

Final Report

AMERICAN PETROLEUM INSTITUTE
PRAC PROJECT 82-45
RHEOLOGICAL CHARACTERIZATION OF FRACTURING FLUIDS

by

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Dr. John Cameron, API Steering Committee Vice-Chairman

I. INTRODUCTION

This is the final report on our research conducted under the American Petroleum Institute's PRAC Project 82-45 entitled "Rheological Characterization of Fracturing Fluids". The project was initiated by the American Petroleum Institute (API) because: 1) the expense of hydraulic fracturing makes it desirable to understand the process fully, including the rheology of the fracturing fluid, to ensure a successful fracturing operation, and 2) during a round-robin testing program by several laboratories the viscosities reported by the participants for identical gel formulations varied by 1000%.

The purpose of this report is to provide a working guide to rheology of guar gels. We first provide, in Section II, a summary of the significant results and conclusions from the first year of this investigation. In Section III dynamic oscillatory shear measurements, which are used to study guar rheology and guar gel structure, are described. Dynamic oscillatory shear measurements can be directly related to the number of network crosslinks. These measurements and their interpretation are discussed in detail, since they are probably less familiar to researchers in the oil production research area than are steady shear measurements. In Section IV we describe the rheological instruments used in this study. In Section V the preparation of guar samples is detailed. The composition of the model guar gel used in this study was specified by the API Steering Committee. Our observations on the factors controlling gel rheology, including chemical effects, sample preparation effects, and flow history effects are presented in Section VI. In Section VII a model that describes the rheology of gelling fluids is described. The model is based on the temporary network theories used to describe the rheology of polymer melts and solutions. To this theory we have incorporated the chemical kinetics of metal ion adsorption onto the guar polymer backbone and subsequent polymer-polymer crosslinking. In the final sections recommendations for rheological instrumentation and for future research are presented.

At the quarterly meetings with the API Committee overseeing this work several hundred pages of experimental data were distributed. All of that data are not included in this report. Rather the important conclusions drawn from those data are presented along with the relevant data that support those conclusions. The original data are on file with the API publications department and can be obtained through the API.

II. SUMMARY OF CONCLUSIONS

Dynamic oscillatory and steady shear measurements have been used to study the rheology of guar gels. Dynamic oscillatory measurements have been used to study the slow hydration of guar polymer and the effects of chemical composition and mixing on guar gel structure. Steady shear measurements have been used to simulate process conditions. Major conclusions, presented in the body of this report, include the following:

- Results from polymer kinetic theory can be used to relate the measured storage modulus, G' , to the crosslink density in the guar gel.
- Aged titanate solutions produce gels with lower values of G' ; and therefore, dynamic oscillatory measurements can be used to quantify titanate reactivity.

- Adding diketone (that is, acetylacetone) to modify the rate of reaction does not just slow down the reaction, but it also prevents the gel from crosslinking to the same extent at room temperature as gels without added acetylacetone.
- Mixing is shown to play a crucial role in the development of gel structure. Poor mixing appears to produce microscopically inhomogeneous gel networks that have higher levels of elasticity than homogeneous gels.
- To produce intimately mixed fluids we have developed a novel impingement mixing device.
- Measurements of the steady shear viscosity of gels indicate that wall slip is occurring. However, conventional rheological techniques for calculating wall slip velocities have given contradictory results. There is a need for direct measurements of velocity fields in shear flow to clarify the mechanism of wall slip. In the next year we will be conducting laser doppler measurements to address this problem.
- Under quiescent conditions dynamic oscillatory measurements show that the guar continues to crosslink over a time scale of about 15 minutes. The steady shear measurements show that shear increases the rate of reaction.
- A novel network theory coupled with chemical reaction kinetics is proposed; material functions can be expressed analytically. This model provides a framework for modeling and predicting rheological properties of reacting gels.

III. RHEOLOGICAL MEASUREMENTS

A. Dynamic Oscillatory Measurements

Dynamic oscillatory shear experiments, which measure the linear visco-elastic response of materials, are acknowledged to be the most valuable probes of gel or network structure. Though steady shear measurements are necessary to duplicate process conditions, the oscillatory measurements give more insight into the properties of the gel than do steady shear measurements. When interpreted using classical network theory, linear viscoelastic measurements can be used to determine the kinetics of gel formation, the crosslink density of a gel, or the shear degradation of gel structure. The gelation of polyvinyl alcohol and gelatin gels has been studied by a number of researchers (1,2,3), and at Princeton we have used these measurements to study polyacrylamide gels used as permeability control agents in enhanced oil recovery (4,5). For an introduction to the field of linear viscoelasticity the reader is referred to the text by Ferry (6).

In a linear visco-elastic measurement an oscillatory shear strain, $\gamma(t)$, is imposed on a sample,

$$\gamma(t) = \gamma_0 \sin \omega t \quad . \quad (1)$$

where γ_0 is the maximum value of the strain.

Experimentally this is accomplished by placing a sample in a cone and plate geometry, a parallel plate geometry, or between concentric cylinders in a Couette geometry, and then imposing a torsional oscillation on one plate, cone, or cylinder. The resulting stress on the stationary plate, cone, or cylinder will oscillate with the imposed frequency ω , but will be out of phase with the forcing oscillation. The measured stress can be factored into two components, one in phase with the displacement and one 90 degrees out of phase with the displacement:

$$\tau(t) = \gamma_0(G' \sin \omega t + G'' \cos \omega t) . \quad (2)$$

The in-phase stress defines a storage modulus G' that gives information about the elasticity and network structure, whereas the out-of-phase component defines a loss modulus G'' that gives information about the viscous or dissipative properties of the fluid. The frequency and strain dependence of the storage and loss moduli, G' and G'' respectively, provide information about the state of the fluid. For an uncrosslinked guar solution both G' and G'' decrease with decreasing frequency, with G'' lying above G' . As a gel crosslinks G' rises until it is horizontal--independent of frequency. As an example, this progression is shown in Fig. 1 for the gelation of a polystyrene/carbon disulfide solution as temperature is decreased. As we will show in Section VI, G' can be monitored as the amplitude of the strain deformation is increased. If strain destroys the network structure, then G' will decrease with increasing strain.

