

#### Sample preparation

The crosslinking polymer was cast, as shown in Fig. 1, on the lower fixture of the rheometer. The open, upper surface of the sample was kept flat by means of a close-fitting ring around the lower fixture, thereby forming a cup into which the polymer could be poured, and allowed to react. The sample was allowed to react at a constant temperature, typically 35°C. This temperature was chosen so as to avoid the effect of unwanted side reactions [12, 15] at higher reaction temperatures. The reaction was stopped at different extents by spraying the upper, open surface of the sample with the catalyst poison, tetramethylethylene (TMEDA). The stable, non-reacting samples obtained in this manner were then directly mounted in the rheometer. Great care was taken at this stage to keep the delicate sample intact, and avoid any extraneous forces. Rheological characterization commenced once the upper-plate fixture was lowered to contact the free surface of the sample, and the ring pushed down to leave the sample held between the two fixtures.

#### Equipment used

Oscillatory shear measurements were conducted on a Rheometrics Dynamic Spectrometer model RDS-7700, and also on a Rheometrics Mechanical Spectrometer model RMS-800. Measurements of creep under a constant shear stress and viscoelastic recovery after the cessation of shear were conducted on a Rheometrics Stress Rheometer (RSR). Startup of shear flow at a constant shear rate and stress relaxation measurements were conducted on the RMS-800 also. It should be noted that removable fixtures were used

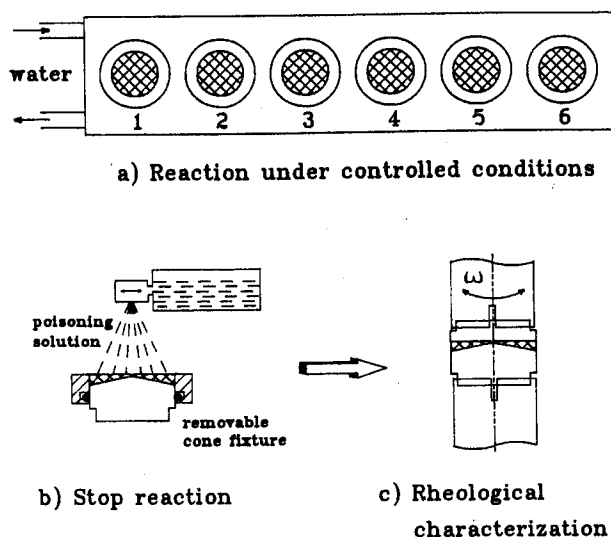


Fig. 1. Molding of the samples directly on the removable fixtures of the rheometer and stopping the reaction at intermediate stages

in all three instruments, in order to enable transfer of the samples from one instrument to the other. This was also necessary to ensure direct comparison of the transient shear data obtained from different instruments.

Typical sample geometries used were: a) parallel-plate geometry with 25-mm-diameter disks 0.6–1.0 mm thick, and (b) cone-and-plate geometry using 25-mm-diameter disks and a cone angle of 0.1 rad. Parallel-plate geometry was used only for the experiments conducted well within the linear viscoelastic region; cone-and-plate geometry was used for the bulk of the experiments in this study to ensure that the material experienced a uniform shear field.

#### 4. Shear experiments

The effect of shear strain has been studied by starting with the linear viscoelastic behavior at small strains, then extending the shear into the finite strain region, and finally studying the material changes taking place under the influence of large strains. The linear viscoelastic behavior is well understood and will not be dealt with in detail here. This study is mainly concerned with the behavior of critical gels at intermediate and large shear strains. Each of these two levels is discussed in greater detail below.

