# Some Rheological Properties of Water-Soluble Hydroxypropylcellulose*

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## Synopsis

Water-soluble hydroxypropylcellulose having a hydroxypropyl molecular substitution (MS) of approximately 4.0 is a thermoplastic which may be fabricated in conventional plastic-forming equipment. Its high-temperature rheological properties have been measured over a wide range of temperatures, shear rates, frequencies, and diluent concentrations, by using the Weissenberg rheogoniometer. The rheological behavior of such hydroxypropylcelluloses is quite different from that of a nonpolar thermoplastic. This behavior may be interpreted in terms of two types of supermolecular structure: a crystalline phase which persists up to at least 215°C (as established by x-ray examination), which is dispersed in an amorphous but highly hydrogen bonded matrix of stiff molecules.

## INTRODUCTION

Water-soluble hydroxypropylcellulose (HPC)† is unusual among the water-soluble cellulose derivatives, in that it is a thermoplastic which may be readily fabricated by use of conventional plastic-forming equipment. Operating temperatures are usually in the range 150–180°C. The preparation and properties of this HPC will be described in detail elsewhere.[1] An idealized structure, showing a molecular substitution (MS) of 4.0 on both anhydroglucose units, is shown in Figure 1. This illustrates two of the many possible ways in which four hydroxypropyl units may add to a chain of anhydroglucose units.

X-ray and microscopic studies have shown that in HPC of MS approximately 4.0, a significant quantity of the polymer is in a crystalline phase, which persists up to at least 215°C.[2]

The unique physical and chemical properties of HPC[1] led to a rheological study of this polymer, both plasticized and unplasticized, over a wide range of temperatures and shear conditions, in order to determine its basic rheological behavior and to gain some insight about its molecular and supermolecular structure.

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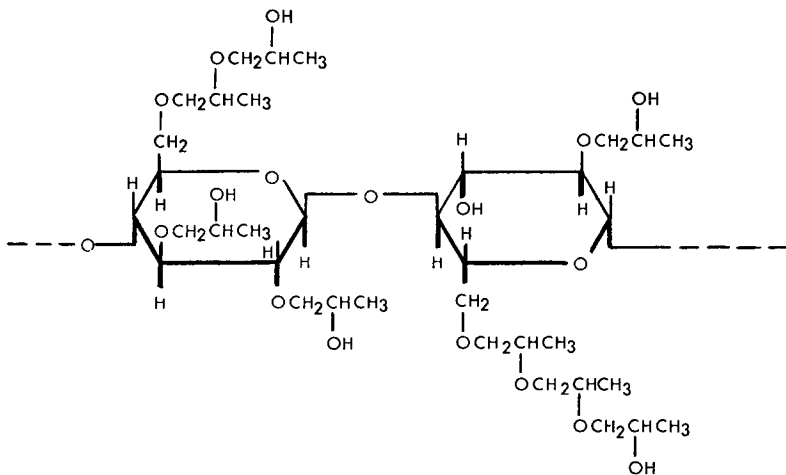† Hydroxypropylcelluloses are being marketed under the trade name Klucel by Hercules Incorporated.

Fig. 1. Idealized structure of hydroxypropylcellulose of MS 4.0.

## EXPERIMENTAL

Samples of HPC having MS values of approximately 4.0 were used in this work. Intrinsic viscosities were determined in 50/50 water–ethanol (by volume) mixtures at 25°C and ranged from 3.1 to 4.2 dl/g. Based upon ultracentrifuge studies of whole polymers,[3] these intrinsic viscosities correspond to weight-average degrees of polymerization of 550 to 700.

The sodium carboxymethylcellulose (Hercules Incorporated) had an average degree of substitution (DS) of 0.4 carboxymethyl groups per anhydroglucose unit.

The following plasticizers and diluents were used without further purification: Atlas G-2240, a sorbitol ethylene oxide adduct (Atlas Chemical Industries, Inc.), octadecanol-1 (Eastman Kodak Co., No. 4053), lauryl alcohol (Alfol 12, Continental Oil Co.).

Unplasticized samples were dried by milling on a 6-in. two-roll mill at 125°C. The resulting sheet was chopped up in a Waring Blendor. Films were pressed from this powder at 163°C. For the Gibbs-Merrill rheometer, films of 12 mils thickness were used; for the Weissenberg rheogoniometer, the thickness was 60–65 mils. The films were held in the press for 5 min under a pressure of 5000–10000 psi.