Classical network theory (7) shows that G' , in the low frequency region where G' is independent of frequency, is proportional to the number density of crosslinks in the gel:

$$G' = g n k T + G_e \quad (3)$$

where g is a constant of order one, n is the number density of crosslinks, k is the Boltzmann constant, T is the absolute temperature, and G_e is a contribution to the modulus from molecular entanglements. For aqueous gels G_e is very small. It is possible to follow the kinetics of gel formation by taking the time derivative of Eq. 3:

$$\frac{dn}{dt} = \frac{1}{kT} \frac{dG'}{dt} \quad (4)$$

Likewise, the destruction of gel structure by shear can be monitored by measuring G' after exposure to steady shear. The results can be interpreted in terms of the breakdown in the number of crosslink points.

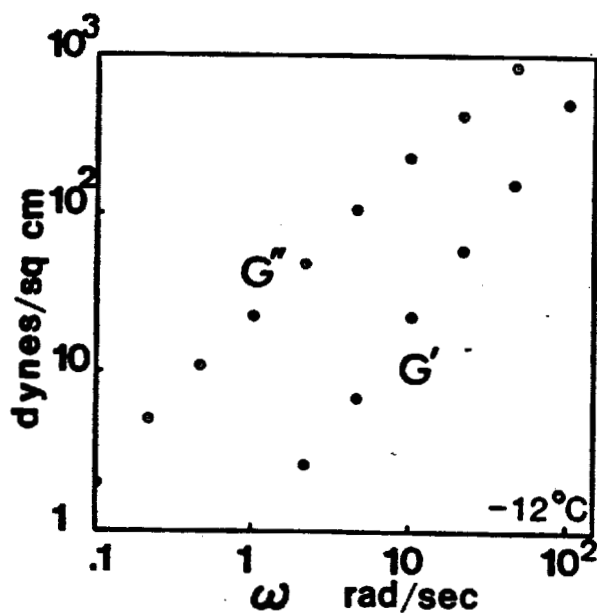


Fig.1a.

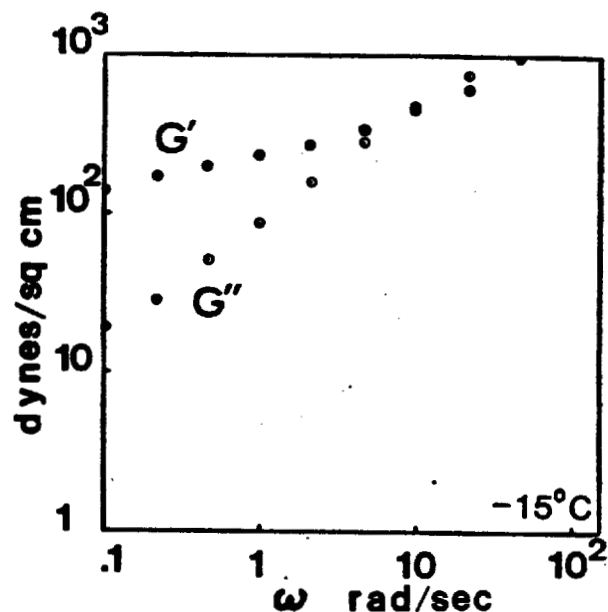


Fig.1b.

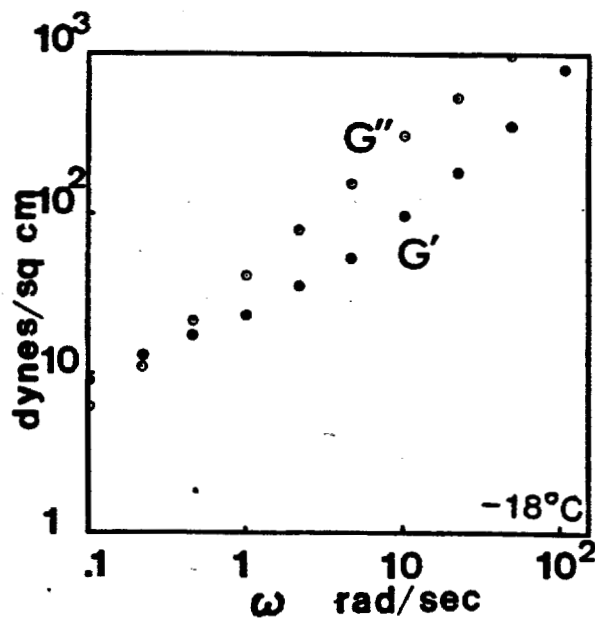


Fig.1c.

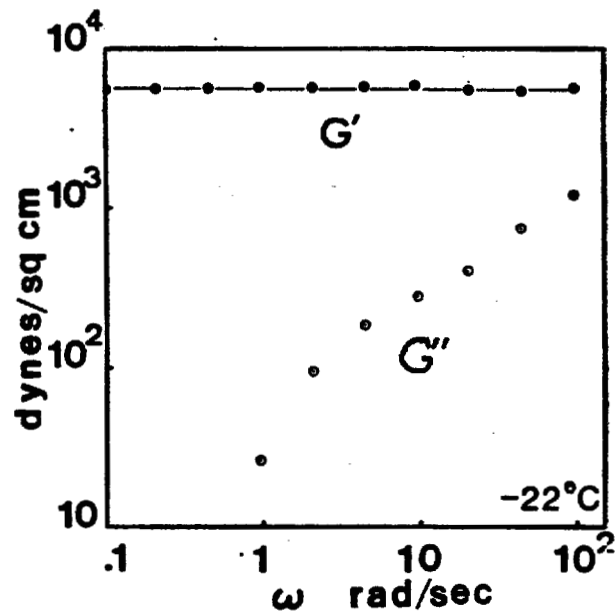


Fig.1d.

Fig.1a-d. Storage (G') and loss (G'') moduli as a function of frequency of a 9.5 wt. % polystyrene (900,000 molecular weight) in carbon disulfide solution at temperature as indicated in each figure and run between parallel plates at 3% strain.(Clark, et.al., Polym Preprints 24,87(1983)).