##### *Behavior at finite shear strain*

Only samples, in which the chemical reaction was stopped very close to the gel point, are selected because that is where the predictions of the Gel Equation can be expected to hold. This is ensured by first conducting a dynamic mechanical test on each of the

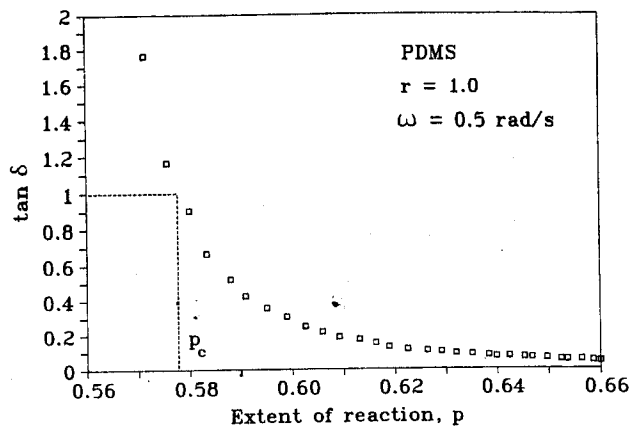


Fig. 2. Evolution of dynamic mechanical properties near the gel point. The loss tangent  $\tan \delta$  is plotted as a function of the extent of reaction  $p$  as measured by FTIR

stable samples to determine the state of their evolution with respect to the gel point. Controlled rheological experiments are then conducted on the stable samples, and the measured stress and strain are compared to the predictions, as discussed in an earlier section of this paper.

Because each set of experiments requires a new sample, and the extent of reaction varies slightly from sample to sample, the linear viscoelastic response of each sample is compared with Fig. 2. The data of Venkataraman et al. [12] is recast in this form to illustrate the dramatic changes taking place in the mechanical properties in the vicinity of the gel point. As can be seen, the loss tangent,  $\tan \delta$ , at a fixed frequency ( $\omega_0 = 0.5$  rad/s here) changes rapidly near the gel point (GP), and is a very sensitive screening tool. Only those samples with extent to reaction  $p = p_c \pm 0.01$  were considered for the comparison between the predictions and the experimental data, but the effect of large strains was considered over a wider range. The linear viscoelastic response of four representative samples is shown in Fig. 3, in terms of the storage modulus  $G'(\omega)$ .

*a) Startup of shear flow:* In a startup-of-shear-flow experiment, the shear stress  $\tau_{12}$  and first normal stress difference  $N_1$  were measured as a function of the shear time at prescribed shear rates  $\dot{\gamma}$ . Figure 4 shows the experimental data for a sample near the gel point that was sheared at  $\dot{\gamma} = 0.5$  s<sup>-1</sup>. Both  $\tau_{12}$  and  $N_1$  evolve in power-laws with time. An easier quantity to follow, the ratio  $[N_1/\tau_{12}\dot{\gamma}]$  can be clearly seen to be close to linear with time, up to strains of about 2 shear units. A marked deviation from linear behavior can be observed at higher strains. This is due to some

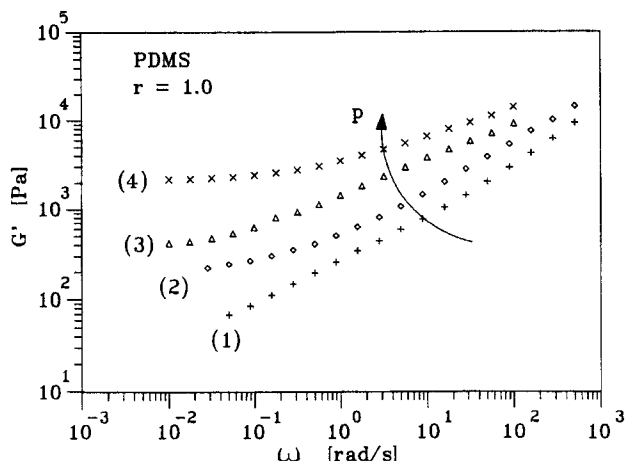


Fig. 3. Storage modulus for four samples with increasing extent of crosslinking beyond the gel point