Plasticized samples were prepared in a similar manner except that the plasticizer was hand-blended with the HPC before the roll mill drying. Octadecanol was added as a solution in ethanol, the ethanol being volatilized in the subsequent operations. All films were stored in a desiccator over $P_2O_5$ before use.

Preliminary rheological measurements were carried out using the Gibbs-Merrill shear creep rheometer.[4] This is a simple instrument in which the sample is subjected to plane Couette flow. It is limited, however, in shear rate ($\dot{\gamma}$) range and the total shear ($\gamma$) to which the sample may be subjected.

Most of the rheological measurements reported here were made using the Weissenberg rheogoniometer.[5] A 2.5 cm cone-and-plate configuration was used. The cone angle $\alpha$ was 4.0°. Steady-shear viscosities $\eta$ were calculated from the measured torque $T$ and rotational velocity $\omega$(in radians/sec) from the basic equation

$$\eta = 3T\alpha/2\pi\omega R^3 \tag{1}$$

where $R$ is the radius of the cone and plate. Oscillatory measurements were made by subjecting the sample to a sinusoidal strain of amplitude $A$ and frequency $f$ (cycles/second). The real component of the dynamic viscosity, $\eta'$, is given by

$$\eta' = (3\ T_0\ \alpha/4\pi^2\ f\ R^3\ A)\ \sin\delta \tag{2}$$

while the real component of the shear modulus $G'$ is given by

$$G' = (3T_0\ \alpha/2\pi R^3\ A)\ \cos\delta \tag{3}$$

$T_0$ is the peak torque (in dyne-centimeters) and $\delta$ is the phase angle between the input sinusoidal strain and the resulting sinusoidal stress. The natural frequency of the measuring system was 132 cps while the highest frequency of the forced oscillation was 30 cps. Thus, no inertial correction was necessary, and eqs. (2) and (3) were used without modification. Strain amplitude in the dynamic measurements was generally 0.15 or lower. Experiments at different amplitudes showed that the measurements were made in the linear viscoelastic region.

## RESULTS AND DISCUSSION

Preliminary experiments at low shear rates and shear stresses $\sigma$ were carried out by using the Gibbs-Merrill shear creep rheometer. As will be apparent when the rheogoniometer results are discussed, the major limitation of the Gibbs-Merrill rheometer is the relatively low amount of total strain to which the sample may be subjected. These measurements may be considered only as qualitative; however, they did demonstrate that HPC shows retarded elasticity, is highly non-Newtonian and gave some evidence of thixotropic breakdown. This is the type of rheological behavior that would be expected from a polar polymer such as HPC.

A very unusual type of behavior, however, was noted. As sample temperature is increased up to 190–200°C, the usual decrease in viscosity was observed. As the temperature was raised higher, however, the viscosity increased irreversibly.

Some sort of crosslinking or chain extension reaction was immediately suspected. This does not appear to be the explanation, inasmuch as the $[\eta]$ of the sample after heating was, within experimental error, that of the unheated material. The same effect was observed with plasticized samples
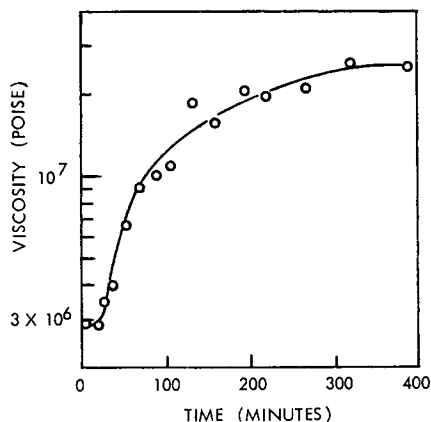
Fig. 2. Change of viscosity of hydroxypropylcellulose at 190°C as a function of time (shear stress 16000 dynes/cm²).

or concentrated solutions, but the minimum in the viscosity temperature curve was shifted to lower temperatures. Similar results were obtained with the CIL viscometer, a capillary instrument.[6]

Reproducibility of these measurements was very poor, and the data presented in Figure 2 show the reason. The viscosity of HPC at 190°C, as a function of time at constant shear stress ($\sigma = 16 \times 10^3$ dyne/cm²), is seen to increase by almost a factor of ten over a period of several hours.

