

Shear effects during the gelation of aqueous gelatin

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Measurements of the viscosity of aqueous solutions of gelatin at a wide range of shear rates during and after gelation are presented. Although the viscosity is shear rate dependent, experiments in which the shear rate was changed during gelation show a shear rate history independence. This implies that shear does not disrupt intermolecular junctions between the gelatin molecules; i.e., the bond probability p is not a function of the shear rate $\dot{\gamma}$. Thus the viscosity is a function of p and $\dot{\gamma}$, i.e., $\eta = \eta(p, \dot{\gamma})$, with the important distinction that p and $\dot{\gamma}$ act independently to determine the state of the system.

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I. INTRODUCTION

Gels are an important and intriguing class of materials in which a small fraction of one component controls a large fraction of another, fluid component. The most common example is gelatin, whose molecules can form a thermally reversible network that can entrain the water of the pregel solution, or sol, even when the gelatin weight fraction is as low as 1% [1–3]. Gelation occurs because the aggregation process in polymeric and colloidal solutions yields nondense, space filling aggregates, often describable as fractals, which eventually fill the volume of the system as they grow. The current theoretical description of gelation uses percolation theory [4–6], which predicts critical-phenomena-like divergences in key parameters such as correlation length, cluster mass, and viscosity as the sol approaches the gel. This approach is parametrized by an extent of reaction parameter or bond probability p and gelation occurs at p_c the gelation critical point.

Perhaps the most observable change as a sol evolves to a gel is the large increases in the viscosity that diverges at the gel point. This observation can be used to infer that the molecules of the gel material are joining together as the sol evolves to the gel to form larger molecular aggregates. The viscosity of gelling solutions is also non-Newtonian such that at large shear rate shear thinning, i.e., a decrease in viscosity with increasing shear rate, is observed. Thus it might be concluded that shear causes a disruption of the molecular aggregates that give rise to the large viscosity. The data presented in this paper indicate that this latter inference is not correct. Data are presented for the viscosity of aqueous gelatin solutions as they evolve from the sol to the gel and also after the gel has set. A wide range of shear rates are used from ca 10^{-5} to 750 s^{-1} . The viscosity evolves during gelation, and by comparing the viscosity measured at fixed shear rate during gelation and the viscosity measured during runs in which the shear rate is quickly changed from one value to another, a shear rate history independence is observed. From these results we conclude that the shear does not disrupt the molecular aggregates that form during gelation and hence in no manner impedes the gelation process. Based on the known behavior of polymer solutions we infer that the observed shear thinning must be due to more fragile intercluster entanglements. Thus the viscosity of the gel can

be described by the extent of molecular aggregate growth, which is quantified by the bond probability p , and the shear rate $\dot{\gamma}$ acting as *independent* variables. This description is also true after the sol has set to the solidlike gel where shear melting and freezing (upon the alleviation of the shear) are observed.

II. EXPERIMENTAL METHODS

Gelatin is a thermally reversible, physical gel, which associates to form agglomerates through hydrogen bonded, triple helix junctions. In our experiments aqueous solutions of gelatin (Aldrich, 300 bloom, $M_w = 1.2 \times 10^5$ determined via ultracentrifuge) were prepared at 3.0% by weight using distilled, deionized water. Once dissolved, the solutions were held at 45°C for 1 h to dissociate the gelatin molecular agglomerates [7]. These hot solutions were then quenched to $28^\circ\text{C} < T_{\text{gel}} \approx 30^\circ\text{C}$ in the viscometer to cause the sol to evolve to the gel. Viscosities were measured as a function of time after quench, the quench time, by either a Wells-Brookfield cone-and-plate viscometer with shear rate $\dot{\gamma}$ variable between 3.75 and 750 s^{-1} or a falling ball viscometer with $\dot{\gamma}$ about 10^{-2} – 10^{-5} s^{-1} . The cone-and-plate viscometer had a 4.8-cm-diam cone with a 0.8° cone angle. Both viscometers were temperature controlled within 0.1°C . In the falling ball measurement a polystyrene ball with an accurately measured diameter, typically $2r \approx 500 \mu\text{m}$, was dropped into the sample contained in a glass tube and its velocity v was measured by timing its fall as seen through a telemicroscope. The viscosity is given by Stoke's law as $\eta = 2\Delta\rho g r^2 / 9v$ and the shear rate is approximately $\dot{\gamma} \approx 3v/2r$. $\Delta\rho$ is the density difference with $\rho = 1.055 \text{ g/cm}^3$ for the polystyrene and $\rho = 1.002 \text{ g/cm}^3$ for the gelatin solutions; the latter was measured with a pycnometer. Run to run reproducibility for the viscosity measurements were $\sim 20\%$ due to its sensitive dependence on temperature and concentration. Gel times were determined by gently tilting a twin sample at an identical temperature and observing when the flow became nonsmooth or lumpy. This method is subjective, but no other methods seems to work better, and it is not critical for the main results of this paper.

