

Rheology of a Cellulose Graft Copolymer. Comparison with Other Closely Packed Gel Thickeners

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Synopsis

Hydrolyzed cellulose-polyacrylonitrile graft copolymer is a polyelectrolyte gel suspension with a high viscosity in water. It is a closely packed swollen gel particle suspension in the appropriate concentration range and has similar rheological properties to other thickeners of this type. Viscosities η in either water or salt solution are reduced to a single master curve by use of the reduced viscosity function η/cQ , where c is weight fraction of polymer and Q is swelling volume in excess solvent of the same ionic strength. The effective molecular weight between crosslinks, M_c , determined from shear modulus, corresponds to M_c values for other closely packed gel thickeners of similar η/cQ . Among all examples of this class of thickener, the plateau values of η/cQ , which occur at $cQ > 2$, are approximately inversely proportional to M_c .

INTRODUCTION

When an acrylonitrile graft copolymer on cellulose is hydrolyzed, it becomes a polyelectrolyte in which the grafted chains are converted to acrylate and acrylamide functionalities. The material is a stiff paste in water suspension, even at a concentration as low as 1% polymer.¹ It is the cellulose analog of hydrolyzed starch-polyacrylonitrile graft copolymer (H-SPAN) which we have examined in earlier papers.^{2,3} We have examined the cellulose graft copolymer (H-CPAN) by the methods developed for H-SPAN to characterize this new substance and to see if its viscosity could be normalized by our reduced concentration variable, cQ , where c is concentration (g/g) in suspension and Q is the swelling (g swollen gel/g polymer) in excess solvent of the same ionic strength.

The mechanism by which H-SPAN and Carbopol-941 act as thickening agents has been described in earlier work.^{3,4} Both materials in water are primarily in the form of highly swollen gel particles with negligible amounts of soluble polymer present. High viscosity is observed when these swollen deformable gel particles are closely packed, i.e., when $cQ > 1$, when solvent is present at levels beyond the swelling capacity of the gel.

The H-CPAN material was expected to be an example of the closely packed gel type. Under a phase microscope, the material in dilute suspension appears mainly as swollen cellulose fibers. There is some soluble material, which can be as small as elementary protofibrils of cellulose,¹ but most of the material is easily centrifuged from the suspension at low speed.

A U.S. patent has appeared on a chemically similar material.⁵ In some practical applications, a thickening agent like H-CPAN can be used at concentrations less than the closely packed condition. Under such conditions, viscosity is increased over that of the solvent, but at much lower levels than would occur at $cQ > 2$.

In the course of this study, we observed an unusually high yield point for H-CPAN, about 600 dynes/cm² for a 1.5% suspension. The high yield point leads to some interesting rheological features which will be discussed further in another paper.

EXPERIMENTAL

The H-CPAN raw material was given us by Pierre LePoutre and A. A. Robertson of the Pulp and Paper Research Institute, Montreal. It was a 1:1 add-on of acrylonitrile. The hydrolyzed product, which had never been dried, was purified to free it of a minor soluble component. The material as a 1% suspension in water was sheared in a Waring Blendor for 20 min. Then, the material was suspended at about 0.3% in 1M NaCl solution, and the gel or insoluble fraction was isolated by centrifuging (2000 rpm for 15 min). The gel was recovered, again centrifuged from 1M NaCl, then acidified to 1M with HCl, and washed by centrifuging six times in water with concentrations of HCl diminishing to about 0.0005M. The gel was then taken up in water and titrated to pH 7.6 with NaOH. Recovery of dry material was about 90% of original dry weight. Two separate batches were prepared. Both had a final polymer concentration of 1.52% and were similar, but not identical, in flow properties. The isolated gel material was not greatly different from the raw material in flow properties and yield point. Other methods have been described.²⁻⁴

RESULTS AND DISCUSSION

Flow Curves

The log apparent viscosity-versus-log shear rate flow curve of the gel suspension shown in Figure 1 is rather typical of a shear thinning fluid. As shear rate increases, the apparent viscosity drops. Such flow curves for polymer melts or solutions are not usually precisely straight; but seldom, if ever, is an inflection point evident as it is in Figure 1 at a shear rate near 0.3 sec⁻¹. Further, in Figure 1, as shear is decreased, there is no apparent trend of the flow curve to a Newtonian region where viscosity is independent of shear rate. Such a Newtonian plateau would be expected both for polymer melts and polymer solutions. In contrast, for H-CPAN as for H-SPAN and Carbopol-941, a yield point is observed at low shear rates. The H-CPAN yield point is high compared to the other materials.

