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# Kinetics of thermal gelation of methylcellulose and hydroxypropylmethylcellulose in aqueous solutions

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Thermal gelation properties, such as gel strength, rate of gelation, gel point, etc, of methylcellulose and hydroxypropylmethylcellulose products play key roles in many applications such as ceramics processing, extrusion of matrix food and manufacture of medicinal capsules. A thorough knowledge of the variables controlling the gelation kinetics is essential. Using a Bohlin VOR rheometer, we have developed a new technique to measure the storage modulus, $G'$, of the gel and the increase in the $G'$ values as a function of time for aqueous solutions of these cellulose ethers when heated above the gelation temperature. This technique utilizes the oscillatory shear mode and a special switching technique to raise the solution temperature as quickly as possible. The initial rate of increase in $G'$ is quite fast and the gel reaches about 95% of the final $G'$ value in about 6 min followed by slow gelation kinetics. The maximum rate of gelation ($dG'/dt$) and the final storage modulus of the gel ($G'_f$) for methylcellulose products were related to various parameters according to the following mathematical model:

$$dG'/dt = KC^{3.3}T^{4.0}(\%\mathrm{MeO})^{3.4}(\mathrm{M_w})^{0.5}$$

$$G'_f = KC^{2.9}T^{0.3}(\%\mathrm{MeO})^{6}(\mathrm{M_w})^{0.8},$$

where $C$, $T$, (%MeO) and ($\mathrm{M_w}$) are the concentration in wt.%, the temperature in °C, the methoxyl content, and the molecular weight, respectively. Hydroxypropylmethylcellulose polymers also exhibit similar gelation behavior with both $G'_f$ and $dG'/dt$ related to nearly the third power of concentration and second power of the ratio of the degree of methoxyl substitution (DS) to the molar substitution (MS) of the hydroxypropyl groups.

## INTRODUCTION

Aqueous solutions of methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) polymers exhibit an interesting phenomenon of thermoreversible gelation (Heyman, 1935), i.e. they gel upon heating and redissolve upon subsequent cooling. The various physicochemical factors involved in this gelation process have been characterized (Sarkar, 1979). Simultaneously, associated with the gelation phenomenon, these polymer solutions also exhibit an entropically induced lower critical solution temperature (LCST) (Elias, 1989) above which precipitation of polymer due to hydrophobic effects is observed (Tanford, 1980). Water, at relatively low temperatures, forms an ice-like structure around the hydrophobic groups, such as the methyl substitution of MC and HPMC polymers. When the solutions are heated, the water structure breaks down with an increase in entropy, thus allowing the hydrophobic groups to interact and causing gelation and precipitation. The initial phase separation upon heating corresponds to a spinodal decomposition and the cooling curve corresponds to a re-dissolution of the binodal curve (Van Dyke, M., Prud'homme, R.K., and Sarkar, N., to be published). From the X-ray diffractions studies of methylcellulose gels it was concluded (Kato *et al.*, 1978) that the crosslinking loci of these gels consist of crystallites of trimethyl glucose sequences. Carbon-13 NMR studies of the high temperature gels of aqueous MC, HPMC, and hydroxypropylcellulose (HPC) solutions revealed (Ibbett *et al.*, 1992) that the substituents and the backbone on MC became immobile due to interchain crosslinks and phase separation. HPC, on the other hand, exhibited a supramolecular helical coil structure of the backbone while maintaining mobility of the substituents. This behavior leads to a very loose, open precipitate with no gel-like properties. In the case of HPMC, an intermediate structure occurs where there are sufficient runs of highly methylated cellulose units for interchain crosslinking, but the structure may be disrupted by intervening helical hydroxypropylated units.

A theoretical study (Stauffer *et al.*, 1982) analyzed the gelation phenomenon using a percolation model and the classical tree model. It was shown that the experimental relationships between elasticity and the fraction of interchain bond formation follow a power law exponent of $3{\cdot}3 \pm 0{\cdot}3$ for various systems. This value is closer to the classical exponent value of 3 than the exponent value of 1·7 predicted by percolation theory. A recent review (Gaunet, 1992) analyzed the behaviors of thermoreversible gels and showed that for many polymers modulus was related to the third power of concentration. Gels can be divided into two broad categories, i.e., chemical gels occurring through covalent or ionic bonds and physical gels occurring through van der Waals interaction. MC and HPMC gels fall in the category of physical gels. This gelation involves co-operativity, i.e., gel junction loci are not point-like but instead involve neighboring group interaction. Since the energy involved in the van der Waals interaction is on the order of $kT$, these gels are thermoreversible. Gel formation or gel melting should follow a first order transition (Gaunet, 1992) arising from the creating of a minimum of molecular order out of an initially disordered solution. In other words, the formation of crosslinking points in physical gel networks can be treated as a binary association between chains (Ohkura *et al.*, 1992) and the rate of formation of crosslinking points is proportional to the square of the concentration of free crosslinking loci.