IV. EQUIPMENT

A. Rheometrics System IV Rheometer:

Most of the measurements reported here were conducted on our Rheometrics Inc. System IV rheometer (Rheometrics, Inc., Piscataway, NJ). This state-of-the-art instrument shown in Fig. 2 has several motor and transducer options. The instrument is fully automated and all data acquisition and manipulation is under computer control. For measurements with the Fluids Transducer a circulating water bath is available with a temperature range from -20°C to 80°C .

For most of the guar solution measurements a Fluids Transducer with a 10 g-cm maximum torque and 100 g maximum normal force was used. This Fluids Transducer allows steady shear measurements of fluid viscosity, dynamic oscillatory shear measurements, and, with a some modification to the drive unit, steady shear followed by oscillatory shear. For polymer solutions and gels the range of frequencies and shear rates over which measurements can be made is usually determined by the minimum torque range of the transducer (about 1/1000 to 1/500 of the maximum torque). Frequencies from 0.01 to 100 rad/s are accessible and steady shear rates from 0.01 to 10,000 s^{-1} . The Fluids Transducers can be run with cone-and-plate, parallel plate, or Couette geometries.

For dynamic oscillatory measurements on guar gels the 10 g-cm transducer is ideal; however, the torque range of this transducer is quickly exceeded if steady shear measurements are attempted on gels. Therefore, for the bulk of the gel measurements a Fluids Transducer with a 100 g-cm torque range was used.

For our System IV rheometer we have a high temperature and pressure cell that allows measurement of fluid viscosity and dynamic moduli under pressures to 450 psi and temperatures to 300°C . However we generally found it more convenient to perform high temperature measurements on a Rheometrics Pressure Rheometer, described below, rather than on our System IV.

B. Rheometrics Inc. Pressure Rheometer:

Measurements of gel properties at elevated temperatures were performed on a Rheometrics Pressure Rheometer located at Rheometrics Inc. laboratories in Piscataway, NJ. The instrument has a unique sealed sample chamber with a Couette geometry. Steady shear and dynamic oscillatory shear measurements over the same range of shear rates and frequencies spanned by the System IV Fluids Transducer are possible. The torque sensitivity of the Pressure Rheometer corresponds approximately to that of the 100 g-cm Fluids Transducer. It is possible to seal and pressurize the sample cell to run samples at temperatures above the normal boiling point of water. It is somewhat awkward to load and mount the sample cup -- the process takes 2-3 minutes. Modifications to allow on-line introduction of the sample to the cup have been suggested to the manufacturer.

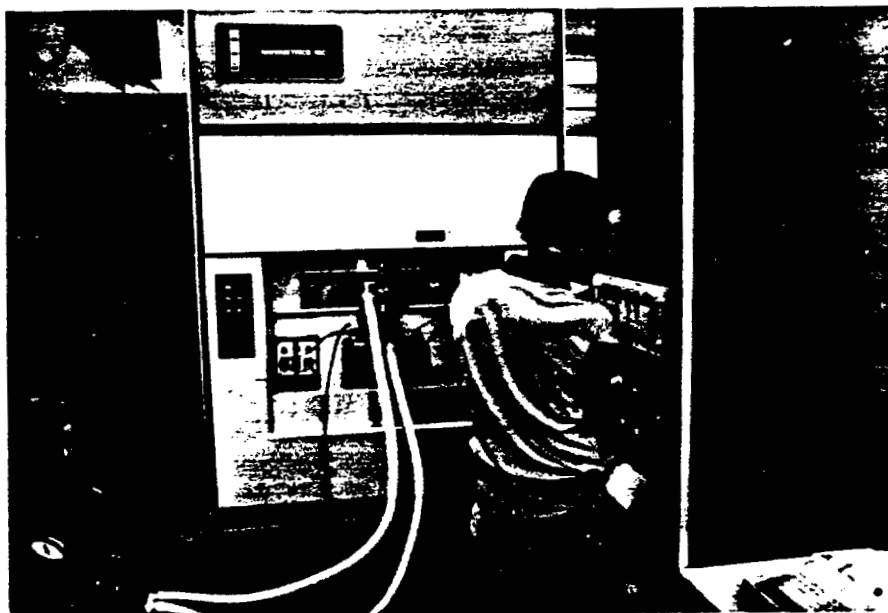


Fig.2. System IV Rheometer.

C. Impingement Mixing Device:

The homogeneity achieved during the mixing of the guar and titanate solutions and shear history of the fluid as it crosslinks determines the gel properties. The recommended procedure of mixing the guar solution and titanate solution in a blender and then transferring the preformed gel to the viscometer yields irreproducible results. This will be discussed below. To circumvent this problem, an impingement mixing device was fabricated that intimately mixes the two streams and injects them directly into the rheometer test cell (Fig. 3). The device consists of a stainless steel double acting pneumatic cylinder that is mechanically coupled to a microliter glass syringe. The pneumatic cylinder is pressurized with nitrogen at 200 psi to force guar solution in the cylinder and titanate solution in the syringe through an impingement mixing head; the mixture then flows through a packed bed mixing section. The packed bed consists of three inches of a 1/4" OD stainless steel tube packed with 24-32 mesh (0.71 - 0.50 mm) sand. During injection through the sand pack the Reynolds number is about one, based on a mean hydraulic radius for the sand pack and the viscosity of the uncrosslinked guar. The connections in the device are made with 1/8" teflon tubing. A three-way valve is used to divert fluid either to waste or to the rheometer cell. The fluid flows directly into the rheometer cell and the dynamic oscillatory measurement can be initiated even before the fluid fills the gap. The total time between the initial contacting of the guar and metal ion solutions and the start of a dynamic oscillatory experiment is on the order of 5 to 10 seconds. For a steady shear experiment the tube connecting the impingement mixer and the rheometer cup must be disconnected so that time to initiate an experiment is less than 1 minute. The schematic and parts list for the impingement mixer is given in Appendix B.

