

Tailoring Closely Packed Gel-Particle Systems for Use as Thickening Agents*

N. W. TAYLOR and E. B. BAGLEY, *Northern Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

When used as a thickening agent in aqueous suspension, hydrolyzed starch-polyacrylonitrile graft copolymer (H-SPAN) has broadly variable rheological properties, such as viscosity, storage modulus, and stress overshoot characteristics. A series of H-SPAN preparations with variable swelling ratio Q were made by pretreating portions of stock material. As 1% suspensions in water, they had viscosities η that were non-Newtonian. At a constant shear rate, η of the suspensions depended on Q and had a sharp maximum in the midrange of Q . In terms of reduced concentration cQ , where c is weight fraction of polymer, the highest η occurred when cQ was approximately 2. With isoionic dilution, each suspension had a constant reduced viscosity function, η/cQ , provided $cQ > 2$. The value of η/cQ fell rapidly when cQ approached 1. All thickeners of the closely packed gel-particle type so far examined have this relation of the reduced variables. The shear modulus calculated from measurements of primary normal force and corrected for solvent swelling, according to theory for rubber elasticity, was essentially constant for each suspension measured during isoionic dilution to $cQ = 2$. The density of crosslinks calculated from the modulus was extremely low for all samples. The variable rheological properties of the preparations resulted primarily from differences in their low effective crosslink densities.

INTRODUCTION

One class of polyelectrolyte thickening agent owes its high viscosity and elastic properties to the presence in suspension of closely packed, highly swollen gel particles. There are two known examples of this kind of thickening agent: hydrolyzed starch-polyacrylonitrile graft copolymer (H-SPAN)¹ and Carbopol 941.² For both materials, viscosity η can be correlated with reduced concentration cQ , where c (g/g) is polymer concentration and Q is swelling ratio (g swollen gel/g polymer) in excess solvent of the same ionic strength. The gel particles are closely packed when $cQ \geq 1$. For values greater than 1, cQ measures the capacity of the gel to swell on dilution.

Viscosity behavior is best described by the reduced viscosity function η/cQ . For both materials, η/cQ is essentially constant (within better than 20%) if cQ is greater than about 2. At lower cQ , η/cQ falls abruptly. This constancy of η/cQ in the plateau region is an important correlation of data, since the wide variation

* Presented at the 18th Canadian High Polymer Forum, Hamilton, Ontario, Canada, August 20-22, 1975.

of η with both ionic strength (sixfold in one example) and polymer concentration is compensated by this transformation.

Once obtained, the value of η/cQ for a material can be used to predict η for any other condition where $cQ > 2$. Since the materials have non-Newtonian viscosities, η does depend on shear rate, but comparisons can be made at a single constant shear rate.

In our study, we examined the effect of polymer structure on the plateau values of η/cQ , as well as other rheological properties. For H-SPAN, such properties as viscosity, elasticity, and swelling volume vary widely, depending either on pretreatment or through unknown sources. A series of H-SPAN samples were made that had a wide range of swelling properties and in which, as will be shown, the structural variable was mainly the amount of crosslinking between chains. Because this structural feature strongly influences desirable rheological properties, it must be rigorously controlled.

In a swollen gel system, in which the polymer has a rubber-like character, two properties of the polymer affect its power to absorb solvent—effective density of crosslinks between molecular chains and dispersibility of the molecular chains of the gel in the solvent. In an ionic polymer, this dispersal power strongly depends on ionic groups on the chain as well as on ions in the solvent. We have emphasized the crosslinking by maintaining ionic properties essentially constant, but the ionic aspects are another important feature of closely packed gel thickeners that should be remembered in controlling the thickening action.

The elastic properties of closely packed gel systems are prominent and can be beneficial or not, depending on their application. We had noted that the elastic shear modulus, as calculated from primary normal force measurements, was more nearly independent of ionic strength of the medium, when plotted against cQ rather than c . Now, we show that these gels can be analyzed as swollen rubber-like materials and that the crosslink densities derived from the modulus are a reasonable representation. According to this analysis, most of the elastic response in steady shear depends on the crosslink density in the gel. Viscosity and elasticity should be closely correlated in the series.