III. RESULTS AND DISCUSSION

Figure 1 displays the results for the viscosity as a function of quench time for different shear rates. The falling ball mea-

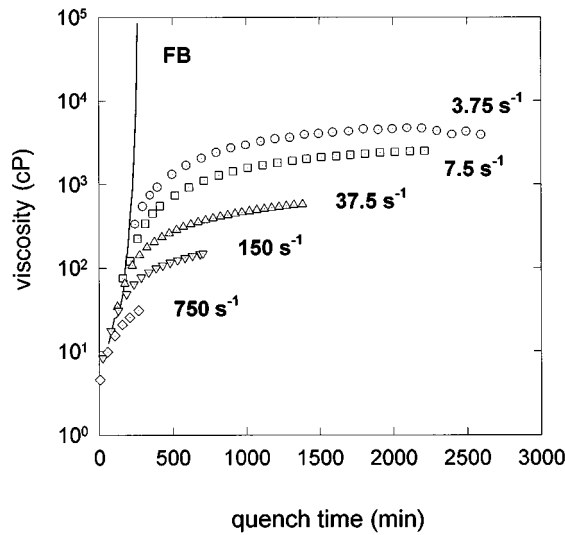


FIG. 1. Shear viscosity vs quench time for various shear rates of a 3% aqueous gelatin solution quenched to 28°C at zero time. The falling ball (FB) measurement is at a shear rate of nearly zero.

surement represents essentially zero shear rate behavior and can be fit with a power law $\eta \propto (t_{gel} - t)^{-x}$ with $x = 2.5 \pm 0.1$ and $t_{gel} = 270$ min, a time that agrees fairly well with the visual gel time of 255 min. This exponent cannot be compared to that predicted by percolation theory (0.7–1.3 [4,8]) because of the unknown relationship between time and bond probability p . The power law behavior, however, is in qualitative agreement with percolation theory and previous experimental results [3]. The implication is that at zero shear rate the viscosity diverges to infinity at t_{gel} . The nonzero shear rate viscosities were obtained by keeping the cone-and-plate viscometer on, starting at zero quench time, for the duration of the experiment. They follow the zero shear rate viscosity at early times, but then successively break away from this dependency at latter times; the larger shear rate viscosities deviate sooner. Figure 1 also shows that at long times all nonzero shear rate viscosities appear to approach a constant, finite value. Figure 2 shows these data again (not

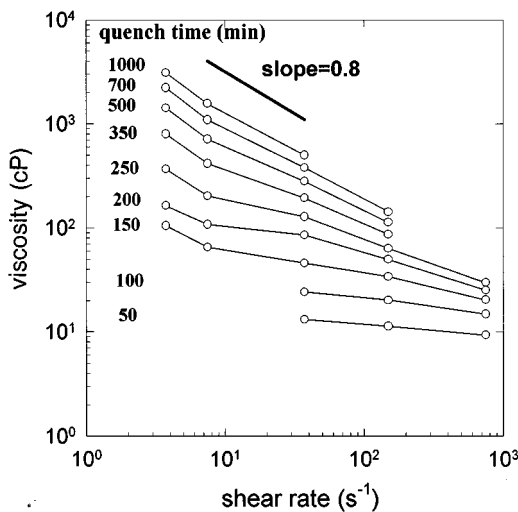


FIG. 2. Shear viscosity vs shear rate for various quench times.