The shear modulus G (Fig. 1) is used to determine the apparent degree of crosslinking in the gel.³ The modulus was calculated from measurements of primary normal force ($P_{11} - P_{22}$) and shear stress τ by the equation

$$G = 2\tau^2/(P_{11} - P_{22})$$

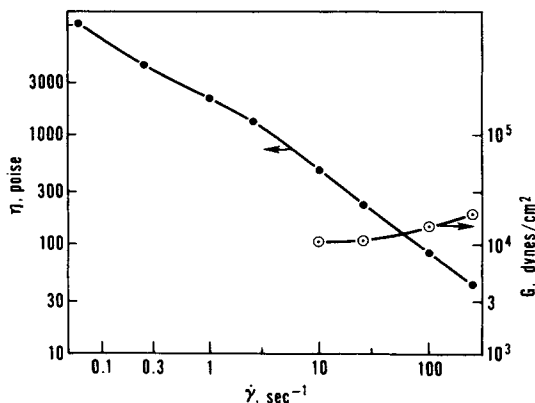


Fig. 1. Apparent viscosity (●) and apparent modulus (○) under steady shear at constant rates for 1.52% hydrolyzed cellulose-polyacrylonitrile graft copolymer (H-CPAN) suspension in water.

The value of G increases slowly with shear rate as it did for H-SPAN and Carbopol gels. The corresponding value of recoverable shear S , calculated as

$$S = (P_{11} - P_{22})/2\tau$$

is about 0.6.

Solvent Swelling

Swelling capacity Q in a solvent is one of the most important properties of a gel in relation to rheological characterization. Q can be determined in various ways. Although we usually determine Q in a ultracentrifuge, we do not imply that this method is ideal. The values obtained depend on the concentration of polymer in the sedimented suspension. They also depend on centrifugation speed. The volume of gel in the centrifuge cell decreases slowly with time, but the volume at infinite time can be obtained by extrapolating the volume versus reciprocal of time. The effect of centrifugal force on Q extrapolated to infinite time is shown in Figure 2. As for H-SPAN and Carbopol, Q is a curved function of centrifugal force. We have arbitrarily chosen a centrifuge speed of 2600 rpm

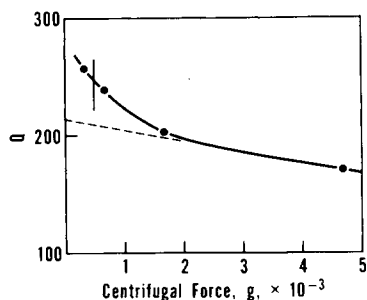


Fig. 2. Swelling volume (extrapolated to infinite time in a centrifuge) as a function of centrifugal force g (\times gravity) for H-CPAN in 0.0179M NaCl. Vertical line indicates g at 2600 rpm, where Q was routinely determined.

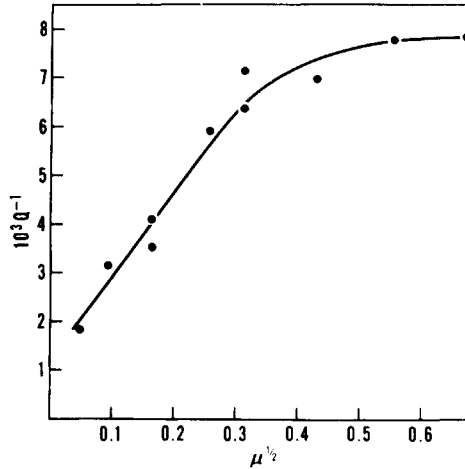


Fig. 3. Reciprocal of swelling volumes Q^{-1} , extrapolated to infinite time, for H-CPAN gel as a function of $\mu^{1/2}$.

(490 \times gravity) to determine relative swelling volumes³; we also try to have a gel fraction in the sedimenting suspension occupy about half the volume of gel plus solvent.

Centrifugal force values reported for Carbopol gel⁴ are a factor of 10 too high. The scale of Figure 2 is the correct one, both for this paper and for the corresponding figure of reference 4.