Sometimes an overshoot occurs in shear stress τ or primary normal force $P_{11} - P_{22}$, at the start of a constant shear treatment. These transient effects are also important in some applications, but are not so clearly understood. Stress overshoot in τ and $P_{11} - P_{22}$ can be built up in some samples by oscillating them.³ Almost no correlation of structure with overshoot function is known, except that it occurs with some elastic liquids. Although mathematical models are available,⁴ the structure and mechanism involved are uncertain. In the current series of samples, we do find differences in this rheological response.

EXPERIMENTAL

The H-SPAN starting material was SGP 502 from General Mills (Minneapolis, Minn.). Approximately 1-g lots (labeled A to I) of this material were taken for pretreatment to modify physical properties. Some lots were steeped in alkali at room temperature at about 1% polymer concentration. All lots were made up to about 1% polymer, pH 7.6, and then were freed of soluble material by centrifuging in 1M NaCl. Soluble material in the supernatant fluid was dis-

carded. Salt was removed from the gels by centrifuging and resuspending them in dilute HCl five times, then making up to 1% weight basis (A, B, and C lots) or dehydrating with absolute ethanol and drying *in vacuo* (D to I lots). The latter were dried at increasing temperature as their pretreatment.

The Rheometrics mechanical spectrometer (Imass, Accord, Mass.) was used in the cone-and-plate mode⁵ and in the eccentric-rotating-disk mode,⁶ i.e., as the Maxwell orthogonal rheometer. Our procedures have been given for rheometry as well as for swelling measurements in the ultracentrifuge^{1,2} and for oscillation to build overshoot.³

Ionic strength μ in the gel suspensions is defined as suggested by Terayama and Wall:⁷

$$\mu = rm + s$$

where m is the equivalent concentration of coions in the swollen gel, and s is the ionic strength of diffusible salt; the value of r depends on linear charge density of the molecular chains⁸ and is about 0.3 for H-SPAN grafted chains.

Even though earlier we used η_{sp}/cQ as reduced viscosity function, because viscosity of the solvent probably influences these systems little, the conceptually simpler function η/cQ was used here. Values of η are much greater than these for the solvent, so both η/cQ and η_{sp}/cQ are essentially constant at $cQ > 2$.

RESULTS AND DISCUSSION

Viscosity and Swelling Power

We knew from preliminary experiments that treating an H-SPAN sample with heat or humidity decreased its swelling ability in water, whereas treating with alkali and neutralizing increased swelling power. Therefore, a series of H-SPAN samples were prepared with varying swelling powers and containing less than 5% soluble material. Viscosity flow curves were determined for these samples, as well as their swelling weight in 0.3M NaCl solution, $Q_{0.3}$.

Alkali pretreatment of samples increased the neutralization titer somewhat,

TABLE I
Pretreatments of H-SPAN^a Samples

Sample	Treatment	Titer to pH 7.6, mM/g	$Q_{0.3}$
A	5M NaOH, 18 hr	6.0	170
B	1M NaOH, 18 hr	5.2	155
C	0.1M NaOH, 18 hr	5.1	99
D	none, dried 88°C	5.2	66
E	none, dried 95°C	5.1	51
F	none, dried 100°C	4.9	54
G	none, dried 105°C	4.9	41
H	none, dried 111°C	4.6	39
I	none, dried 115°C	—	28
S	none	5.3	101
Cb ^b	none	11.8	294

^a H-SPAN = Hydrolyzed starch polyacrylonitrile.