In the past (Sarkar, 1979), we have used a cone penetrometer to study the gel strengths of MC and HPMC gels. That method did not allow the determination of time dependent properties. In this study we used a dynamic oscillatory technique to measure the shear modulus during the thermal gelation process. Oscillatory measurements have been used in the past to study the gelatin gels (Ferry, 1948) and to follow the gelation of polyacrylamide/$Cr^{+3}$ systems (Prud'homme *et al.*, 1983). When a viscoelastic material is sheared by imposing a sinusoidal strain ($\gamma$) according to:

$$\gamma(t) = \gamma^\circ \sin \omega t, \tag{1}$$

where $\gamma^\circ$ is the maximum strain, $\omega$ is the angular frequency and $t$ is the time, the resultant shear stress ($\tau$) is given by:

$$\tau(t) = \tau^\circ \sin(\omega t + \delta), \tag{2}$$

with $\delta$ being the phase angle between 0 (for ideally elastic solids) and $\pi/2$ (for ideally viscous liquids), and $\tau^\circ$ is the maximum shear stress. Expansion of this sine function in equation (2) gives:

$$\tau(t) = \tau^\circ(\sin \omega t \cdot \cos \delta + \cos \omega t \cdot \sin \delta) \tag{3}$$

$$= \gamma^\circ(G' \sin \omega t + G'' \cos \omega t). \tag{4}$$

$G' = (\tau^\circ/\gamma^\circ)\cos\delta$ is called the storage modulus and measures the elastic property of the material. $G'' = (\tau^\circ/\gamma^\circ)\sin\delta$ is called the loss modulus and measures the viscous property of the material. A gel, according to a mechanical definition, should display solid-like behavior characterized by a storage modulus, $G'$, which is substantially larger than the loss modulus, $G''$, and is independent of frequency, i.e., the stress in the gel cannot relax over any time scale. Gelation kinetics can, therefore, be monitored as a function of time by monitoring the $G'$ values. We have modified a method developed by Prud'homme (Prud'homme *et al.*, 1983) that allows us to study the gelation properties at small strains in the linear viscoelastic region where the gel network should remain undisturbed during the measurement of the storage modulus.

The theory of rubber elasticity (Pearson & Graessley, 1980) gives the relationship between the storage modulus ($G'$) of the gel and the density of the crosslink, $n$, by the equation:

$$G' = gnkT + G_{en} \tag{5}$$

where g is a constant with a value between 0·4 and 1 (Gottleib *et al.*, 1981), k is the Boltzman constant, $T$ is the absolute temperature, and $G_{en}$ is the contribution to the modulus arising from chain entanglement. For 2% MC solutions, the $G'$ value for solutions below the gelation temperature should correspond to $G_{en}$ which is normally much smaller than the $G'$ values for gels. The rate of change of $G'$ is, therefore, proportional to the rate of change of crosslink density. Therefore, dynamic mechanical measurements can be used to follow the kinetics of gelation of MC and HPMC solutions in water. In this paper, we will report the method development as well as the relationship of the pseudo-equilibrium storage modulus of the gel (called the final gel strength, $G'_f$, in this paper) and the maximum increase in $G'$ values with time (called the maximum rate of gelation, $dG'/dt$, in this paper) with various factors such as the degree of substitution of methyl and hydroxypropyl groups, polymer concentration, temperature and the molecular weights of cellulose ethers.

## MATERIALS

All the MC and HPMC samples used in this paper were either of commercial grade or made in the laboratory. Commercial samples were obtained from The Dow Chemical Company under the tradename of METHOCEL* brand cellulose ethers (METHOCEL cellulose ether is a trademark of The Dow Chemical Company) having different viscosity grades (i.e. the viscosity of 2% aqueous solution at 20°C measured using Ubbelohde capillary viscometer) and substitutions.

Laboratory samples were made by essentially the same commercial process by allowing cellulose to react with aqueous sodium hydroxide and subsequently with methyl chloride and propylene oxide (Greminger & Krumel, 1980). Degree of methoxyl substitution (DS) and the hydroxypropyl molar substitution (MS) of all the samples were determined using a Zesel gas chromatographic technique (Hodges *et al.*, 1979).