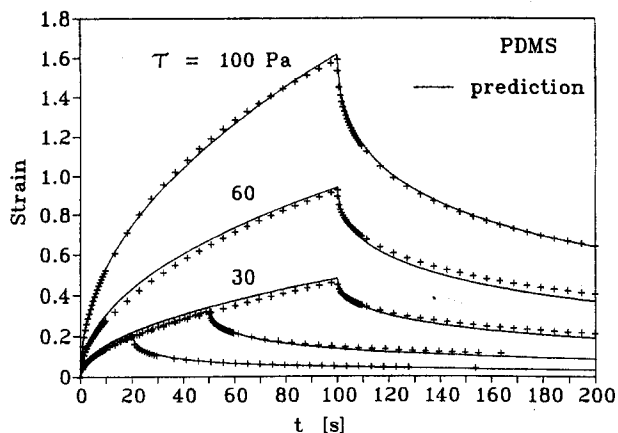


Fig. 5. Measured shear strain during creep under a constant shear stress and viscoelastic recovery after the cessation of shear for PDMS near the gel point. The solid lines are predicted by the Gel Equation for finite strain

change in the fragile network structure, and will be explained in greater detail in the following section. The value of the relaxation exponent  $n$  calculated from the intercept of this curve, agrees extremely well with that obtained from the dynamic mechanical experiment conducted earlier on the same stable sample. Therefore, the proposed constitutive equation predicts the stresses ( $\tau_{12}$  and  $N_1$ ) in a startup of shear.

*b) Creep and recovery behavior:* In a creep-and-recovery experiment, the shear strain during creep under a constant shear stress and the viscoelastic recovery after the cessation of shear are monitored as a function of time. In the first series of experiments,

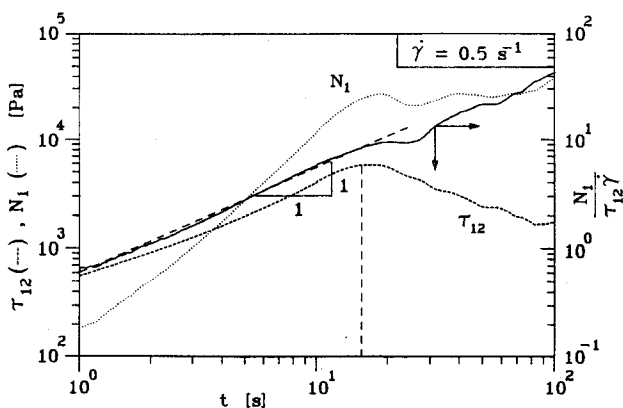


Fig. 4. Shear stress and first normal-stress difference during a start-up of shear flow at a constant rate  $\dot{\gamma} = 0.5 \text{ s}^{-1}$  for PMDS near the gel point. The dotted line is predicted by the Gel Equation for finite strain. The critical strain value for network rupture is the point at which the shear stress attains a maximum value

the shear stress  $\tau_0$  was kept constant at 30 Pa, and the creep time  $t_0$  was varied. The sample was allowed to recover fully before the commencement of the next creep experiment. The experimental data from three consecutive experiments on a sample very near the gel point, with creep times of 20, 50, and 100 s, is shown in Fig. 5. In the second series of experiments on the same sample, the creep time was kept constant at 100 s, and the shear stress was increased from 30 to 60 Pa, and then to 100 Pa. The experimental data is again shown in Fig. 5. An excellent agreement is seen with the predicted strain using values of the parameters  $S$  and  $n$  from the dynamic mechanical measurements conducted on the same sample. The agreement between the predictions and the experiments extends to strains of about 2 shear units.

When the creep-and-recovery experiments are repeated at increasingly higher stress values, to attain increasingly higher shear strains on the polymer samples, abruptly non-linear creep response is seen above some critical stress value. This phenomenon can be clearly observed in the representative set of creep compliance curves plotted in Fig. 6. At low stress values, increasing the applied stress has no effect on  $J(t)$ , indicating that the deformation was in the linear range.  $J(t)$  deviates from linear behavior above a critical stress value. This can be attributed to mechanical rupture of the fragile network structure near the gel point, causing the material to deform more easily.