^b Carbopol 941 gel.²

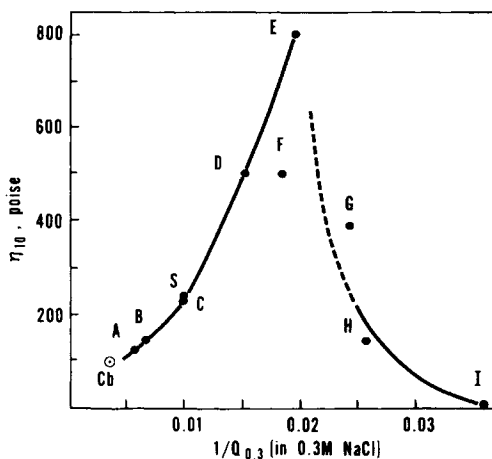


Fig. 1. Viscosity η_{10} at shear rate 10 sec^{-1} and 1% polymer concentration as a function of reciprocal of swelling volume $1/Q_{0.3}$ in 0.3M NaCl solution for hydrolyzed starch polyacrylonitrile (H-SPAN) gel (S), and samples A to I of modified H-SPAN (see Table I). Carbopol 941 gel (Cb) is included for comparison.

whereas heating decreased it (Table I). In this series, there was not enough change to affect ionic properties.

The values of $Q_{0.3}$ are markedly affected by the pretreatment. Samples A to I, the current series, were selected to have the desired range in $Q_{0.3}$. Sample S is an H-SPAN gel not pretreated. Data on Cb, a Carbopol-941 gel² previously reported, is repeated for comparison with H-SPAN. Carbopol has a greater density of ionic groups along the chains than does H-SPAN and is not strictly comparable in the current series.

Viscosity flow curves of all the H-SPAN samples were the usual non-Newtonian, shear-rate thinning type as experienced previously. To characterize the different H-SPAN preparations, viscosities of the 1% dispersions at a shear rate of 10 sec^{-1} , η_{10} , were plotted (Fig. 1) as a function of the reciprocal of $Q_{0.3}$. It is evident that the H-SPAN gels with the larger swelling powers, on the left-hand side of Figure 1, had relatively low values of η_{10} .

As swelling power $Q_{0.3}$ of the gels diminishes, proceeding toward the right in Figure 1, η_{10} increased to a maximum value. On further decrease in swelling power, η_{10} dropped again to a low value. In sample I, the swelling power of the gel was insufficient to fill the available suspension volume even in water, and in a few minutes the gel phase settled out.

Samples F, G, and H were rubbery, tended to creep out of the rheometer, and were otherwise difficult to measure. The dotted lines in Figure 1 indicate the uncertainty. These samples were particularly difficult to measure at higher shear rates, so the comparison presented in Figure 1 was made at a shear rate of 10 sec^{-1} instead of our customary 100 sec^{-1} .

The experiments in Figure 1 demonstrate clearly that for thickening agents of the closely packed gel type, viscous properties depend on structural relationships within the gel particles. Variation in this gel structure was inserted by pretreatments in the current series of H-SPAN gels, and is detectable as differences in swelling power. Under the conditions of Figure 1, i.e., 1% sus-

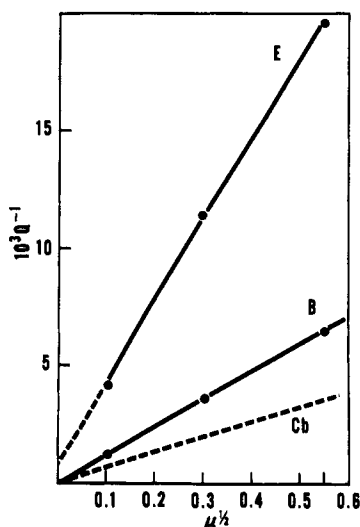


Fig. 2. Reciprocal of swelling volume Q^{-1} as function of $\mu^{1/2}$ for samples B and E of modified H-SPAN. The Cb curve is included for comparison.

pensions in water, sample E is a more effective thickening agent than A or Cb. For other conditions, different relative effective action would prevail, as will be shown.

The appearance of a maximum η_{10} in Figure 1 can be understood in terms of variation of η with the reduced concentration parameter cQ . Obviously, the gel in sample I could not absorb all the solvent at 1% concentration even in water, and therefore that cQ was less than 1. We suspected that the fall in η_{10} to the right of the maximum is related to the progressive decline in cQ to and below the critical value 1 as swelling power of the gel decreases.