## EXPERIMENTAL

Oscillatory shear measurements were carried out using a Bohlin VOR rheometer (Bohlin Instruments, Cranbury, NJ) interfaced with an MS-DOS, Intel 80286 based computer. This is a fully computer controlled couette rheometer capable of running in steady shear, oscillation and relaxation modes. In our experiment, a serrated bob and cup system was used to minimize slippage. The temperature of the sample is controlled by circulating water/glycol mixture from a constant temperature circulator (CTC) through the jacket of the rotating cup. The constant temperature circulator is interfaced with the rheometer controller and the computer allowing us to run either temperature ramps or at constant temperatures. The shear stress in the sample is measured from the deflection of the bob which is connected to an interchangeable torsion bar. The deflection of the torsion bar is measured using an LVDT (linear variable differential transformer). The phase angle shift is automatically computed from the time displacement between the sine waves of stress and strain. Different moduli are then calculated from the phase angle and the maximum stress and strain amplitudes. In oscillatory measurements, one first runs a strain sweep at a fixed frequency. This enables one to obtain the linear viscoelastic region where $G'$ and $G''$ are independent of applied strain. Once the linear region is established, measurements are made at a fixed frequency and at an amplitude in the linear region as a function of time or temperature.

In order to measure the kinetics of gelation of MC and HPMC solutions, one should be able to heat the solution as quickly as possible. To do that, we placed a three-way valve in the tubing between the CTC and the jacket of the cup so that the circulating fluid could be either circulated through the jacket or returned back to the CTC unit. The CTC unit and the rheometer jacket have fluid capacities of about 5 l and 0·6 l, respectively. In order to heat and control the MC solution at some temperature, 65°C for example, the rheometer was controlled at 30°C initially. The three-way valve was then turned to return the fluid back to the CTC, and the CTC fluid temperature raised to 90°C. As soon as the CTC fluid temperature reached 90°C, the three-way valve was opened to allow the 90°C, water–glycol mixture in the CTC to rush into the rheometer jacket and raise the temperature of the MC solution. Simultaneously, the rheometer was started to control the temperature at 65°C and start gathering data. Figure 1 illustrates the rate at which both temperature and $G'$ of the sample increase as a function of time. In this experiment, the actual temperature of the solution was measured using a second thermocouple in the sample. It is seen that it takes about 150 s before $G'$ begins to rise corresponding to a temperature of about 60°C which is slightly above the onset of gelation of the particular MC sample.

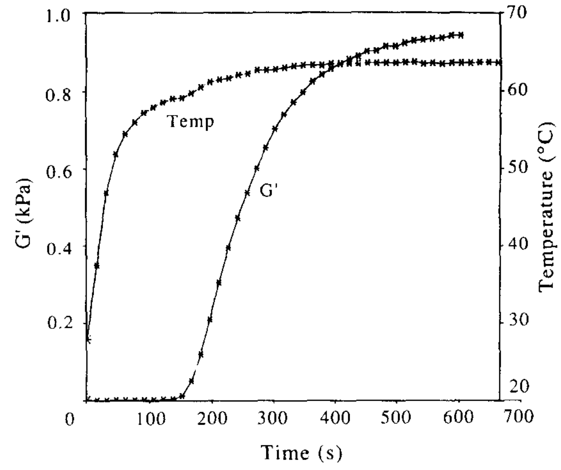

**Fig. 1.** $G'$ and actual sample temperature vs time for a 2% methylcellulose solution when suddenly heated to reach a final temperature of 65°C.

In the case of most MC and HPMC samples, both $G'$ and $G''$ are initially low. The $G''$ values remain low while $G'$ typically displays the S-shaped curve shown. The slopes of the $G'(t)$ curve provide a measure of rate of gelation reflecting network formation. The curve $G'$ vs $t$ shows that there are two gelation processes, a fast gelation followed by a slow gelation or annealing of the gel. In our experiment, we measured the maximum rate of increase in $G'$ (called the rate of gelation). Examination of Figs 1 and 2 reveal that the time when the fastest

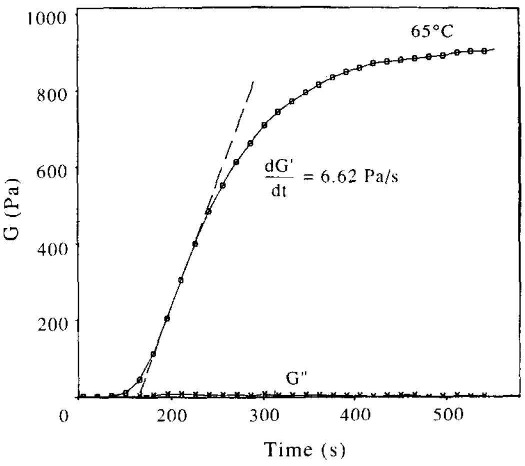

**Fig. 2.** Rate of change in $G'$ and $G''$ values of a 2% methylcellulose solution suddenly heated to reach a final temperature of 65°C.

rate of increase in $G'$ is measured is when the solution reaches a temperature slightly lower than the final temperature of the gel. It is seen that the methylcellulose gels reach about 95% of the final gel strength in about 6 min after the start of the experiment or about 3 min after the solution reaches gel temperature. This initial rapid gelation is followed by the slow gelation stage. The gels may require about 30 min of ageing before reaching the final gel strength values.

