

Stress Yield Value in Closely Packed Gel Suspensions

INTRODUCTION

Closely packed gel thickeners are systems of swollen gel particles that completely fill the available suspension volume. Efficient thickening action occurs when there is no excess solvent present, i.e., when the reduced concentration cQ is greater than 1. Here, c is concentration (g polymer/g suspension) and Q is swelling weight (g swollen gel/g dry polymer) in excess solvent of the same ionic strength.

In the closely packed condition, these systems usually have a stress yield value. When the surface of the suspension is disturbed with a spatula, the imposed irregularities remain indefinitely if they are not too high. Most of the examples of closely packed gel systems that we have examined had a yield value at great enough concentration, but hydrolyzed cellulose polyacrylonitrile graft copolymer¹ (H-CPAN) had one of the largest yield values for its 1.5% polymer concentration. Obviously, the yield value would be an important property affecting practical use of these systems, and the H-CPAN suspension offers an opportunity to examine yield value and its effects in somewhat more detail.

EXPERIMENTAL

The H-CPAN raw material was given to us by Pierre Le Poutre and A. A. Robertson of the Pulp and Paper Institute, Montreal. The gel fraction was isolated from the small amount of soluble material by a centrifugation treatment.¹ The purified stock preparation, containing 1.52% polymer, was the same one described in reference 1. The rheological properties were measured in a Rheometrics Mechanical Spectrometer (Union, N.J.) with a 3.6-cm radius cone-and-plate set, with a 0.04-radian cone angle. Gel swelling and flow rheology are given in reference 1.

RESULTS AND DISCUSSION

Shear Stress Yield Value

Yield value can be determined quantitatively by observing shear stress τ as a function of shear rate $\dot{\gamma}$. In a cone-and-plate viscometer during shear at steady rates, τ is linear with $\dot{\gamma}$ at low values of $\dot{\gamma}$ (Fig. 1) for the stock preparation of H-CPAN. At higher $\dot{\gamma}$ the values of τ deviate below the straight line.

In Figure 1 the yield stress τ_0 is obtained by extrapolation to $\dot{\gamma} = 0$. So far as we could discern, τ is linear for H-CPAN down to the lowest values of $\dot{\gamma}$ attainable on our instrument (Fig. 1). Such

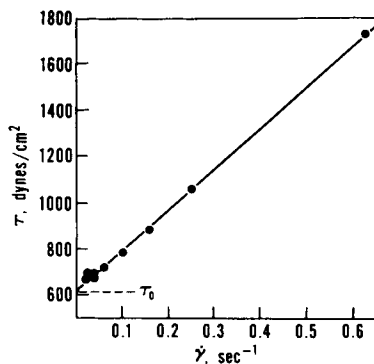


Fig. 1. Shear stress yield value of H-CPAN at low shear rates. Shear stress τ is a linear function of shear rate $\dot{\gamma}$, and the intercept at $\dot{\gamma} = 0$ is the yield value τ_0 .

behavior is typical of a plastic material or Bingham body.² When τ_0 is exceeded, flow will occur according to the Bingham model. Actually, stresses higher than τ_0 could remain in the stationary gel suspension after appropriate shear treatments, as will be discussed below. However, during treatment at finite $\dot{\gamma}$, the material did behave as a Bingham body.

Most closely packed gel suspensions do not have the linear behavior displayed in Figure 1. They may have yield values or apparent ones, but precise values of τ_0 are often unobtainable, and we have not previously reported them. Patton³ as well as Jeanes and Pittsley⁴ have described some responses of natural gums at low shear rates, based on the technique of Patton in which the released, unwinding spring of a Brookfield microcone-and-plate viscometer permits observations of τ at descending low shear rates. The value of τ at an arbitrary low shear rate, i.e., $\dot{\gamma} = 0.01$, is defined as a working yield value.

Elliott and Ganz⁵ noted that some samples of carboxymethyl cellulose gel behave as Bingham bodies and that the behavior appears when degree of substitution of carboxyl groups is reduced. They relate the yield value to the presence of fringe micelles of unsubstituted cellulose which act as crosslinks.