In polyelectrolyte materials, swelling volume depends on ionic strength μ in the swollen gel. To include contributions from both the polyelectrolyte and added salt,^{2,4} $\mu = r \cdot M + [\text{NaCl}]$, where r is a factor depending on linear ion density in the polymer and is 0.3 for H-SPAN and H-CPAN, M is the molarity of Na from the polymer, and $[\text{NaCl}]$ is the molarity of added salt. The effect of μ on Q is

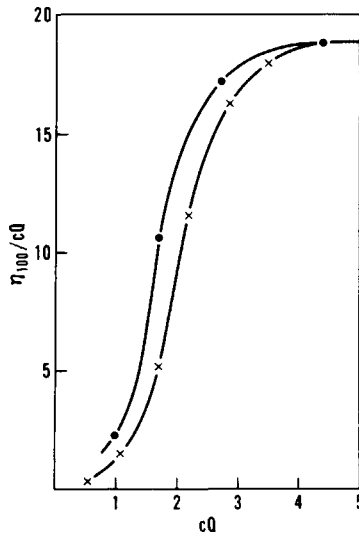


Fig. 4. Reduced viscosity functions η_{100}/cQ for dilutions of H-CPAN in water (●) and in NaCl solution of $r = 0.3$ (x) (isoionic dilution³). Data are for a shear rate of 100 sec^{-1} .

shown in Figure 3 where the values of Q^{-1} at 2600 rpm after extrapolation to infinite time are given as a function of $\mu^{1/2}$. The relationships observed in earlier work for H-SPAN and Carbopol were nearly linear on this kind of plot, and the curves approached the origin, except for less swelling H-SPAN preparations.³ The relationship for H-CPAN is much more curved, and there is a minimum value of Q which is approached at high values of μ . That is, H-CPAN is salt tolerant at high μ .

Dilution Effects

The reduced viscosity function at a shear rate of 100 sec^{-1} , η_{100}/cQ , was determined for two series of dilutions, in water and in isoionic NaCl solutions. The isoionic series was prepared by diluting the original stock of H-CPAN in NaCl solution with a concentration of Na which was 0.3 times that of the H-CPAN stock ($r = 0.3$). In both series (Fig. 4), η_{100}/cQ decreases as cQ decreases and appears to be reaching a constant value as cQ increases. H-CPAN has only a moderate swelling power in water, so that our 1.5% stock had a cQ value of 4.5. It would appear that the plateau value of η_{100}/cQ is reached at this cQ , but this point is not clearly established with the present sample. The curves for both dilution series (Fig. 4) are nearly identical; the function η_{100}/cQ is effective in describing H-CPAN as a closely packed gel suspension.

In comparing η_{100}/cQ curves of H-CPAN with H-SPAN and Carbopol, some minor differences may be partly due to difficulties in measuring Q accurately or may be real differences. The plateau region of η_{100}/cQ is reached at $cQ = 2$ for H-SPAN and Carbopol, but it begins at about $cQ = 4$ for H-CPAN.

Variation of shear modulus G was determined in the same series of dilutions (Fig. 5). The variable $G_{100}/c^{1/3}$ is the appropriate reduction for modulus if the theory of rubber-like elasticity holds.⁶

Our interpretation may be seen more easily by comparing similar experiments with Carbopol-941 gel⁴ (Fig. 5). In these, it is evident that $G_{100}/c^{1/3}$ is approximately constant for dilution with water or salt solution, provided cQ is not too small. Values decrease at cQ less than 3, except for water, where values in-

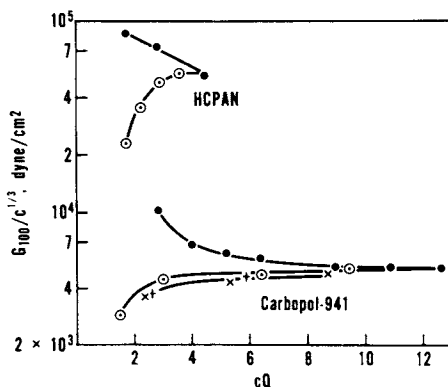


Fig. 5. Reduced shear modulus $G/c^{1/3}$ for dilution series of H-CPAN in water (●) and isoionic NaCl solution, $r = 0.3$ (○). Data are for a shear rate of 100 sec^{-1} . For comparison, data⁴ for Carbopol-941 gel are also given in water (●), isoionic NaCl, $r = 0.17$ (○), $r = 0.3$ (x), and $r = 0.67$ (+).

crease at low cQ . The plateau value is the apparent dry modulus of the gel particles. Although increase with dilution in water is not explained, it may be related to the increase in modulus that occurs in rubbers when molecular chains are stretched beyond the region of Gaussian statistics.⁶

The limited data on H-CPAN are consistent with the interpretation for Carbopol. There is a definite trend toward a plateau value at higher concentrations.