Swelling Curves

The relation of Q to μ was examined earlier.^{1,2} The value of Q^{-1} was linear with $\mu^{1/2}$ for an H-SPAN gel and for Carbopol-941 gel. Figure 2 shows data for a few of the current series of H-SPAN preparations. For all samples examined (A to E, S, and Cb), a linear relationship occurred, but slopes differed. Also, there appears to be a positive intercept on Q^{-1} for the samples of lower swelling power. These curves were used to determine the value of Q for a given μ in order to calculate cQ .

Reduced Viscosity Function

A series of isoionic dilutions for samples A to E (Fig. 3) disclosed the same type of behavior experienced earlier for H-SPAN gel and Cb gel. Values of η and $P_{11} - P_{22}$ were measured as functions of shear rate for each isoionic dilution series. The reduced viscosity function, η_{100}/cQ and reduced concentration cQ were calculated from Q values corresponding to μ values of the stock preparations. Q is constant during an isoionic dilution since Q is a function only of μ .

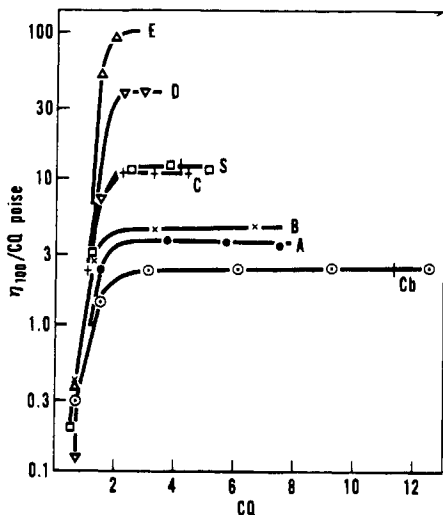


Fig. 3. Reduced viscosity function η_{100}/cQ of S, modified H-SPAN samples A to E, and Cb during a series of isoionic dilutions. η_{100} is measured at $\dot{\gamma} = 100 \text{ sec}^{-1}$. Ordinate scale is logarithmic. Initial concentration of samples A to E was 1%; of S, 1.5%; and Cb, 1.23%. Values of cQ at 1% in water are marked on the curves of S and Cb by vertical lines.

Figure 3 data plots confirm our earlier observations. Over the measurable range of viscosity, η_{100}/cQ is essentially constant for all samples, provided $cQ \geq 2$. Near $cQ = 1$, η_{100}/cQ drops precipitously. In other words, for all samples, thickening action is efficient only when the gel particles are closely packed, absorbing all available solvent in the system.

The individual preparations described in Figure 3 differ greatly. These differences reflect the underlying structure in the gel, which we tentatively ascribe to variability in an effective crosslinking density.

The reduced viscosity function curves of Figure 3 were measured only during isoionic dilution, but they are a complete description for all ionic strengths within about 20% precision, as we noted for Cb² and for an H-SPAN gel such as S.¹ We expect that similar relations hold for all the gels measured. In any general ionic conditions, Q would be found for the ionic strength in the gel system, or knowing μ and the curves of Figure 3, η_{100} could be calculated for any suspension.

The relationships in Figure 3 can now explain the sharp maximum in viscosity observed in Figure 1 as $Q_{0.3}$ varies. Starting with sample A, as crosslinking increases and $Q_{0.3}$ decreases, plateau values of η_{100}/cQ increase; η_{100} and η_{10} also increase, though not so rapidly since Q is decreasing in this series. However, in sample E, a 1% suspension is already as low as $cQ = 2$; and for any further decrease in swelling power, the plateau value would not be reached, but a lowered value of η_{10}/cQ as cQ diminishes to 1 would be anticipated.

At higher degrees of crosslinking, a continuing higher plateau value of η_{100}/cQ would occur, but the c necessary to reach it would also increase rapidly. Thus, sample E has nearly the highest η possible for 1% suspensions of closely packed, crosslinked gel particles (Fig. 1).

For any other series at constant conditions of differing polymer concentration and μ , there will be a similar effect on η when swelling power of the gel varies. The maximum in η should occur under conditions when $cQ = 2$.