### Rheogoniometer Measurements

**Steady Shear.** Measurements made at a constant shear rate over a period of time, subject the sample to large total shear strain. Changes in shear stress with time (which is proportional to total strain at constant $\dot{\gamma}$) provide considerable information about delayed elasticity and thixotropic structure breakdown. In this work, $\dot{\gamma}$ was limited to about 0.2 sec$^{-1}$ and below. At higher shear rates, the sample fractures and is no longer retained in the gap.

The curve shown in Figure 3 is typical of the behavior of HPC under steady-shear conditions. The shear stress rises to a maximum and then decreases to a steady value. When shearing is stopped, the stress decays rapidly at first and then approaches zero quite slowly. This type of curve was obtained with HPC over wide ranges of temperature, shear rate, and concentration. The presence of a maximum in the $\sigma$ versus $t$ curve is indicative of a thixotropic structure breakdown in the system. Such a maximum was observed in all the HPC systems examined with the exception of measurements made at low shear rates (ca. 10$^{-3}$ sec$^{-1}$) on relatively dilute systems. This occurrence of a maximum is far more common with polymer melts and concentrated solutions than is generally realized, and it has been considered in some detail by Russian workers.[7,8] On making the
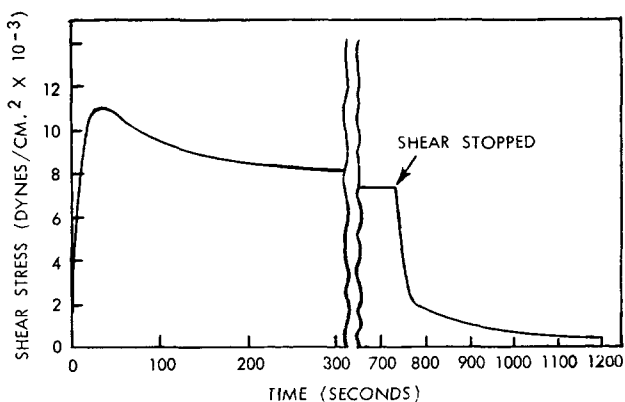
Fig. 3. Shear stress as a function of time for 90:10 hydroxypropylcellulose–Atlas G-2240 at 154°C (shear rate 5.40 × 10$^{-2}$ sec$^{-1}$).

reasonable assumption that relatively weak junction points between polymer chains exist in the system, which result in the formation of a three-dimensional structure, the $\sigma$ versus time curve can be interpreted as follows. At low strains (the ascending branch of the curve), the shear stress builds up primarily by an elastic deformation until it reaches a value at which the three-dimensional structure begins to break down to relax the stress. The descending branch of the curve may be considered from a kinetic viewpoint[9,10] as two opposing rate processes, structure breakdown and buildup. When these rates become equal, equilibrium, corresponding to a given shear rate, is established, $\sigma$ is constant, and the sample is flowing viscously. When shearing is stopped, the stress relaxes and after sufficient time has elapsed, the three-dimensional structure is reformed.

Junction points between polymer chains may occur by entanglement, hydrogen bonding, or by way of the fringe micelles which are present when crystalline material or gel centers are present in the system.[11,12]

This general type of stress–time behavior occurred whether or not there was any crystallinity present in the system, as judged by examination with a polarizing microscope. One would expect HPC of MS 4.0 to be a rather expanded or elongated molecule. The molecular weight of a substituted anhydroglucose unit of length 5.15 Å is approximately 400, and a polymer composed of such bulky units would not be very flexible. The expanded configuration is confirmed by the value of 0.90 for the exponent in the Mark-Houwink equation for HPC in water.[3,13] The fact that the intrinsic viscosity, and the slope constant in the Martin equation, are the same in water, ethanol, and water–ethanol mixtures is consistent with the view that HPC has an extended configuration. On remembering that HPC is a highly polar molecule, having three OH groups per 5.15 Å of backbone chain length, a high degree of hydrogen bonding would be expected. This, combined with an expanded configuration, would give rise to a three-dimensional

structure whose rheological behavior in steady shear would be that which was found experimentally.