The extent of damage of the network structure can be evaluated by conducting another small amplitude oscillatory shear experiment on the same sample after

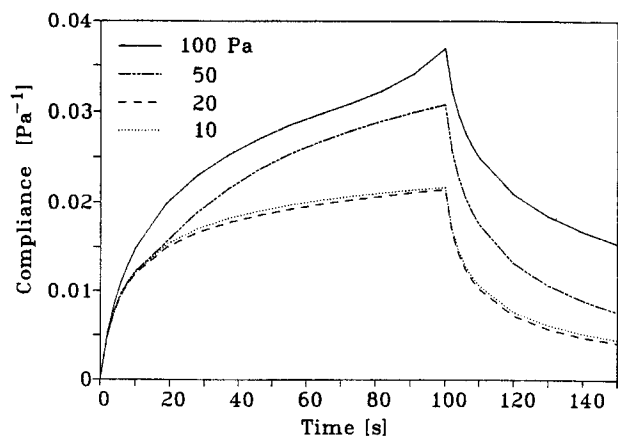


Fig. 6. Deviation of the creep compliance from linearity during successive creep-and-recovery experiments at increasing stresses on PDMS near the gel point

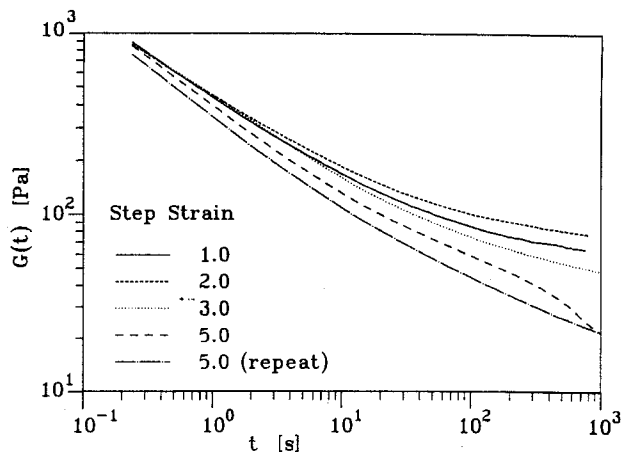


Fig. 8. Estimation of the critical strain for network rupture from stress-relaxation experiments after large-step shear strains

the large-strain experiments. Figure 7 compares the linear viscoelastic response of the material before and after the imposition of large strains. It can be seen that while the material originally behaved like a typical viscoelastic solid, it later behaves like a critical gel, where the complex moduli exhibit a power-law dependence on the frequency of oscillation. Therefore, the breakage of the network structure causes an apparent reversal of the gelation process in this stable sample. A mechanical gel point could possibly be defined, independent of the chemical gel point, which then depends on the kinetics of the crosslinking reaction, and on the mechanical treatment.

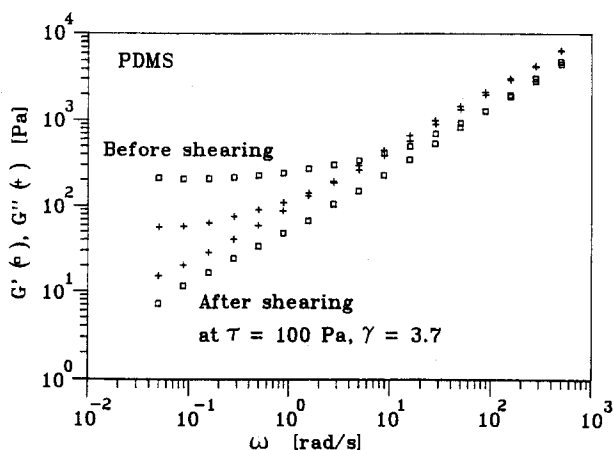


Fig. 7. Storage and loss moduli of the sample before and after the imposition of large shear strains. The material behavior, in this case, proceeds from that of a viscoelastic solid to that of a critical gel

#### Critical strain for network rupture

The large-shear-strain experiments indicate that the network rupture takes place above some critical strain measure. This critical strain measure is difficult to estimate using the creep-and-recovery experiments, where the shear stress and shear time are prescribed before the onset of the experiment. Therefore, the critical strain value for network rupture has to be estimated using other techniques, where the strain level can be controlled. Some of these are detailed below.