## RESULTS AND DISCUSSION

Methylcellulose solutions at temperatures below their gelation point exhibit the usual linear viscoelasticity, i.e. both $G'$ and $G''$ are independent of strain, with $G''$ values considerably larger than $G'$ values. By the same token $G''$ and $G'$ values for methylcellulose solutions show normal increase as a function of frequency with $G'' > G'$. On the other hand strain sweep experiments for full three-dimensional gels formed at temperatures above the gelation points exhibit $G'$ much larger than $G''$ reflecting that the elastic properties are dominant over viscous properties. Figure 3 shows a typical strain sweep for a gel formed at 65°C. Here, $G'$ values show slight initial increase indicating strain hardening followed by yielding at a critical strain when $G'$ decreases sharply upon further increase in strain. As expected, $G'$ values of these gels were found to be independent of frequency since the stresses in the gel do not relax over any time scale and the gel is much more elastic than viscous. As a solution passes from a fluid state to a full gel state, a gradual transition of the elastic modulus, $G'$, takes place from a frequency dependent value lower than $G''$ to a frequency-independent value higher than $G''$ (Clark *et al.*, 1983).

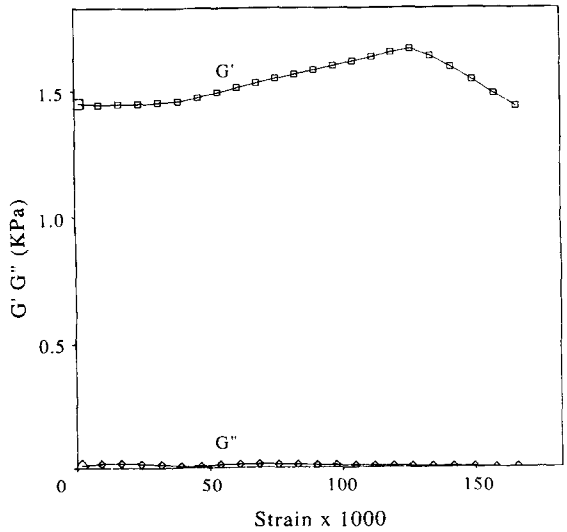

**Fig. 3.** $G'$ and $G''$ values of the gel of 2% solution of a 4000 mPa viscosity grade methylcellulose at 65°C as a function of strain at a frequency of 1 Hz.

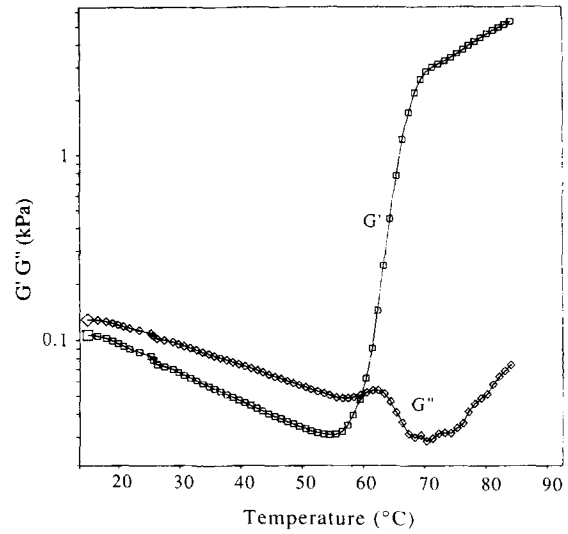

**Fig. 4.** $G'$ and $G''$ values vs temperature for 2% solution of a 4000 mPa viscosity grade methylcellulose at a frequency of 10 Hz and 10% amplitude heated at a rate of 1°C/min.