It was observed that the maximum shear stress in steady shear occurred at a remarkably constant value of the total strain ($\gamma = \dot{\gamma}t$). Over two decades of shear rates, 100°C range in temperature, and HPC concentrations from 23 to 100%, $\gamma$ ranged from 0.8 to 2.0. Strictly speaking, the maximum in the $\sigma$–time curve is not necessarily the point of onset of structure breakdown, but this is a reasonable approximation. The constancy of $\gamma$ for the maximum value of $\sigma$ strongly suggests that, over a wide range of concentrations, temperature, and $\dot{\gamma}$, the same basic three-dimensional structure is present, which requires an imposed strain of 1–2 before significant breakdown. The strain corresponding to the equilibrium portion of the curve is much larger, being of the order of 10 or greater.

Stress relaxation, after equilibrium is reached, requires a spectrum of relaxation times, some of which are very long, for its description.

The low shear-rate behavior discussed above would not be observed in the fabrication of HPC in commercial equipment. Here the shear rates and total strains are sufficiently high that the maximum in $\sigma$ would not be detected and the material would appear to have a constant viscosity at a given shear rate.

**Dynamic Measurements.** In contrast to steady shear, dynamic measurements permit the rheological examination of a sample which has been subjected to very small shear strains. Hence effects due to orientation, disentanglement, or thixotropic breakdown are minimized, and the material
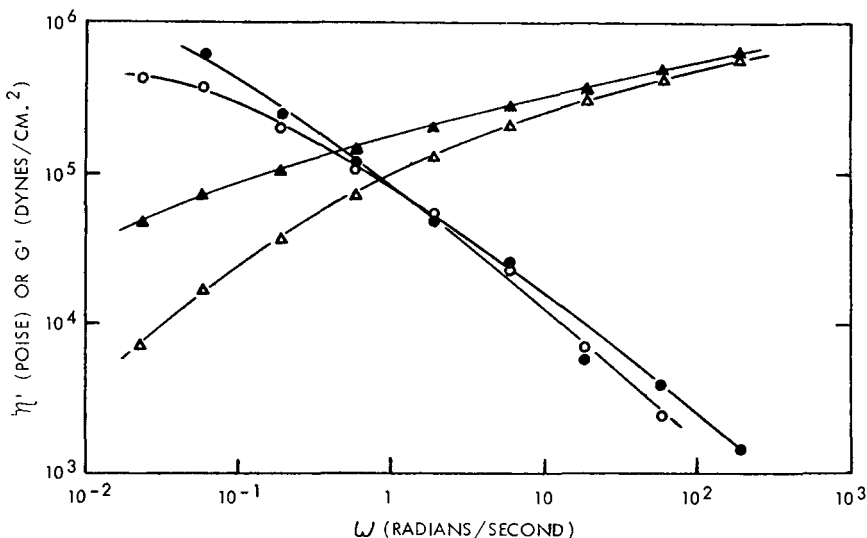


Fig. 4. Dynamic viscosities and moduli of 5:1 hydroxypropylcellulose–octadecanol-1 as a function of frequency after 1 and 4 hr at 190°C. O-$\eta'$, $\triangle$-G' in first hour, ●-$\eta'$, ▲-G' in fourth hour.

may be considered to be in an essentially undisturbed state. Figure 4 shows the effect of aging at 190°C on a HPC sample containing 16.7% octadecanol-1 as plasticizer. The expected decrease in $\eta'$ and increase in $G'$ with angular frequency is observed. The effect of aging on $\eta'$ is not great, wheras $G'$ values after 4 hr at 190°C are markedly higher, particularly at low frequencies. Figure 5 shows the loss tangent as a function of frequency for the same experiment. While there is some scatter of the experimental points, it is quite clear that aging causes a marked change in mechanical properties. The higher values of $G'$ and lower values of tan $\delta$ indicate that the sample behaves more elastically after aging.

Figure 6 shows $\eta'$ and $G'$ values for unplasticized HPC after 1 hr at 190°C and after 1 hr at 220°C. Here there is a marked difference between the dynamic mechanical properties at the different temperatures. The unusual feature is that both $\eta'$ and $G'$ are higher at the higher temperature. Other thermoplastics (e.g., polyolefins) show the opposite effect. The observed results, however, are consistent with the preliminary shear creep results discussed earlier.

At 150°C there is little change in dynamic properties of HPC with time. A comparison of an unplasticized sample with one containing 10% Atlas G-2240 showed lower $G'$ values as would be expected, but the $\eta'$ values were substantially unchanged.