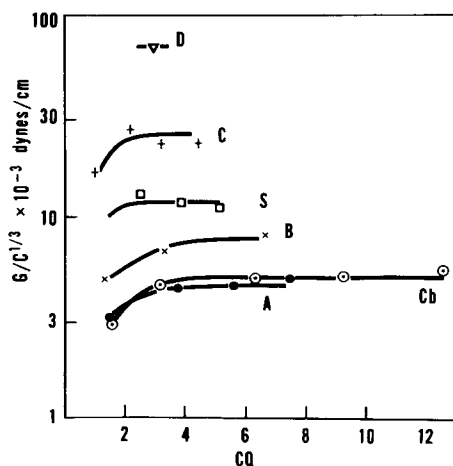


Fig. 4. Reduced modulus, $G/c^{1/3}$ during series of isoionic dilutions of S, Cb, and modified H-SPAN samples A to D. G was determined at 100 sec^{-1} . Ordinate is a logarithmic scale. The interpolated positions of 1% S and Cb in H_2O are indicated on their respective curves by vertical lines.

The relationships noted here can be applied to tailoring a gel for use as a thickening agent for any particular need. If a certain value of η is desirable, then the most efficient use of polymer would prescribe a value of cQ equal to about 3, i.e., higher than 2, to allow for some unknown variability. If any contact is possible with salt solutions, $cQ > 3$ may be necessary. Choice of cQ then leads to a value of η/cQ in the plateau region, which can be obtained by adjusting the crosslink density of the polymer.

This formula should have fairly general application; that is, it should apply to any closely packed gel system whether nonelectrolyte or electrolyte in character. Only a few measurements of η and Q should permit predicting which direction to adjust crosslink density. Of course, other aspects of thickening action also must be considered in practical applications, such as presence of soluble polymer material, interaction with other constituents, and time effects. Lotion formulas⁹ containing Carbopol-941 at 0.1% have a cQ value of approximately 3, presumably achieved by experiment.

Shear Modulus and Estimation of Crosslink Density

In the theory of rubber-like materials, the shear modulus G depends only on the density of crosslink points in the rubber sample. In solvent-swollen rubbers, experimental results agree closely (about a factor of 3) with theory when a correction for swelling volume is applied. The value of G is related to the average molecular weight of chain between crosslinks, M_c , by the equation

$$G/\phi_2^{1/3} = \rho RT/M_c$$

where ϕ_2 is volume fraction of polymer. The equation is derived from eq. (4.26) and (5.11) in Treloar.¹⁰ Conversion to weight concentration c gives

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

The reduced modulus $G/c^{1/3}$ is an apparent modulus of the solvent-free material.

The values of G for our H-SPAN gel samples and Cb were calculated from the observed values of $P_{11} - P_{22}$ and τ at shear rate of 100 sec^{-1} by the equation

$$G = \frac{2\tau^2}{P_{11} - P_{22}}$$

Values of G for our samples were approximately constant with shear rate or increased moderately with shear rate over the range we examined.

In our earlier study of Cb, we noted that G as a function of cQ was influenced little by μ , except for dilute water solutions. The curves of Figure 4, therefore, would be good descriptions of the G for most H-SPAN suspensions.

The values of $G/c^{1/3}$ do appear to be nearly constant during the series of isoionic dilutions (Fig. 4). As was true for reduced viscosity function, the reduced modulus also decreases abruptly as cQ approaches 1. Although values at low cQ are not precise, we can be confident that $G/c^{1/3}$ does turn down.

To consider M_c , we must assume G measured on the gel paste is essentially equivalent to G of the actual gel particles. Though this assumption is yet to be established, preliminary information from studies with eccentric rotating disk mode,⁶ in which the loss modulus G'' and storage modulus G' are obtained, tend to confirm it. Hydrated H-SPAN films were examined by this technique and, afterward, were crushed to a paste with minimal shearing by squeezing through a fine screen. Values of G' and G'' over a range of shear rates were approximately the same (30%) for film and paste. This agreement was found with several different films having different moduli. Also, G calculated from $P_{11} - P_{22}$ agreed essentially with values of G' . Unfortunately, data are not so precise at the low distortions needed for linear behavior with displacement, but we do conclude tentatively that G is mainly a measure of modulus of the gel particles in these purified preparations, provided $cQ > 2$. This subject will be examined further in a subsequent report.