Figure 4 shows a typical temperature sweep experiment for 2% solution of a 4000 mPa viscosity grade MC exhibiting the $G'$ minimum at which gelation takes place. There is a certain degree of controversy about the exact gel point of a crosslinking polymer solution (Winter, 1987). It was proposed that the gel point (GP) of a crosslinking polymer occurs at the instant where $G'$ and $G''$ values cross each other, i.e., $\tan \delta = 1$ (Tung & Dynes, 1982). However, this is true (Winter, 1987), only when reaching GP;, power law relaxation $G(t) \sim t^{-n}$ has a specific exponent value of $n = 1/2$ in the presence of a surplus of crosslinkers and a stoichiometrically balanced network. In the cases where weakly crosslinked networks are formed (lack of crosslinker) the value of $n$ becomes greater than 1/2 and the GP occurs earlier than the crossover. In the case of MC and HPMC solutions, we believe the GP is represented by the minimum in the $G'$ vs temperature curve which is always found to be at a temperature a few degrees below the temperature at which $\tan \delta = 1$.

Quite often we have observed an interesting phenomenon of a sharply decreasing spike in the $G''$ value at a specific temperature shortly after gelation. This is most likely caused by the matching of the resonance frequency of the combination of the transducer, sample and the bob with the frequency of the measurement (Ferry, 1961), when energy is stored in the spring changing the phase shift. Running the experiment at a different frequency or using a different fixture eliminates this artifact.

In contrast to Fig. 4, where $G'$ values exhibit a well defined minimum, Fig. 5 shows that at lower frequencies and using a lower molecular weight sample there

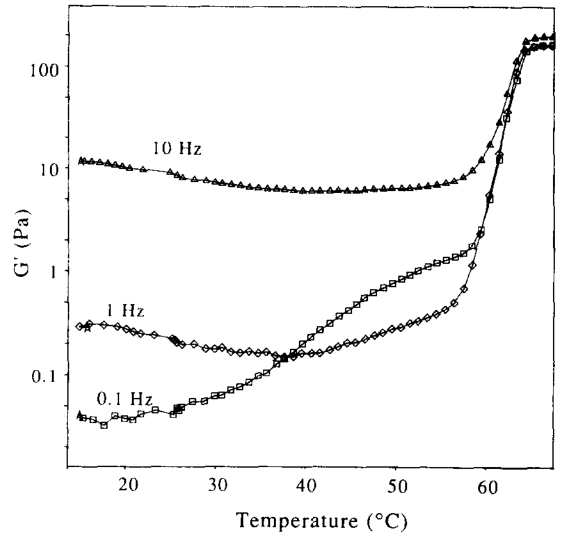

**Fig. 5.** Temperature course of thermal gelation of 2% solution of a 400 mPa viscosity grade methylcellulose at an amplitude of 5% and at different frequencies.

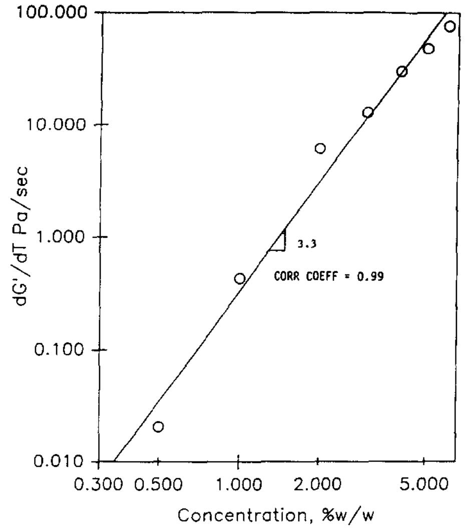

**Fig. 6.** Maximum values of $dG'/dt$ vs concentration for solutions of a 400 mPa viscosity grade methylcellulose at 65°C.

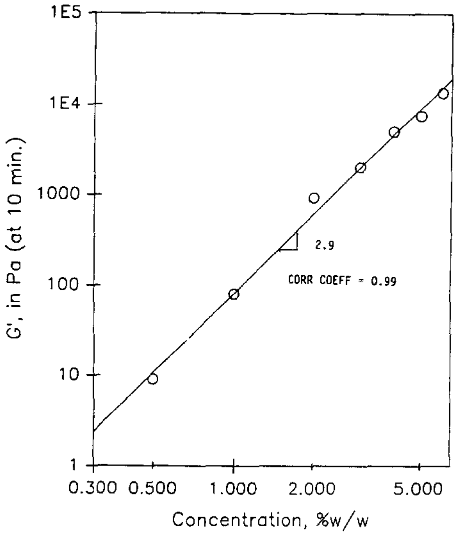

**Fig. 7.** $G'$ values after 10 min of heating at 65°C ($G'_f$) vs concentration for solutions of a 400 mPa viscosity grade methylcellulose.

are two distinct waves in the $G'$ vs temperature curve. This was also reported earlier by other researchers (Owen *et al.*, 1992; Haque & Morris, 1993). The interpretation (Haque *et al.*, 1993) of this dual wave phenomenon is apparently due to entanglement coupling originating from the differences between the relaxation time of the polymer in solution and the time element of the frequency of the measurement. Running the experiment at a higher frequency or using polymers with higher molecular weight, i.e. lower relaxation time, eliminates this interaction.