*a) Startup of shear flow:* Shear stress  $\tau_{12}$  and first normal-stress difference  $N_1$  were measured as a function of the shear time at a constant shear rate  $\dot{\gamma}$ , as shown in Fig. 4. As before, at low strain levels, both  $\tau_{12}$  and  $N_1$  had power-law relationships with time. As the strain level was increased, deviations from the power-law behavior could be observed.  $\tau_{12}$  was seen to peak at some critical strain level and then decrease. This value of the critical strain for network rupture was in the same range as in the creep-and-recovery experiments. Direct comparison was not possible, as independent samples need to be used for each experiment, since they were destroyed during the experiment. Also, the strain level is not controlled directly in the creep-and-recovery experiments.

*b) Stress relaxation after large-step shear strains:* The relaxation modulus  $G(t)$  of a material can be measured in a step-strain experiment, in which an instantaneous step-shear strain  $\gamma_0$  is imposed on the material, as shown in Fig. 8. At low strain levels,  $G(t)$  is independent of the strain and is a characteristic material quantity. Deviations from linearity can be seen at higher strain levels, where network rupture takes

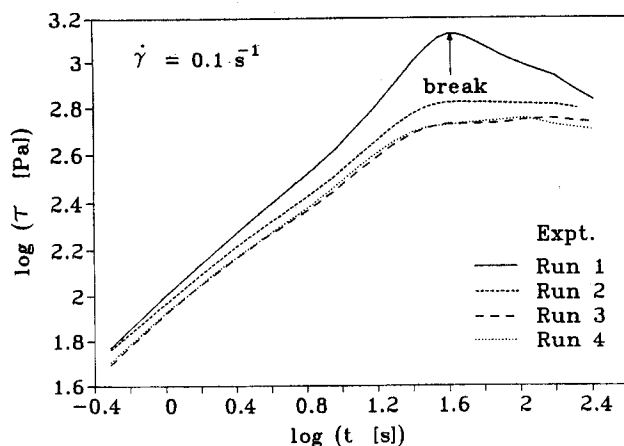


Fig. 9. Shear degradation of the network in a startup of shear flow at  $\dot{\gamma} = 0.1 \text{ s}^{-1}$ . Repeated deformations to  $\gamma = 14$  show no further decrease in  $\tau_{12}$

place. Also, repeated experiments at the higher strain levels indicate that the material settles into a new equilibrium state at each  $\gamma_0$ .

Data from all the different shear experiments indicate that the Gel Equation for finite strains accurately predicts the material response up to strains of about 2 shear units. Increasing the shear strain above this level causes the network to rupture, drastically changing the linear viscoelastic behavior. Significant changes in the small amplitude oscillatory shear behavior, as shown in Fig. 7, are observed independently of the actual deformation technique used to apply large strains. This shows that the experimental data is consistent and the changes observed in the material behavior are systematic.

The effect of network rupture on the linear viscoelastic properties of the material has been observed to be insensitive to the actual deformation path of the sample. The controlling factor appears to be the level of shear strain applied. This observation has been substantiated by applying repeated deformations on a single sample, as shown in Fig. 9. The sample was sheared in a startup of shear flow, and an evolution in the shear stress  $\tau_{12}$  similar to that in Fig. 4 can be observed.  $\tau_{12}$  reaches a peak at  $\gamma \approx 4$  and then decreases. The sample was allowed to relax fully between experiments in order to erase the effects of previous shear history. On repeated deformations to  $\gamma = 14$ ,  $\tau_{12}$  can be observed to increase at low shear strains, but then level off at the same stress. This indicates that no further degradation of the network takes place. Further degradation is possible, however, by increasing the level of shear strain. In this manner,

it is possible to change the linear viscoelastic response of the material from a viscoelastic solid to that of a critical gel, and further down to that of a typical viscoelastic liquid, as shown in Fig. 10.