A reasonable interpretation of the dynamic results and the increase of apparent viscosity around 190°C with time (Fig. 2) may be based on the fact that there is a crystalline phase present in HPC which persists up to at least 215°C. This crystalline phase is dispersed in the amorphous but highly structured phase discussed above. These crystallites can serve as major junction points for the three-dimensional structure, based on the
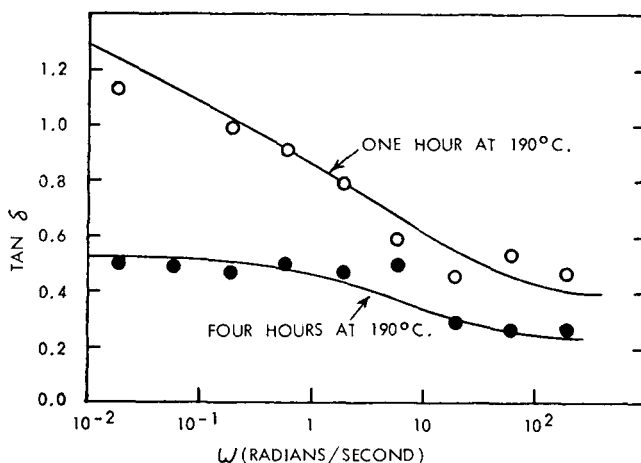


Fig. 5. Loss tangent as a function of frequency of 5:1 hydroxypropylcellulose–octadecanol-1 after 1 and 4 hr at 190°C.
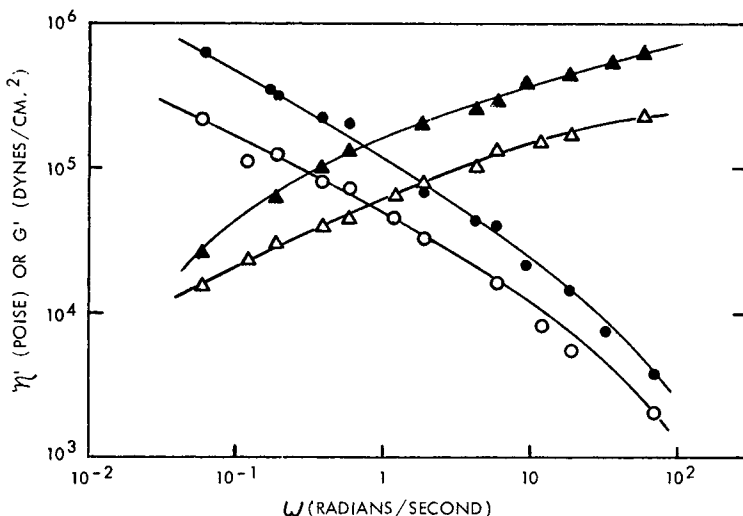
Fig. 6. Dynamic viscosities and moduli of hydroxypropylcellulose after 1 hr at 190°C and after 1 hr at 220°C.   190°C, $\eta'$-0, G'-$\triangle$;   220°C, $\eta'$-●, G'-▲.

fringe micelle picture.[11,12]   At temperatures approaching the melting point, approximately 235°C,[2] two processes could occur.   First, there could be an increase in the overall crystallinity.   High temperature x-ray studies indicated that there was no change in total crystallinity with time, in the temperature range 170–210°C.   However, the specimens were heated for 1 hr before the measurements were made, so this possibility is not necessarily ruled out.   The second, and more likely process would be a disaggregation of the crystallites and dispersion of these crystallites throughout the amorphous thixotropic matrix, with the total crystallinity remaining constant. Rheological properties of aqueous solutions of carboxy-methylcellulose have been discussed in terms of this concept earlier.[11,12]   Such a disaggregation of crystallites would give rise to a much larger number of junction points in the structure.

The dynamic measurements are consistent with this view.   At 190°C and below, G' changes markedly with time of heating, while $\eta'$ is relatively unaffected.   Disaggregation of the crystallites should increase the rigidity (G') of the system without introducing any additional loss mechanism which would be reflected in a change in $\eta'$.   The results with plasticized polymer at 150°C tend to confirm this inasmuch as the presence of plasticizer lowers G' but $\eta'$ is unaffected.   Thus the plasticizer makes the structure less rigid (lower G') but does not introduce new loss mechanisms and $\eta'$ is the same with or without plasticizer.

In Figure 6, dynamic values at 190 and 220°C are compared.   The rise in G' at 220°C is consistent with the above picture.   It is seen, however,

that $\eta'$ is higher at 220°C than at 190°C. This is not in agreement with the observations at lower temperatures, and it may well be that as measurements are made close to the crystalline melting point, other morphological changes in the HPC may be occurring.