D. Capillary Viscometer:

A preliminary capillary viscometer has been designed and assembled. The shear history dependence of these gels, as shown in Section VI, convinced us that rather than making a circulating loop using a pump, a better design for our very small scale lab work would be a long capillary in which the fluid is pumped back and forth. In this way the fluid is under constant shear (excluding the short times needed to reverse the direction of the flow). The viscometer is being controlled by an IBM personal computer with a Tecmar Inc. A/D and D/A board. Further details and results on this device will be presented in future progress reports under next year's research project. The schematic of the capillary viscometer is given in Appendix C.

V. MATERIALS AND PREPARATION

The exact formulation of the guar gel was specified by the API Committee monitoring this project. Special lots of hydroxypropyl guar and Tyzor AA titanate were reserved for this study by Celanese and DuPont, respectively. The following formulation was used to produce a 40 lb/Mgal gel:

500 ml distilled water

2.4 g hydroxypropyl guar (Celanese SCN 9574)

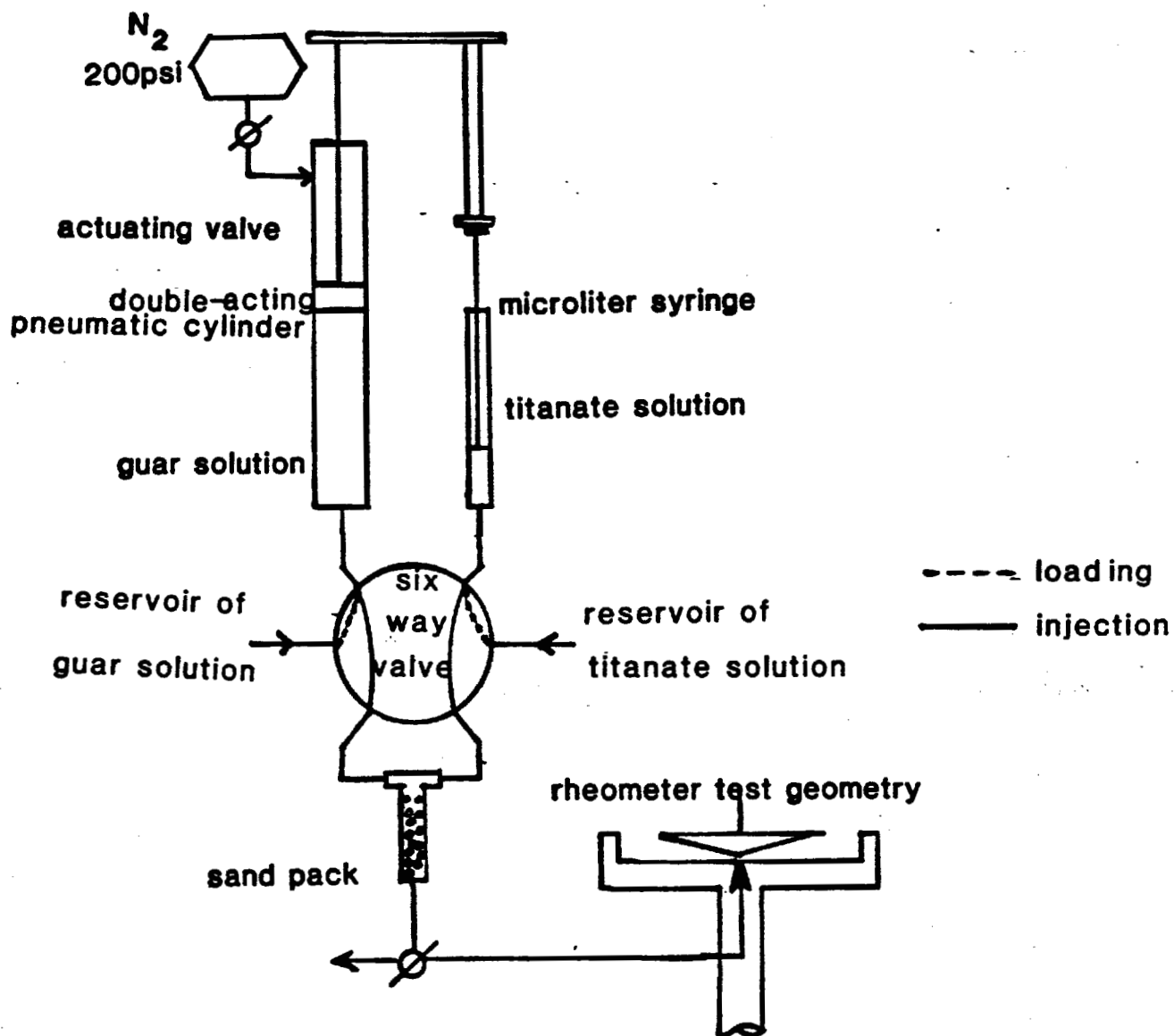


Fig.3. Impingement mixing device

- 0.6 g sodium diacetate buffer (Celanese SCN 9744)
- 10 g analytical grade KCL (Fisher lot 722797)
- 0.125 ml 25% glutaraldehyde in water (Eastman Kodak lot E11A)
- 2 ml of (9:1) solution by volume isopropyl alcohol (JT Baker) and Tyzor AA titanate (DuPont)

The base guar (without crosslinking agent) is prepared using an Osterizer blender set at low speed. A timer and variac are connected with the blender in series to control mixing time and speed. The solution is prepared in the following way. The blender, with 500 ml of water in the pitcher, is set at a low speed to produce a shallow vortex. The hydroxypropyl guar is sprinkled slowly on the free surface to produce a uniform dispersion. The potassium chloride, sodium diacetate and glutaraldehyde are quickly added. The total mixing time is three minutes. The solution is then transferred to another container and allowed to mix for about 20 hours on a low shear tumbling mixer.