Methylcellulose gelation kinetics were then investigated as a function of different variables. The maximum $dG'/dt$ and the final gel strengths, $G'_f$ (at $\geq 10$ min of heating) were measured. At the 95% confidence level, the relative error of measuring $dG'/dt$ and $G'_f$ were found to be 11 and 8%, respectively. While classical chemical reaction order is related to the concentration, we have also explored the relationship of both $G'_f$ and $dG'/dt$ as a function of other variables and obtained power law relationships. Figure 6 shows the maximum $dG'/dt$ values of a 400 mPa viscosity grade MC solution at 65°C as a function of concentration in a log–log scale. It is found that the maximum $dG'/dt$ is proportional to the 3·3 power of the MC concentration indicating an approximate third order gelation process. Interestingly enough, gelatin also exhibits (te Nijenhuis, 1981) third order gelation kinetics related to three crosslink sites for every triple helix crosslink. In the case of MC solutions, the third order relationship is not obvious but the crosslinking mechanism involving trimethyl substitutions of glucose may be relevant (Kato *et al.*, 1978). Figure 7 shows that $G'_f$ values of a 400 mPa viscosity grade MC solution at 65°C also exhibit an approximately third power dependency on concentration. This agrees with the values reported in the literature.

Figure 8 shows $G'_f$ as a function of temperature indicating that at or above GP the gel strength increases sharply until the temperature reaches about 65°C above which there is only a moderate increase in gel strength. Above 65°C, the slope of the log $G'_f$ vs log (temperature) curve is 0·3. The maximum rate of increase in $G'$, as shown in Fig. 9, shows similar behavior but the slope of log $dG'/dt$ above 65°C is 4·0 indicating that the maximum rate of gelation has a greater dependence on temperature than does the final gel strength.

Figures 10 and 11 show that neither the $G'_f$ nor the maximum values of $dG'/dt$ are a strong function of molecular weight. Up to a molecular weight of about

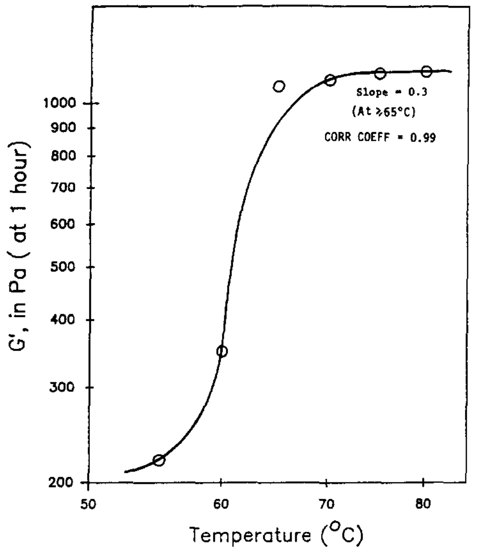

**Fig. 8.** $G'$ values after 1 h of heating at different temperatures ($G'_f$) for 2% solution of a 400 mPa viscosity grade methylcellulose.

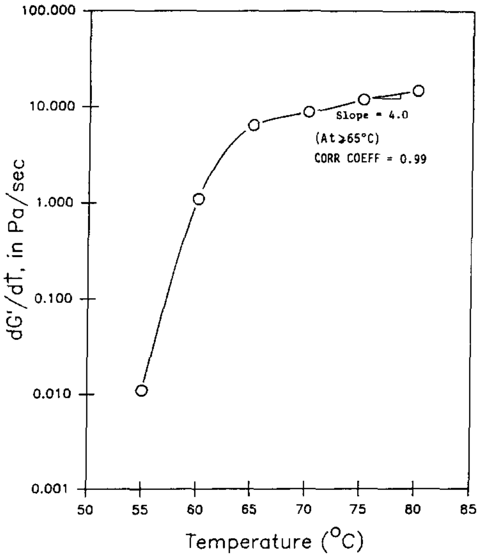

**Fig. 9.** Effect of temperature on the maximum values of $dG'/dt$ for 2% solution of a 400 mPa viscosity grade of methylcellulose at 65°C.

500 000, the slopes of log $G'_f$ vs $M_w$ and log ($dG'/dt$) vs $M_w$ are only 0·8 and 0·5, respectively. Above a molecular weight of about 500 000, $G'_f$ and maximum values of $dG'/dt$ show a reduction in responsiveness to changes in molecular weight. This finding is similar to those reported earlier in the literature (Sarkar, 1979).