The behavior of G for H-CPAN and other closely packed gel particles can be differentiated from that for a carboxymethyl cellulose gel which forms by self-association of molecules when concentration becomes high enough. Hermans⁷ noted that in such a system the shear modulus, obtained by stress-strain measurements, varied as c^2 . This behavior is clearly different from our observations on closely packed gel particle suspensions with relatively permanent crosslinks within the particles.

Relationship Between Viscosity Function and Degree of Crosslinking in the Gel

H-CPAN is a third kind of polymeric material, which can be described by the use of reduced variables cQ and η/cQ . It thus appears as expected that the relationships apply generally to closely packed gel thickeners. As the gels become more densely crosslinked, the plateau values of η_{100}/cQ versus cQ increase.³ Furthermore, all the examples so far examined seem to follow nearly the same relationship in Figure 6, where the apparent molecular weight between crosslinks, M_c , is plotted against $G_{100}/c^{1/3}$. M_c is calculated from the equation for rubber-like elasticity:

$$M_c = \rho^{2/3}RT/(G/c^{1/3})$$

where ρ is polymer density, R is the gas constant, and T is temperature.

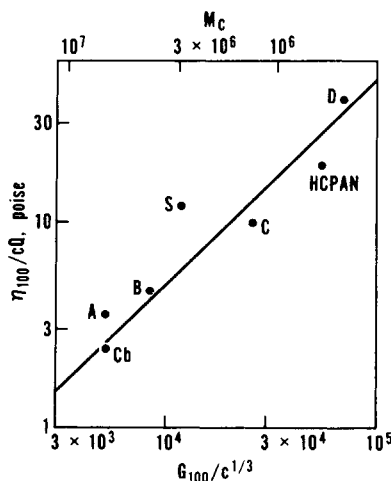


Fig. 6. Relation between plateau values of η_{100}/cQ and $G_{100}/c^{1/3}$ for all known examples of closely packed gel thickeners. A, B, C, D, S, H-SPAN³; Cb, Carbopol-941⁴; H-CPAN, The straight line was drawn with a slope of 1.

Figure 6 is a logarithmic plot. The straight line, drawn with unit slope, demonstrates that the values of η_{100}/cQ are approximately proportional to the first power of $G_{100}/c^{1/3}$, or to M_c^{-1} . It is clear, then, that M_c^{-1} , i.e., the degree of crosslinking, influences viscosity directly in closely packed gel particle thickeners. A greater M_c^{-1} results in proportionately greater η_{100}/cQ if $cQ > 2$.

The recoverable shear, defined above, can be restated in terms of the variables in Figure 6 for $\dot{\gamma} = 100$:

$$S = \frac{\eta_{100}/cQ}{G_{100}/c^{1/3}} \cdot 100 c^{2/3}Q.$$

Since the ratio of experimental variables is approximately constant, S will be proportional to $c^{2/3}Q$. The suspensions will have lower S , i.e., be shorter, toward the right side of Figure 6, where Q decreases, or toward lower c . We confirmed this relation during casual observation of the suspensions.

Another feature of these materials that can influence viscosity is the chemical composition of the polymer, which would determine the swelling power of the gel in a given solvent. Viscosity would vary in proportion if M_c and η/cQ remains constant. Ionic functionalities in the polymers are the most prominent in increasing swelling (in water); but other solvent-solute interaction parameters would be expected to have an effect, especially for slightly ionized or nonelectrolytic polymers. As yet, though, we have not examined the parameters which affect solvent swelling experimentally.

Whether nonelectrolyte and other polymers with different chemical interactions with a solvent would have the same relation with M_c , as given in Figure 6, has not been completely investigated. The three kinds of polymeric materials shown in Figure 6 are all highly ionic polyelectrolytes, which are too similar to test this point. We do know that changes in viscosity with ionic strength of the medium are predictable by the η/cQ reduction, and, therefore, the η/cQ reduction should be constant through a range of chemical composition of the polymers. Further work will be done on this possibility. Meanwhile, it is evident that the η/cQ relation expressed in Figure 6 is rather general in application.

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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