To prepare crosslinked guar for rheological studies two procedures were used. During the first half year the solutions were mixed by hand, and in the last half year the impingement mixing device was used. In mixing by hand, 10 ml of base guar solution is placed in a beaker, followed by a proportional amount of Tyzor AA (diluted with isopropanol). The solution is stirred vigorously with a glass stirring rod for 30 seconds and transferred into the rheometer cup. The rheometer stage is then closed to set the proper gap and the test begins. This technique proved more reproducible than mixing the guar and titanate in a blender. The good reproducibility of dynamic oscillatory measurements for samples mixed by hand is shown in Fig. 4. However, variation in the hand mixing resulted in inadequate homogenization and time delays which caused variations in steady shear measurements. This led to our development of the impingement mixer. Subsequent studies with the impingement mixer have shown that mixing also influences dynamic oscillatory measurements (Section VI.B.1a). Because it was not possible to get the cross-sections of the guar cylinder and titanate syringe in exactly the correct ratios, extra isopropanol was added to the titanate solutions to obtain the correct titanate volume for the syringe. The added isopropanol did not affect the gelation kinetics (Section V.A.5). In all cases the Tyzor AA concentration in the final gel corresponded to that specified in the recipe above.

For experiments lasting more than about 10 minutes, the free liquid surface is covered with mineral oil to prevent evaporation. The mineral oil is immiscible in the guar solution and does not affect the torque signals. Between runs the rheometer tools are cleaned with water, followed by alcohol. Thorough cleaning is required to remove oil films or the gel will prematurely slip at the tool surfaces during measurement.

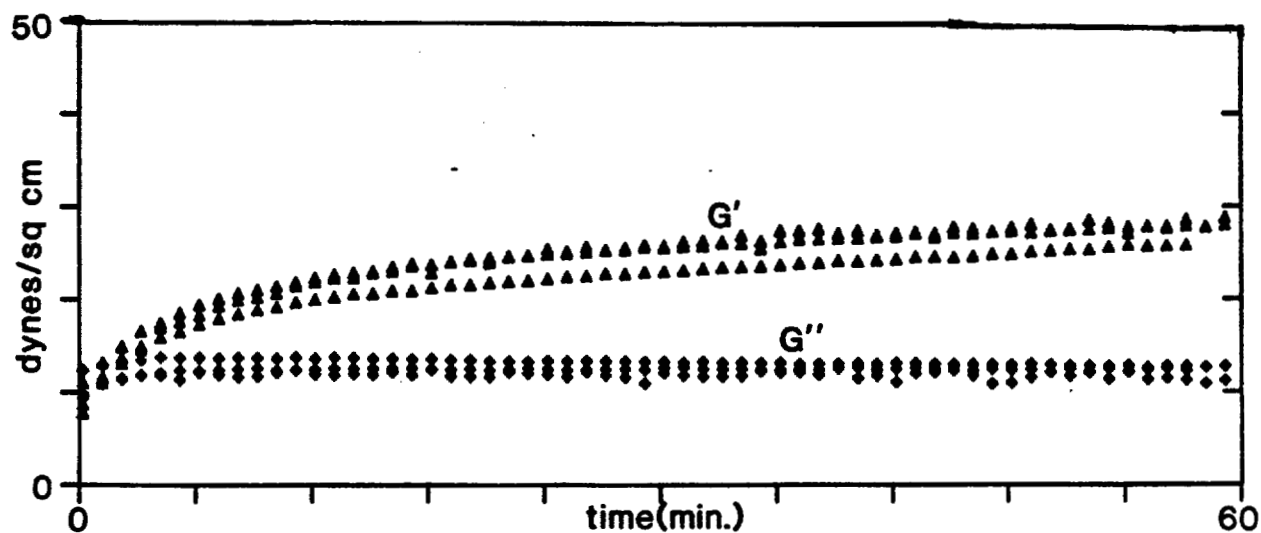


Fig.4. Test of reproducibility of gel mixing and formation at different times by different operators. Samples were .48% HP guar (G + K + N) mixed with Tyzor AA (.04%) by hand. Tests began immediately after mixing at 1rad/sec & 100% strain (runs 51983 3, 61083 4 & 61583 1).

VI. RESULTS AND DISCUSSION

The properties of guar gels depend on the chemistry chosen, the mixing of the components, and shear history of the gel. In this section we present the results of studies on these effects.

A summary of all of the measurements performed this year and reported to the API Committee at quarterly review meetings has been prepared by Dr. John Cameron, the Committee Vice-Chairman (Appendix D). The significant conclusions are presented here.

A. Chemical Effects

1. Hydration of HP-Guar

HP-guar molecules are not present as isolated entities but are rather contained inside an intact cell about ten microns in diameter (8). The guar derivatization is done in such a way that the cell wall is not disrupted. When the HP-guar is added to water, water penetrates the cell wall and begins to hydrate the guar. During hydration microcrystalline cellulose domains are dissolved, the cell swells, and finally the cell wall ruptures releasing the guar. The rate at which this occurs depends on pH, temperature, and the osmotic pressure difference across the cell wall. An experiment was conducted to test how long it took to fully hydrate the guar. A guar solution was prepared and mixed in the blender for 30 minutes under strong agitation. Immediately thereafter dynamic oscillatory measurements were run as a function of strain amplitude. The results in Fig. 5 show that G' decreases as strain amplitude increases. This indicates that there are three-dimensional structures in solution, probably arising from association of the unhydrated guar domains, that are easily broken down by shear. This is not observed if the guar is allowed to age 20 hours after the initial mixing. This same phenomenon is shown in Fig. 6 where, for the solution mixed 30 minutes, the steady shear viscosity increases at low shear rates, whereas for the aged solution the viscosity reaches a Newtonian plateau. This increase in low shear viscosity also indicates aggregation and structure in solution. It is important to note that at higher shear rates the viscosities of the two fluids are identical since moderate shear fields can disrupt these weak aggregates. We see that dynamic oscillatory or low shear rate measurements are sensitive probes of structure in solution.