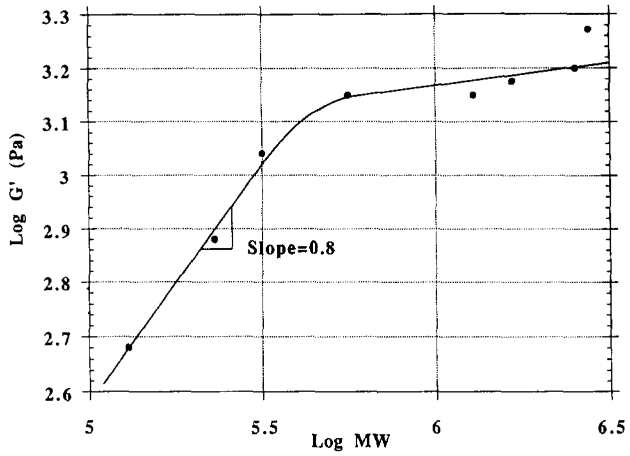

**Fig. 10.** $G'$ values after 10 min of heating at 65°C ($G'_f$) for 2% solutions of methylcellulose as a function of their weight average molecular weight.

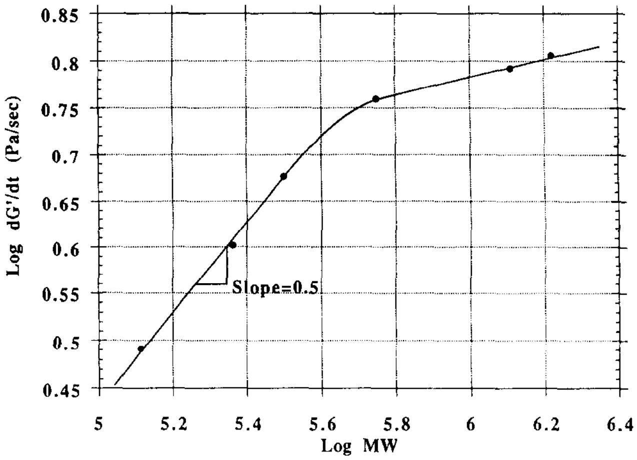

**Fig. 11.** Maximum values of $dG'/dt$ for 2% solutions of methylcellulose at 65°C as a function of weight average molecular weight.

Gel strengths and maximum rates of gelation as a function of methoxyl degree of substitution showed considerable scatter in the data, presumably due to variations in the process conditions giving rise to variations in the substituent distribution along the backbone of the polymers. In order to avoid that problem, several samples were produced in a research pilot plant under identical process conditions. Figures 12 and 13 show $G'_f$ and the maximum values of $dG'/dt$, respectively, as functions of the % methoxy (%OMe) content of the samples. It is seen that the gelation properties are strongly affected by methoxyl content.

The overall gel strength ($G'_f$) and the maximum rate of gelation ($dG''/dt$) expressions for methylcellulose polymers produced under normal manufacturing conditions are then given by the following mathematical model:

$$G'_f = KC^{2{\cdot}9}\, T^{0{\cdot}3}\, (\%\mathrm{MeO})^6\, (M_w)^{0{\cdot}8} \qquad (6)$$

and

$$dG'/dt = KC^{3{\cdot}3}\, T^4\, (\%\mathrm{MeO})^{3{\cdot}4} (M_w)^{0{\cdot}5} \qquad (7)$$

where:

$C$ = concentration in wt.%

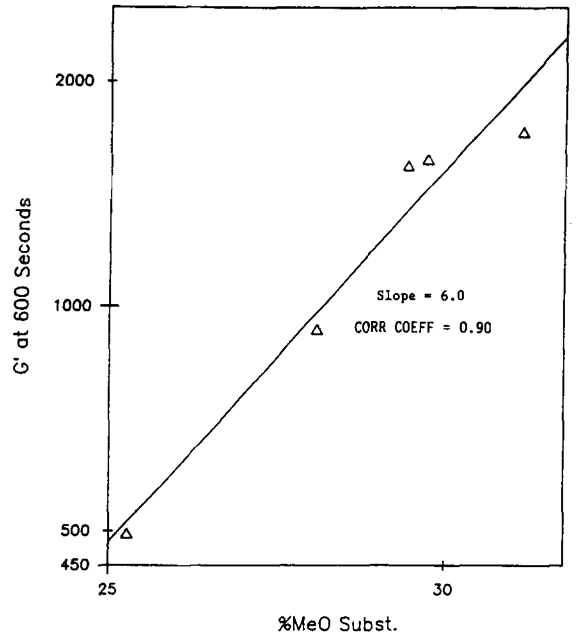

**Fig. 12.** $G'$ values after 10 min of heating at 65°C ($G'_f$) for 2% solutions of ~30,000 mPa viscosity grade methylcellulose samples as a function of % methoxyl content.