The large-strain experiments to cause network rupture have been repeated on several different samples with increasing extents of reaction. Figure 11 shows that the shear stress at network rupture increases with the extent of reaction, the polymer does not deform as easily when the strands are more densely crosslinked. Because the extent of reaction could not be measured directly, the value of the complex modulus,  $G^*$  at a frequency  $\omega = 0.01 \text{ rad/s}$  was chosen to be representative of the state of the sample. The open symbols denote the highest stress for a linear response in a series of creep experiments to 100 s on each sample; the filled symbols represent the stress applied to obtain a clearly nonlinear response. Network rupture, therefore, occurs somewhere between these two stresses.

#### Effect of large strains on the relaxation exponent

The breaking of the network by large strain does not reverse the gelation process in the sense that the polymer is brought back to earlier crosslinking states. This can be seen on the relaxation exponent of the polymer network. In Fig. 12, the effect on a stable, non-reacting sample, in which the reaction has been stopped a little past the gel point, can be seen. Before breaking, this sample exhibited the typical dynamic mechanical behavior of a viscoelastic solid. Increas-

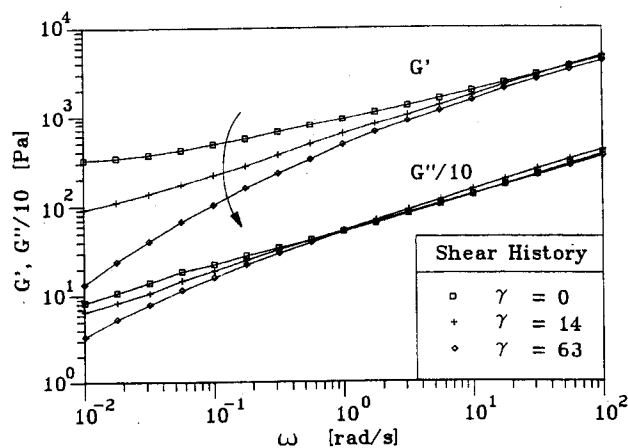


Fig. 10. Effect of increasing levels of shear on the storage-and-loss moduli of a typical sample. The rheological behavior of the stable sample changes from a viscoelastic solid to a critical gel, and then to a viscoelastic liquid, by the application of shear.  $G''$  has been shifted down to avoid overlap

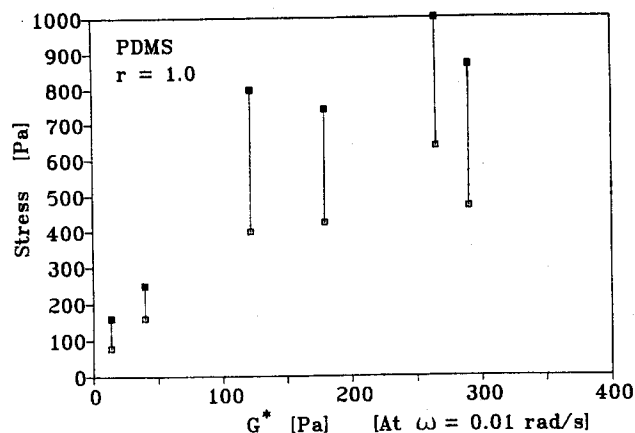


Fig. 11. Stresses imposed during a series of creep-and-recovery experiments on a set of samples with increasing extents of reaction. The open symbols denote the highest stress imposed for a linear response; filled symbols denote nonlinear response

ingly large-shear strains were then applied, until non-linear behavior, as in Fig. 6, could be seen. After shearing with 10 shear units, the dynamic mechanical behavior of the sample was already markedly different. Power-law relaxation behavior now governed the entire experimental window of four decades in frequency. The relaxation exponent  $n$  was now 0.36, while it was found (in a separate experiment on a similar sample) to be 0.5 when crosslinking in a quiescent state and stopping the reaction at the gel point. The value of the relaxation exponent was therefore decreased by the flow. This is not unexpected, because the effect of the deformation has been to cause the gelation to occur at later times, thereby decreasing the value of the exponent. As a direct consequence, the strength of the network at the gel point  $S$  is increased.