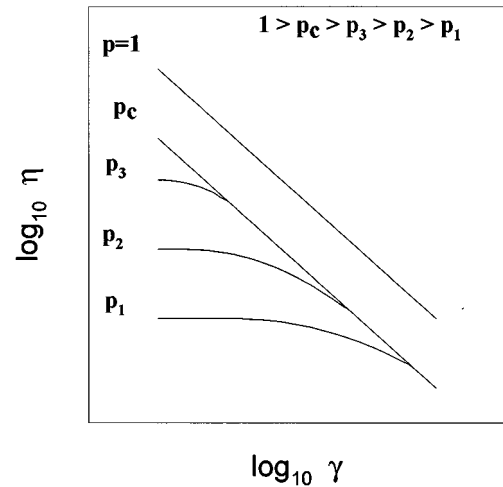


FIG. 3. Schematic diagram of shear viscosity vs shear rate for various bond probabilities p with $0 \leq p_1 < p_2 < p_3 < p_c < 1$. The bond probability is monotonically directly related to quench time and mass.

shown are the falling ball data) but as a function of shear rate. Although the data are limited by the range of the cone-and-plate viscometer, a distinct pattern occurs. Early after the quench, there is very little shear rate dependence. As the gelation proceeds, non-Newtonian behavior (i.e., shear rate dependent viscosity) increases until a limiting dependency is obtained described by $\eta \sim \dot{\gamma}^{-y}$ with $y = 0.8 \pm 0.05$.

These figures imply that the complete picture of η versus $\dot{\gamma}$ would look like Fig. 3. Figure 3 is parametrized by the bond probability p , which increases monotonically with quench time and hence represents quench time when compared to Fig. 2. As time evolves, p increases, hence η increases. At finite shear rate, this increase eventually slows as the non-Newtonian regime is entered. Then η would turn off from the zero shear rate divergent behavior. This describes the data in Fig. 1 qualitatively.

The next series of figures demonstrates a remarkable shear rate history independence of the viscosity. Figure 4

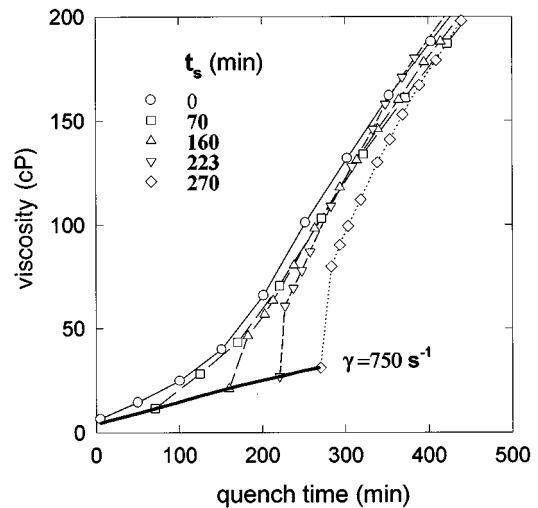


FIG. 4. Shear viscosity vs quench time. The viscometer shear rate was switched from 750 to 37.5 s^{-1} at different t_s .

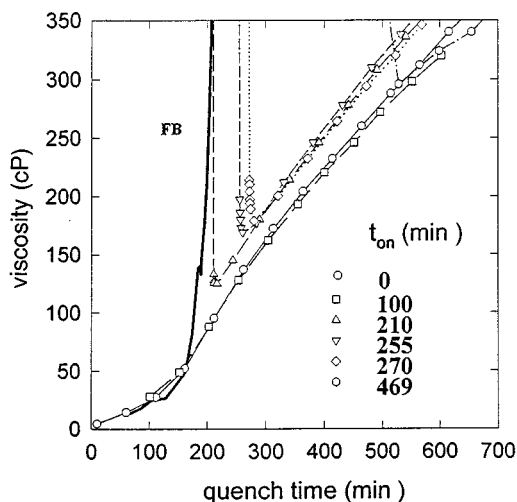


FIG. 5. Shear viscosity vs quench time. The viscometer is off, thus shear rate is zero, until various times t_{on} when it is turned on to a shear rate of 37.5 s^{-1} . The falling ball (FB), essentially zero shear rate curve is shown for comparison. The visual gel time is 255 min.