2. Order of Addition

We were surprised to find that the order of addition of ingredients to the original base guar solution had an effect on the gels that were ultimately formed. Dr. William Stivers of Celanese (8) has suggested that this might be related to the hydration of the guar, the osmotic pressure in the solution during hydration, and the number of cells that fail to rupture. The order of addition of the sodium diacetate buffer (N), potassium chloride (K), and guar (G) was varied in a series of tests. Though no differences in the rheology of the guar solutions prepared using different orders of addition could be measured, certain orders of addition led to gels with lower levels of network structure (i.e., lower G'). The results are shown in Fig. 7 for different orders of addition. The differences in G' are quite noticeable, though G'' data

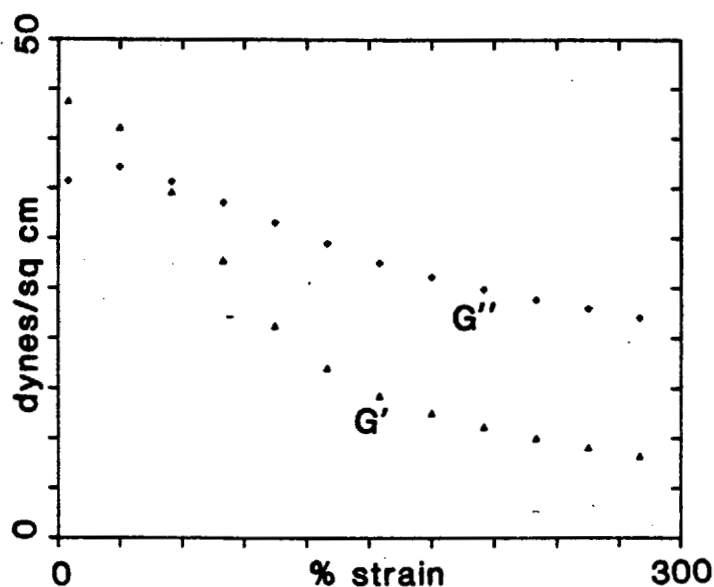


Fig. 5. Storage(G') and loss (G'') moduli as a function of strain of a .48% HP guar solution (30 minutes agitation) at 10 rad/sec : (run 21783 2).

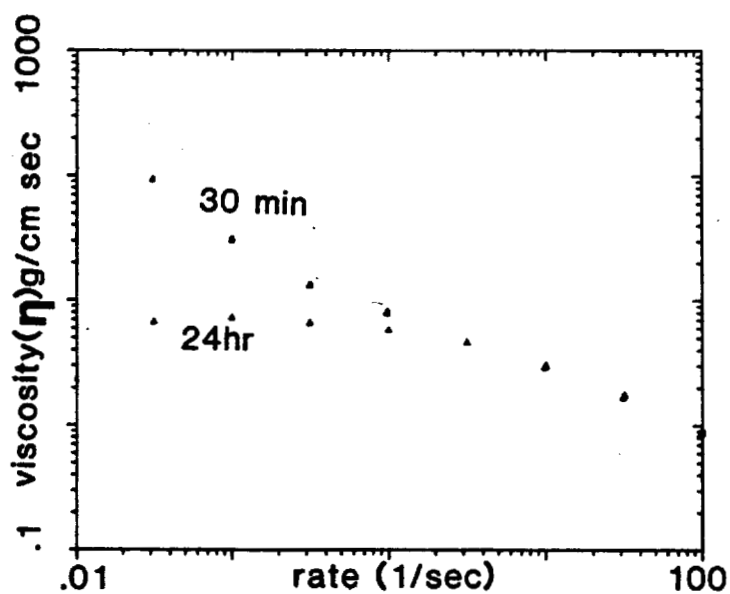


Fig. 6. Viscosity (η) as a function of shear rate of .48% HP guar solutions at different ages (runs 21683 and 21883 2).