It was observed some years ago[11] that if a solution of sodium carboxymethylcellulose (CMC) of low DS was subjected to high power input stirring, it would form a rigid gel on standing. This behavior was interpreted in terms of disaggregation and dispersion of fringe micelles arising from crystallite residues in the CMC. A 5% aqueous solution of CMC of average DS 0.4 was prepared by slow tumbling. A portion of this solution was sheared for several minutes in a Waring Blendor, which produced a rigid gel. The dynamic properties of the solution and gel are shown in Figure 7. Disaggregation and dispersion of the crystallite residues in the CMC system give changes in dynamic properties which are qualitatively very similar to those observed in HPC after prolonged heating. In the case of the CMC gel, $G'$ shows a marked increase. As shown in Figure 8, the loss tangent (tan $\delta$) was zero for the gel, and hence $\eta'$ could not be determined. The similarity is very evident when Figures 4 and 7 and Figures 5 and 8 are compared. These CMC results tend to confirm the hypothesis that the unusual behavior of HPC on prolonged heating arises as a result of the disaggregation and dispersion of the crystalline material which is present.
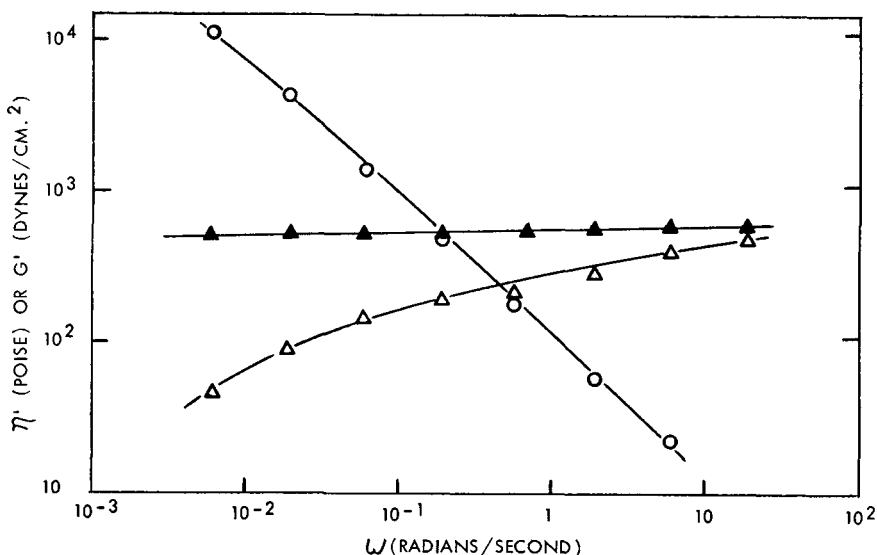


Fig. 7. Dynamic viscosities and moduli as a function of frequency for 5% sodium carboxymethylcellulose (DS 0.4) solution before and after high-power shearing. Before high power shearing, O-$\eta'$, $\triangle$-$G'$; after high power shearing, $\blacktriangle$-$G'$.
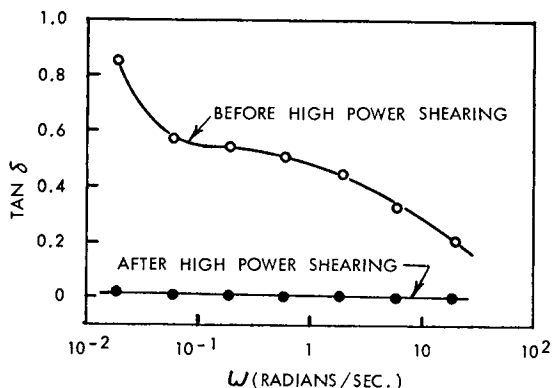
Fig. 8. Loss tangent as a function of frequency for 5% sodium carboxymethylcellulose (DS 0.4) solution before and after high-power shearing.

## CONCLUSIONS

Results of dynamic and steady shear rheological measurements on HPC systems at elevated temperatures indicate that there are two types of super-molecular structures present; a crystalline phase which persists up to 215°C, which is dispersed in an amorphous but highly hydrogen-bonded and entangled matrix. Changes in rheological properties of HPC as a function of time at elevated temperatures can be interpreted in terms of the disaggregation and dispersion of this crystalline material.

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