Values of τ_0 in H-CPAN depend on both c and ionic strength μ in the suspension. τ_0 decreases on dilution in either water or isoionic salt solution, but the values of τ_0 form one continuous curve when plotted against cQ (Fig. 2). For H-CPAN and other closely packed thickeners, when $cQ > 1$, then η/cQ , where η is viscosity of the suspension, is approximately constant for varying c and μ . For a specific polymer sample, then, η (or τ) is a function only of cQ at constant $\dot{\gamma}$. The data of Figure 2 indicate that τ_0 , too, is a function only of cQ , at least for this H-CPAN sample. τ_0 is influenced by salt (μ), but apparently only through the effect of μ on Q .

For comparison, we may note that shear modulus G in a closely packed thickener is not a function of cQ but depends on $c^{1/3}$ and to a lesser degree on μ , since the reduced modulus $G/c^{1/3}$ is approximately constant. Theoretical explanation for the relationship of τ_0 to cQ is not available.

Equilibrium Stress After Shear

For H-CPAN suspensions, the shear stress remaining after a shear treatment does have an unusual feature. When rotation of the cone of the rheometer is initiated, τ rises to a peak and then declines somewhat to a steady value (Fig. 3). This response is commonly observed in polymeric materials. When the cone is stopped, τ falls rapidly to a minimum and then recovers to a somewhat higher value, designated as τ_e in Figure 3. This last response is unusual. In an ideal Bingham body, one would expect that after a shear cycle, the value of τ would drop or decay slowly to $\tau_e = \tau_0$. The τ_e values after stopping (i.e., at time C in Fig. 3) were highly variable, probably because our instrument did not perform a perfectly smooth stop.

It was also unexpected that some τ_e values were larger than τ_0 , i.e., 1000 dynes/cm² compared to 600 dynes/cm² for τ_0 (Fig. 4). τ_e seemed to increase with $\dot{\gamma}$, and the larger values also required extensive shear. During shear in the direction opposite to the immediately preceding treatment, or after oscillatory pretreatment, τ_e built up to maximum values (at constant $\dot{\gamma}$) only after strains of approximately 100 or more. The values of τ_e in Figure 4 were determined after shear strains of at least 100. Even though quantitative results could not be acquired, the shape of the curve in Figure 3 and the higher τ_e values in Figure 4 indicate that some structure in the suspension is perturbed

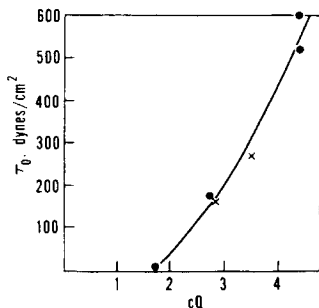


Fig. 2. Shear stress yield values τ_0 for dilution of H-CPAN in H₂O (●) and in isoionic NaCl solution ($r = 0.3$) (x).

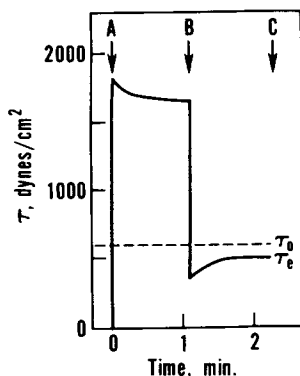


Fig. 3. Shear stress in H-CPAN in the rheometer during and after a cycle of steady shear at a shear rate of 1 sec^{-1} , starting at A and stopping at B. τ_0 for this suspension is compared to the equilibrium stress τ_e after shear.