The relaxation exponent is related to the distribution of cluster sizes in the material. The effect of a shear force on a cluster of molecules is directly proportional to its size. The larger clusters are broken up into smaller ones by the application of shear forces, changing the overall distribution and therefore the relaxation behavior. This is manifested by the change in the relaxation exponent. This behavior is similar to that of micro-networks studied by Antonietti et al. [16], where relaxation exponents between 0.2 and 0.5 are reported. In our case, shear breaks the larger clusters into smaller ones. Breaking is assumed to occur preferably at regions of low-crosslink density. This could create the so-called microgels, which can still be crosslinked into a network at later stages in the reaction.

### Bond dissociation energies

It can be surmised that the non-linear behavior of the network at large strain levels is due to the cleavage of molecular strands in the network. This cleavage may occur by the dissociation of certain bonds in the backbone of the network, thereby decreasing the ability of the network to transfer forces through it. The backbone chains in this case are comprised of C-C, C-Si, and Si-O bonds only. These will be the only bonds affected by the large deformations. The various bond dissociation energies are given by Walsh [17] to be 88 kcal/mol and 89.4 kcal/mol for the C-C and C-Si bonds, respectively, and 128 kcal/mol for the Si-O bond dissociation. Because the Si-O bond-dissociation energy is significantly higher than either the C-C or the C-Si bond-dissociation energies, the probability of chain cleavage occurring at these sites (Si-O sites) is low. All the breaking is assumed to occur at either the C-C or the C-Si bonds.

The energy input per unit volume during a shear formation is given by:

$$e = \int_{t'}^t \tau(t) : \dot{\gamma}(t'') dt'' \quad (14)$$

In a creep experiment at a constant stress  $\tau_0$ , this reduces to:

$$e = \tau_0 \gamma_{\max} \quad (15)$$

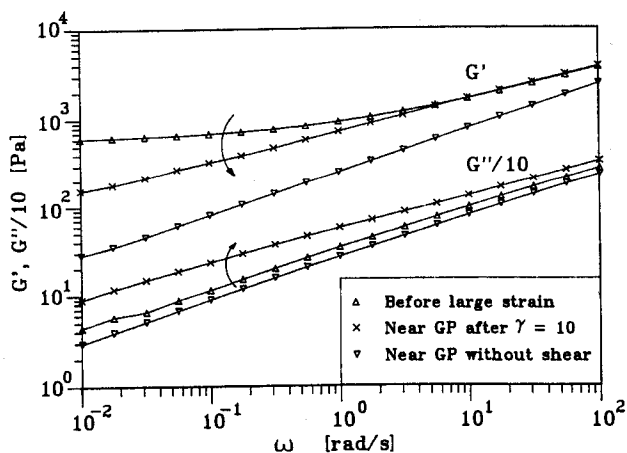


Fig. 12. Reversal of the gelation process has a significant effect on the relaxation behavior. The top curve ( $\Delta$ ) shows a sample, which was crosslinked beyond the gel point. It is a solid. A shear of 10 units transforms the network into a critical gel ( $\times$ ). However, this critical gel is different from the critical gel, which was formed during the initial sol-gel transition when crosslinking in the quiescent state ( $\nabla$ ). The exponent  $n$  is seen to decrease from 0.5 to about 0.4 after the imposition of a strain of 10 shear units



where  $\gamma_{\max}$  is the maximum strain imposed during the creep experiment. In viscoelastic materials at low-strain levels, this energy for deforming the material is partially recoverable. At higher strain levels, part of the energy is also used in dissociating bonds, and is therefore not immediately recoverable. A measure of this dissociation energy can be obtained as the difference between the actual energy input during the deformation in a creep experiment and the energy required for a pure deformation at the same stress level. An upper estimate for the number of bonds dissociated by this extra energy can then be calculated from the known bond-dissociation energy is known. For example, in a typical set of creep-and-recovery experiments, the deformations at all stresses up to 400 Pa were seen to be linear. At 400 Pa, a strain of 3.44 was obtained after deforming for 100 s. The first non-linear creep response was observed at 800 Pa, where a strain of 11.42 was obtained at 100 s. For a purely linear response, the strain should only have been 6.88. The extra energy input during the deformation is about:

$$e = 800(11.42 - 6.88) = 3.64 \times 10^3 \text{ J/m}^3 .$$

This energy is used for network rupture, and the number of bonds broken can be calculated.