shows the viscosity as a function of quench time for two different shear rates. The gelatin solution was quenched in the viscometer and the viscometer was set to a shear rate of 750 s^{-1} . Then at a series of different times after quench (including initially, i.e., no 750-s^{-1} period) the shear rate was changed to 37.5 s^{-1} , a factor of 20 decrease. In every case the viscosity quickly changed to the value, within the 20% run-to-run reproducibility, it would have had at that time (hence at that particular bond probability and cluster mass) had the viscometer been set to the lower shear rates at zero time. After the change, the viscosity continued to evolve with the 37.5-s^{-1} curve. This implies that the measured viscosity is independent of shear rate history. Figure 5 shows a situation in which the gelatin solution was quenched in the viscometer, but the viscometer was not turned on, i.e., $\dot{\gamma}=0$. The implication is that η increased as described by the essentially zero shear rate, falling ball measurements drawn in the figure. At a series of different times, the viscometer was turned on to $\dot{\gamma}=37.5 \text{ s}^{-1}$. In each case the measured viscosity quickly fell to the value it would have had if the viscometer had been on continuously at $\dot{\gamma}=37.5 \text{ s}^{-1}$ since $t=0$. This includes *two situations after the system has gelled*; hence what appears to be a shear melting phenomenon is observed. We have also seen the converse, a “shear freezing;” that is, for $t > t_{gel}$ once the shear is removed, the solidlike gel is present in the viscometer immediately after opening. Finally, Fig. 6 shows a run in which the viscometer was initially at $\dot{\gamma}=7.5 \text{ s}^{-1}$ switched to 37.5 s^{-1} and then switched back to 7.5 s^{-1} . This run is compared to two runs for which $\dot{\gamma}=7.5$ or 37.5 s^{-1} continuously. Once again complete history independence is seen.

The results above imply that the shear does not disturb the sol to gel evolution; i.e., it does not disrupt or break the growing gelatin molecule clusters. In the language of percolation theory, the bond probability p is not a function of $\dot{\gamma}$. Instead the viscosity is a unique function of these two variables, acting independently, and we write

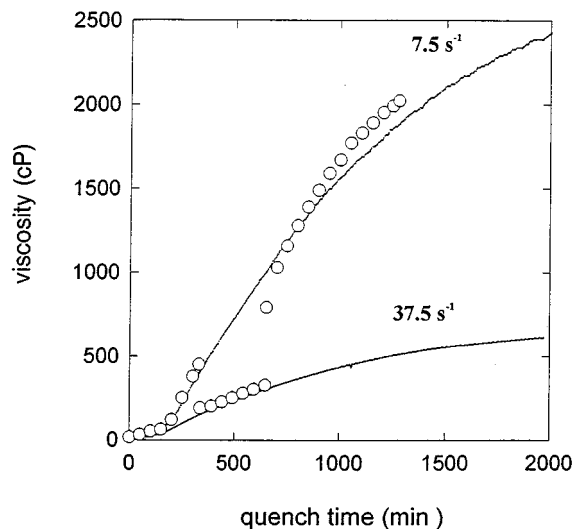


FIG. 6. Shear viscosity vs quench time. Circle represents when the shear rate is 7.5 s^{-1} from time zero to 331 min, switched to 37.5 s^{-1} at 331 min, then switched back to 7.5 s^{-1} at 646 min. Curves represent viscosity runs measured continuously at either 7.5 or 37.5 s^{-1} .