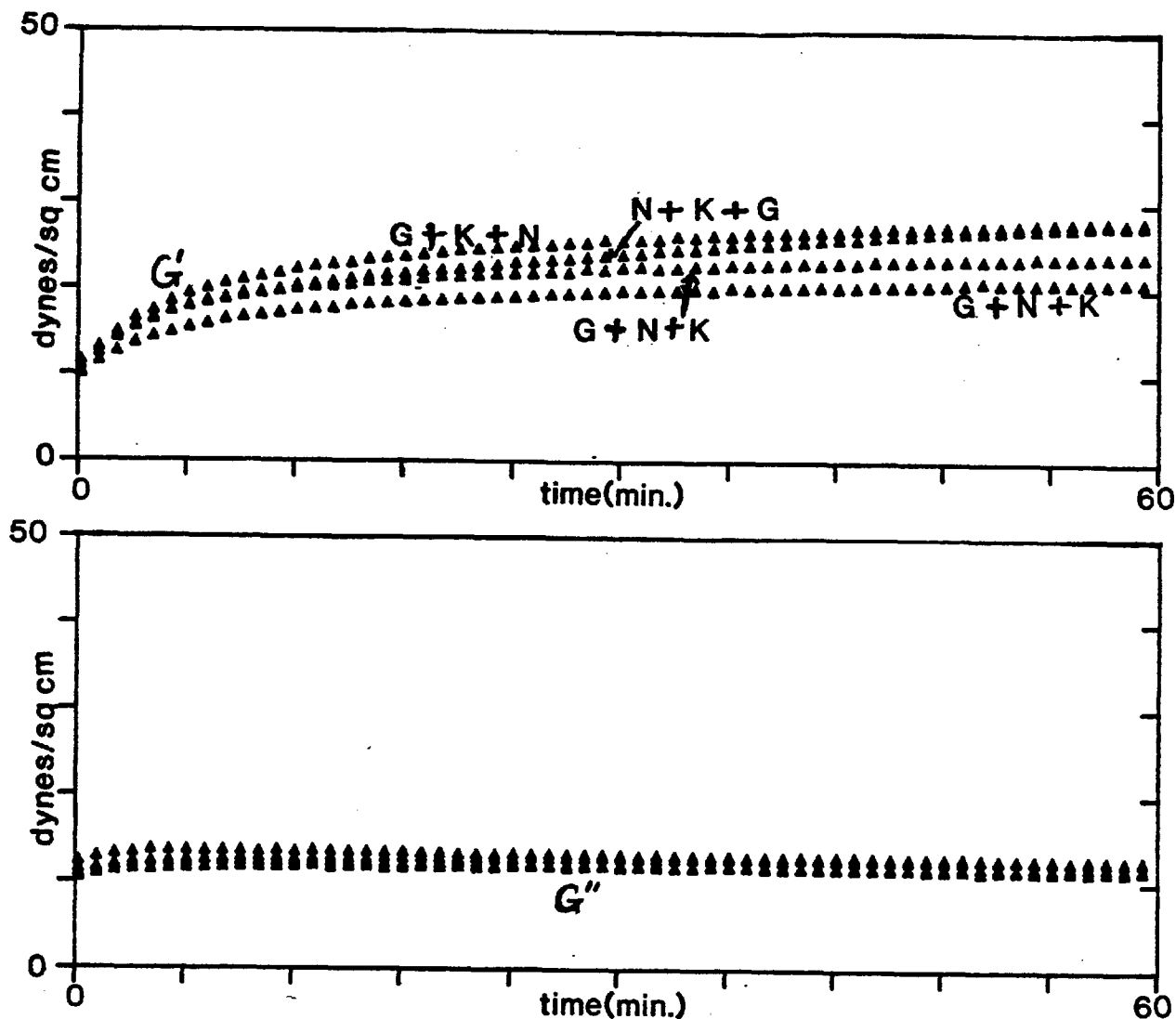


Fig.7. Effect of order of addition on G' and G'' of .48% HP guar mixed with Tyzor AA by hand. Measurements began immediately after mixing at 1 rad/sec and 100% strain (runs 61583 1, 61583 2, 61583 5 & 7683 2).

are similar for all runs. We have not at the time of this report duplicated these runs with the impingement mixing technique. For all subsequent studies we used the mixing order [G+K+N]. Further work on this phenomenon is underway.

3. Aging of Tyzor AA Solutions

Tyzor AA solutions change color from light yellow to orange or brown over a period of time. Dr. Donald Putzig of DuPont has suggested three mechanisms of Tyzor aging (9):

- a. Photo-reduction of Titanium. This will give a green/blue color. Keeping solutions in brown bottles eliminates this problem.
- b. Oxidation of Acetylacetone by Oxygen. This will give an orange color. However, Dr. Putzig did not think this would affect the crosslinking reaction.
- c. Hydration of Titanium by Water from the Air. This will give a white titanium dioxide precipitate.

Dr. James Steinmetz of Kay-Fries, Inc. has suggested that color change is related to acetic acid impurities present in the acetylacetone chelate (10).

We found that gels made from Tyzor AA solutions that had been opened many times over a several month period made gels with lower values of G' . Figure 8 shows the storage modulus of gels made from newly opened bottles of Tyzor AA and from bottles that had been used for several months. To eliminate these problems the large pint bottles of Tyzor AA were divided into several smaller vials and sealed. Brown vials were used and molecular sieves (W.R. Grace 3A) were added to the vial to scavenge water. This worked well and gave reproducible results that did not show the effects of aging over a period of months.

4. Diketone Addition

The most straightforward way of measuring gelation kinetics is to measure the maximum slope in the plot of G' versus time and to apply Eq. 4, as we have done previously in our study of polyacrylamide/Cr(III) gelation (5). However, as can be seen from Figs. 4, 7-9, and 13-14, the reaction rate of these guar/titanate gels is so fast that the maximum rate cannot be determined with confidence -- it occurs at too short a time.

It has been suggested that diketones can be used to slow the rate of crosslinking (11). Our results, taken at room temperature, show that not only does the addition of acetylacetone (a diketone) slow the reaction rate, but it also prevents the gel from crosslinking fully. With the addition of diketone, as shown in Fig. 9, the final value of the storage modulus is decreased. It has been suggested that increasing the temperature of these solutions might activate crosslinking. Further studies of delayed crosslinking are being pursued.