It is reasonable to assume that only those strands that are part of a permanent network (elastically effective strands) will be forced to stretch, and later break, by applying a large deformation. This will necessitate the formation of three- and four-functional junction points in the network. Using the recursive theory of Macosko and Miller [18], the number of three- and four-functional junctions in the material at any extent of reaction can be calculated, because this polymer system has been shown earlier to be a model system [12]. The fraction of these junctions that are broken due to a non-linear deformation can then be calculated. It was found that for a typical sample near the critical extent of reaction, the breakdown of even 0.01% of the bonds is sufficient to cause a dramatic change in the dynamic mechanical behavior. The number would be even smaller as a fraction of all the possible junction points. This demonstrates the sensitivity of dynamic mechanical techniques to small changes in the molecular structure of polymers.

The rupture of the crosslinking network by shear creates free radicals. The presence of free radicals can be detected by electron spin resonance (ESR) spectroscopy, but their number is difficult to estimate experimentally. These free radicals can recombine over

time, releasing the energy used for bond dissociation. However, the recombination of the broken bonds depends on the ability of the network strands to diffuse towards each other which is hindered to a great extent by the crosslinks. Samples that have been subjected to large strains were observed to partially (but not fully) recover their structure over a period of 48 h, as manifested by their linear viscoelastic response.

## 5. Conclusions

The crosslinking PDMS at the gel point, the critical gel, has been shown to exhibit power-law relaxation behavior, not just in the linear viscoelastic region, but also at finite shear strains up to about 2 shear units. The validity of the power-law relaxation modulus at the gel point has been confirmed by several independent rheological measurements: creep-and-recovery, startup-of-shear-flow, and stress-relaxation.

Critical gels can also be prepared by crosslinking a polymer beyond the gel point and then breaking it by applying large strains. A suitable strain has to be chosen so that the material is transformed to the critical gel. The power-law exponent of the critical gel is lower (higher front factor  $S$ ) than that of the virgin critical gel (see Fig. 12).

Large shear strains ( $\gamma > 2$ ) have been found to irreversibly alter the network structure of the crosslinking polymer. For crosslinking during flow, this results in a mechanical delay of the gelation process. The rheologically altered gel point of the polymer occurs at a higher extent of reaction than if allowed to react in a quiescent state. The relaxation exponent  $n$  at the gel point is shifted towards lower values. Such a change was expected, because the breaking of network bonds affects the distribution of molecular cluster sizes, which is directly related to the relaxation exponent. It should be emphasized that these relatively small strains (compared to those in typical processing flows) have a drastic effect on the rheological behavior of the crosslinking polymer network. This is due to the extremely large molecular clusters formed during gelation.

It is not surprising that the networks rupture when subjected to large deformations, but the linear viscoelastic response of the broken networks brings to light possible applications. The material properties can be controlled, not just by the chemistry, but also by the processing, to suit the need of specific applications. For example, by causing a viscoelastic solid to attain the linear viscoelastic material behavior of a critical gel, we have created a new material that has

the rheological properties of a critical gel, but with increased strength. Such materials find increasing application as adhesives, damping materials, sealants, superabsorbers and catalyst supports.

Large shear strains on the fragile network structure near the gel point can also be expected to affect the mechanical properties of the fully cured network. For example, the tenuous network structure may be broken down by processing flows, resulting in a final product with a lower modulus. The resulting network is more lossy (damping material) than originally prescribed by the stoichiometry of the components, due to the presence of a greater number of dangling ends. This effect needs to be accounted for during the material and process design.

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