$$\eta = \eta(p, \dot{\gamma}). \quad (1)$$

This “equation of state” for the viscosity is described graphically in Fig. 3. The shear rate behavior shown in Fig. 3 is also seen in nongelling polymer solutions and melts parametrized by molecular weight [9–11] rather than bond probability. In these systems the viscosity at low shear increases with increasing molecular mass. The non-Newtonian power law regime in these polymeric systems has an exponent $\gamma = 0.8\text{--}1.0$, equal to that observed for gelling gelatin, Fig. 2. Thus we proposed a simple model based upon this empirical resemblance. One may envision the gelatin molecules as clustering together after the quench with increasing cluster mass as quench time proceeds, i.e., as p increases. It is expected that these clusters act the same as polymer molecules in a solution or melt with viscosity dependent on cluster mass M and shear rate exemplified by Fig. 3. At zero shear rate as $p \rightarrow p_c$, the cluster mass $M \rightarrow \infty$, hence $\eta \rightarrow \infty$. At nonzero shear rate we propose that p and hence M evolve as they did at zero shear rate. Thus η at finite shear rate would equal η at zero shear rate until p increased to the point where the non-Newtonian regime in Fig. 3 is entered. Then shear thinning is observed but p and M continue to evolve independent of shear rate. Observe in Fig. 1 and Fig. 2 that at and after the gel time when $p \geq p_c$, the nonzero shear rate viscosity continues to evolve. This implies that the $p = p_c$, $M \rightarrow \infty$ line for the polymer solution must continue to evolve towards the $p = 1$ line in Fig. 3. Although the average cluster mass is infinite at $p = p_c$, percolation theory shows that the fraction of molecules involved in the infinite cluster is zero at p_c , but this fraction grows to unity as $p_c \leq p \rightarrow 1$. It is reasonable to propose that while the zero shear rate viscosity is infinite for all $p \geq p_c$, the nonzero shear viscosity, being finite, would be larger as the fraction of molecules involved in bonding increased. This is supported by observations that the helicity of the gelatin gel,

which can be used as a measure of p , [3,12] continues to evolve with time long after the gel point [3]. Finally, as the $p=1$ line is approached, the viscosity will approach a constant value.

Perhaps the most remarkable properties observed are the shear melting and freezing as the cone-and-plate viscometer is turned on and off after t_{gel} . The system gels when $p=p_c$, hence $M \rightarrow \infty$. An infinite mass polymer solution has infinite viscosity at zero shear rate, but according to the viscosity equation of state represented in Fig. 3, it has finite viscosity at finite shear rate. This explains the “shear melting” phenomenon in Fig. 5. However, we now see that the terms “shear melting” and “shear freezing” are misnomers because there is no change of phase. The state of the gel viscosity is given by p and $\dot{\gamma}$. Instead we should view the liquid nature of the gel as merely the state of the gel at finite shear.

We have argued above that the shear rate history independent behavior of the viscosity implies that shear does not disrupt the aggregation or gelation process. Consider, however, what would happen if shear did break the junctions between individual molecules. Then the decrease in viscosity would be the result of the competition between the aggregation that is occurring as the sol sets to the gel and the fragmentation of the clusters due to finite shear. Our results, however, are inconsistent with an aggregation-fragmentation mechanism. In such a mechanism our previous work [13,14] shows that changes of shear rate, hence a purported fragmentation rate, would lead to much slower changes to the new equilibrium values of viscosity than the very rapid changes we observed. Also the viscosity changes would be monotonic in an aggregation-fragmentation scenario [13,14], whereas experimentally they were not.

What then is the cause of the observed shear rate dependent viscosity? It has been proposed that for polymer sys-

tems shear affects intermolecular *entanglements* and hence reduces the viscosity [9–11]. Certainly the mass of the polymer is not changed by the shear. These entanglements are weaker than the junctions that occur between gelatin molecules as they aggregate. Thus we propose that whereas the shear does not disrupt the intermolecular junctions (intracluster bonds) formed during gelatin aggregation, it does affect the entanglements between the ever growing molecular clusters (intercluster entanglements).

IV. CONCLUSIONS

In conclusion, the shear viscosity of a gelling physical gel, aqueous gelatin, is independent of shear history. This implies that shear does not disrupt the *intermolecular* clusters that form and grow as gelation proceeds. In other words the *intermolecular* bond probability p is not affected by shear; the shear does not disrupt the gelation process. Shear thinning is due to disruption of the more fragile *intercluster* entanglements. The viscosity of the gel system is determined by the independent variables p and $\dot{\gamma}$, described qualitatively by the model proposed in Fig. 3. The macroscopic solid nature of the gel is due to the infinite viscosity at zero shear rate. At finite shear rate, however, the gel is a liquid with finite viscosity. It is relevant to ask if the behavior we see in aqueous gelatin is universal. We have preliminary data for atactic polystyrene in carbon disulfide, a physical gel, that show the same behavior. Whether the chemical gels show the same behavior or not remains to be determined by future experiments.

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