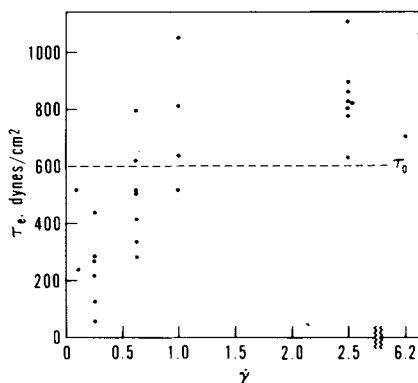


Fig. 4. Equilibrium stress τ_e remaining after shear treatments at various shear rates $\dot{\gamma}$ to a shear strain $\gamma \geq 100$, after which shear was stopped. τ_0 is given for comparison.

or oriented at higher $\dot{\gamma}$. This perturbed state appears to have a higher yield value than the unperturbed one.

Phase Relationships During Oscillation

The existence of the shear stress yield value affects the behavior of the suspension during oscillatory treatment. When the cone of the rheometer is oscillated sinusoidally (Fig. 5), τ follows the oscillation of angular position, p , with a displaced phase as expected. The primary normal force, $P_{11} - P_{22}$, also oscillated but depended strongly on the immediately preceding treatment of the sample. Oscillation after shear treatments in either direction of rotation resulted in peaks in $P_{11} - P_{22}$ which had the same frequency as angular position, but their phase depended on the previous rotation direction (experiments A and B, Fig. 5).

In polymer solutions, the response of $P_{11} - P_{22}$ to oscillatory motion is a symmetrical sinusoidal curve with twice the frequency of the oscillation.^{6,7} The $P_{11} - P_{22}$ curve of the H-CPAN suspension could be converted to this response; but to do this, the sample had to be oscillated at high amplitude (strain amplitude 20), and then the amplitude had to be gradually reduced to the final low level of the experimental oscillation. In all three experiments of Figure 5, the oscillatory responses were stable for as long as we observed them (about 30 min). Oscillatory response with twice the frequency but unequal amplitudes could also be produced by other pretreatments. The amplitude of τ was hardly affected by the pretreatments, except that in experiment C there was a decrease of about 20%. Other closely packed gel systems can show at least a minor dependence of $P_{11} - P_{22}$ during oscillation on pretreatment, so this response may occur commonly in closely packed thickeners.

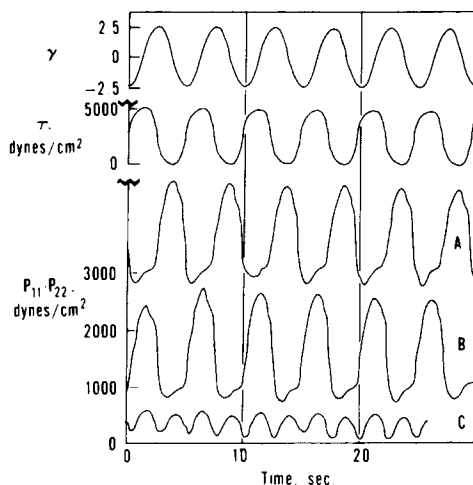


Fig. 5. Phase relationship of shear stress τ and primary normal force $P_{11} - P_{22}$, to shear strain γ during sinusoidal oscillation of H-CPAN suspension. Upper curve is γ during oscillation at a frequency of 0.2 sec^{-1} and an amplitude of 0.2 radian. $P_{11} - P_{22}$ is shown: A, during oscillation after 1 min shear clockwise at $\dot{\gamma} = 25$; B, after 1 min shear counterclockwise at $\dot{\gamma} = 25$; C, after oscillation at an amplitude of 2 radians for a few cycles and then decreasing gradually to 0.2 radian in about 1 min.

The oscillatory experiment indicates that there is a structure or alignment which can be built into the H-CPAN suspension which has minor influence on the value of τ but which is important in the elastic response as indicated by $P_{11} - P_{22}$. Polymer melts commonly show elastic effects that are not disclosed in measurements of τ . Even though the H-CPAN suspension examined here is mainly gel particles with some long fibers, the aligned structure persists through strains up to 5 or greater. Persistence through this large strain is unusual for a suspension of gel particles. The long fibers may enhance the yield value and cyclic $P_{11} - P_{22}$ properties of H-CPAN, but since other closely packed thickeners without fibers also have yield values, some other structure may be the source of yield value.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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