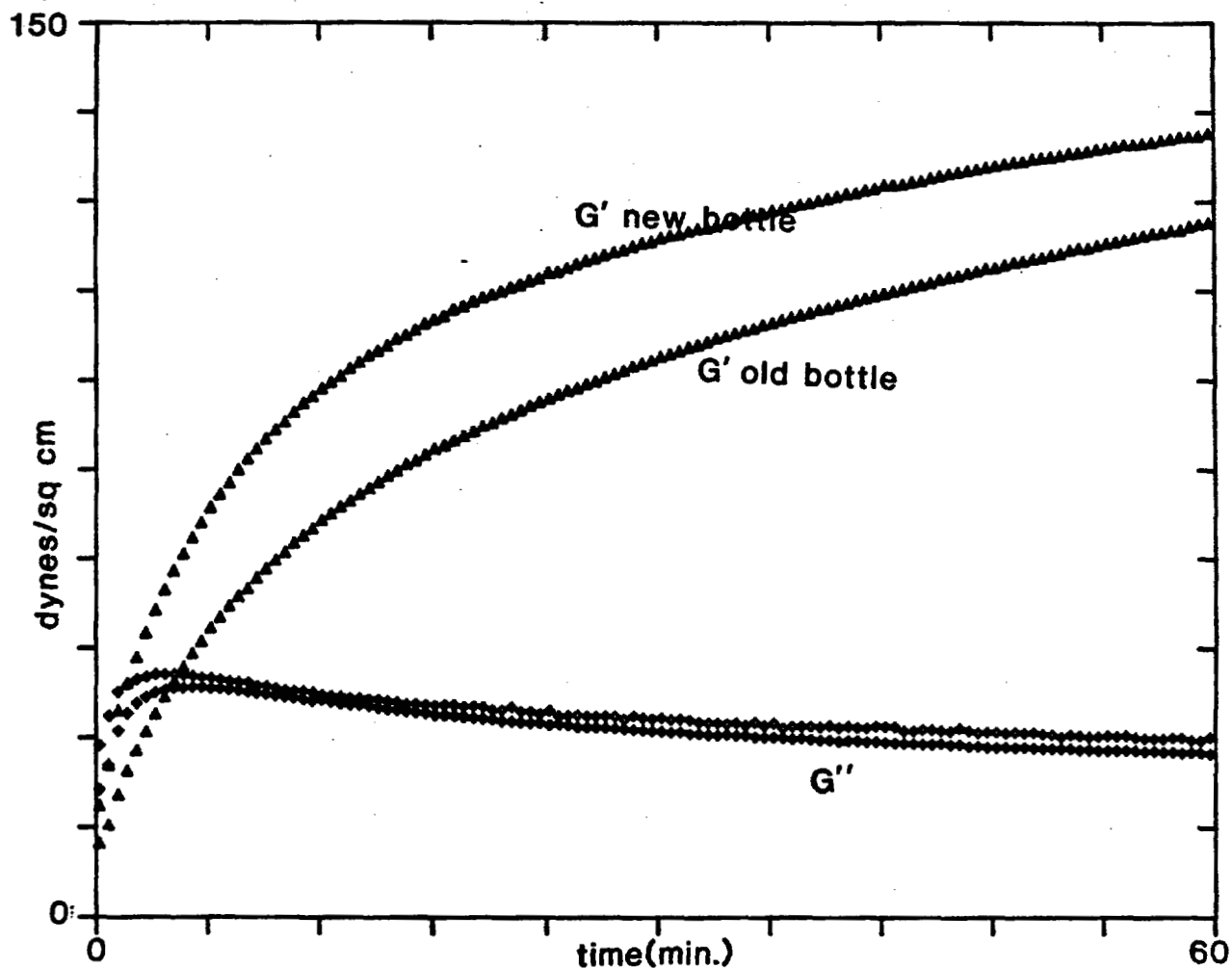


Fig.8. Storage (G') and loss (G'') moduli of HP guar gel (.48% guar (G + K + N) and .04% Tyzor AA) made from a newly opened bottle of Tyzor AA and from a bottle that had been used for several months. Impingement device was used and tests began immediately after mixing at 10 rad/sec 100% strain (runs 121583 1 & 122983 3).

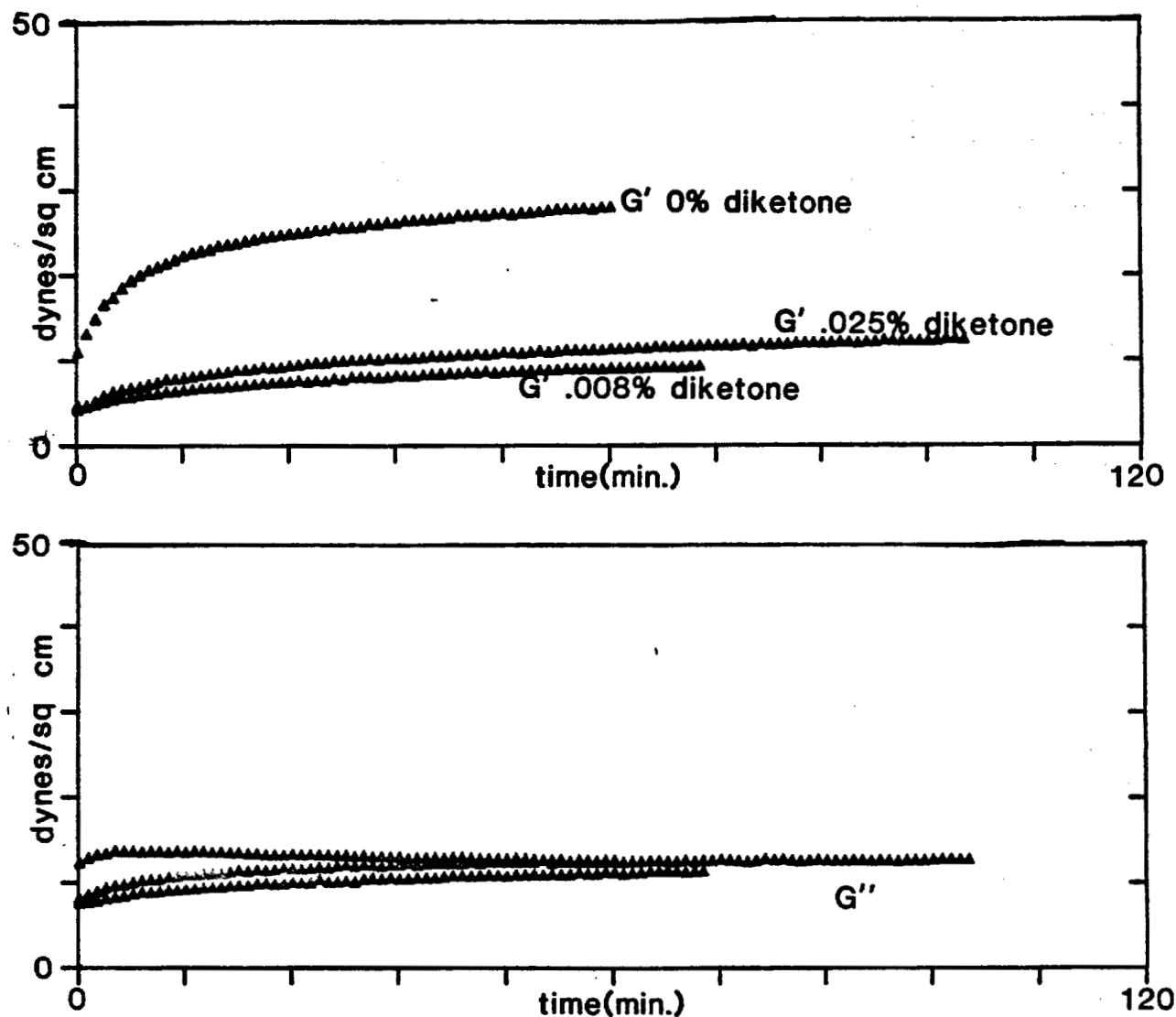


Fig.9. Effect of diketone on G' and G'' of HP guar gel (.48% guar (G† K† N) and .04% Tyzor AA). Tests began immediately after mixing by hand at 1 rad/sec and 100% strain (runs 52483 2, 52483 4 & 61583 1).