The value of M_c calculated for H-SPAN gel sample S is 3.4×10^6 daltons. For sample D, M_c is 0.58×10^6 ; for A, 7.8×10^6 . These values are only an apparent molecular weight between crosslinkages and do not necessarily characterize the true structure. Particularly, because the polyelectrolyte chains of H-SPAN are grafts on starch chains, the H-SPAN structure should have numerous free chain ends. This structure would have a reduced modulus, or increased value calculated for M_c , compared to the values of an ideal network with the same M_c .

The starch component of H-SPAN is present to about 43% (for the usual 1:1 add-on). The molecular weight of the hydrolyzed grafted chains^{11,12} is about 1×10^6 . From these figures, the average molecular weight in the starch component between grafts is about 0.7×10^6 . While the state of the starch component is unknown, except that it has been gelatinized, it must be a fairly loosely knit aggregate.

Different preparations of pretreated H-SPAN from the same starting material can absorb as much as 1400 times its weight of water or as little as 100 times. All this variation need not occur in the starch only, but in the current series A to D, of high swelling power, a lightly crosslinked starch fraction is implied. The experimental value of M_c for sample S, 3.4×10^6 is in agreement with these ideas.

The importance of high molecular weight between crosslinks in the gel needs reemphasizing. This structural feature is the key in developing either highly

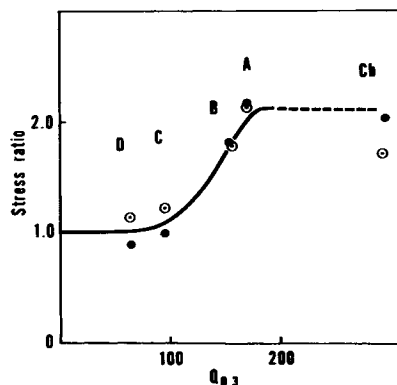


Fig. 5. Ratios of peak value (overshoot) of stress to the value after one revolution (i.e., near steady state) for shear stress (●) and primary normal force (○) for samples A to D and Cb.

swollen gels or effective thickening agents of the closely packed gel type. This feature requires that the molecular weight of the "original" chains be higher than M_c and that these chains be mostly free coiling.

Overshoot in Shear Stress and Normal Force

We had noted³ that some rather special samples of H-SPAN can develop an overshoot in both τ and $P_{11} - P_{22}$. On starting the rheometer at a constant shear rate, τ and $P_{11} - P_{22}$ rise to a maximum and then fall to the steady-state level. Both Carbopol-941 and its gel fraction can develop an overshoot.²

The overshoot phenomenon is particularly sensitive to sample history and to preconditioning of the final sample in the rheometer. Oscillation in the rheometer at a slow rate builds up the overshoot condition, whereas a rather small extent of shear will greatly diminish it.

The current series of samples was examined after a constant oscillation treatment for 18 hr at a strain amplitude of 4 and a frequency of 0.2 sec^{-1} . They were tested at a shear rate of 25 for one revolution of the cone. The data (Fig. 5) disclose that only the gels with high swelling power develop an overshoot. There is a rather sharp change from no overshoot to high overshoot in the mid-range. Overshoot is not correlated in a simple way with either G or Q , but it appears to be an indication of a much subtler property. The curve between A and Cb is uncertain, since H-SPAN and Cb gel are different materials.

There is still no satisfactory explanation for the overshoot phenomenon. It occurs in some polymer solutions, and now we know that it occurs in some polyelectrolyte gels. It undoubtedly is important in application of gels to particular uses. Furthermore, it is an indication either of a rather elusive aspect of structure in gels or of interaction among neighboring gel particles.

The mention of firm names or trade products does not constitute an endorsement by the U.S. Department of Agriculture over other products or firms not mentioned.

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Received January 15, 1976