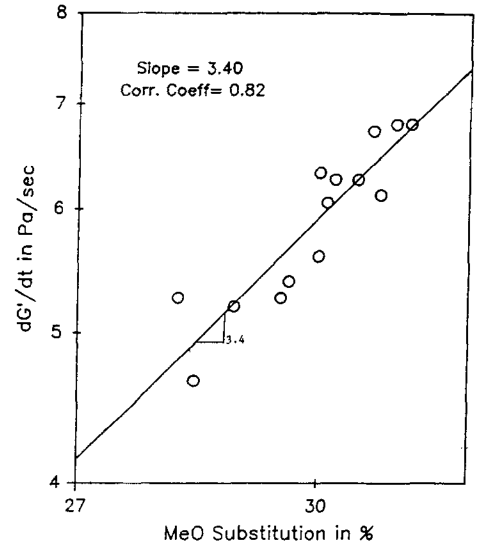

**Fig. 13.** Maximum values of $dG'/dt$ at 65°C for 2% solutions of ~30,000 mPa grade methylcellulose samples as a function of % methoxyl content.

$T$ = temperature in °C, above 65°C
(%MeO) = % methoxyl content
$M_w$ = molecular weight (when below ~500,000).

These equations demonstrate the relative importance of different variables and should be very useful in selecting a MC product for a particular application. It is seen that the rate of gelation is strongly dependent on concentration, temperature and methoxyl content and only marginally dependent on molecular weight. On the other hand, gel strength is strongly dependent on concentration, very strongly dependent on methoxyl content and only marginally dependent on temperature (at temperatures sufficiently above GP) and molecular weight.

Gelation behavior of HPMC is considerably different from MC polymers depending on the molar substitution of the hydroxypropyl groups (MS). It was reported earlier (Sarkar, 1979) that the gel strength decreases drastically as the degree of hydroxypropyl substitution increases. As was seen in Fig. 4, high molecular weight MC solutions show only one minimum in the $G'$ vs temperature curve as gelation takes place. Figure 14, on the other hand, exhibits two inflection points for an HPMC solution. As the temperature is increased the solution shows the usual lowering of $G'$ and $G''$ values followed by a sharp decrease at a temperature, $T1$, presumably indicating the precipitation of certain fractions of HPMC polymers. Upon further increase in the temperature, the solution begins to gel at a temperature, $T2$, when $G'$ begins to increase very sharply. $G''$ values also follow a similar trend with $G''$ being greater than $G'$ below $T2$ and vice versa above $T2$.

Figure 15 shows the isothermal rate of gelation of an HPMC solution indicating only a moderate rate of gelation and final gel strength compared to those of MC solutions as shown in Fig. 4, It is seen that, although the $G'$ values of the gel are higher than those of $G''$, the $G'$ value of the solution (at zero time) is actually somewhat higher than the $G'$ value of the gel. This phenomenon is highly dependent on the relative degree of methoxyl substitution (DS) compared to the molar substitution (MS) of the hydroxypropyl groups.

Figures 16 and 17 show the $G'_f$ and the maximum

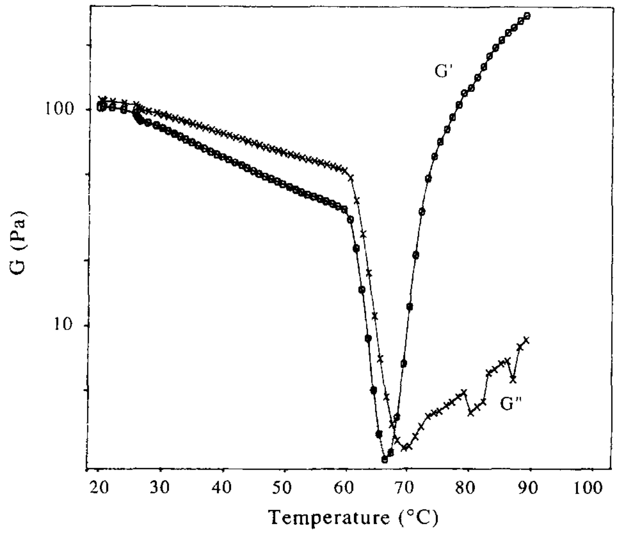

**Fig. 14.** $G'$ and $G''$ values for 4% solution of a 4000 mPa viscosity grade HPMC polymer with DS of 1·85 and MS of 0·16 as function of temperature at 1 Hz and 8·5% amplitude.

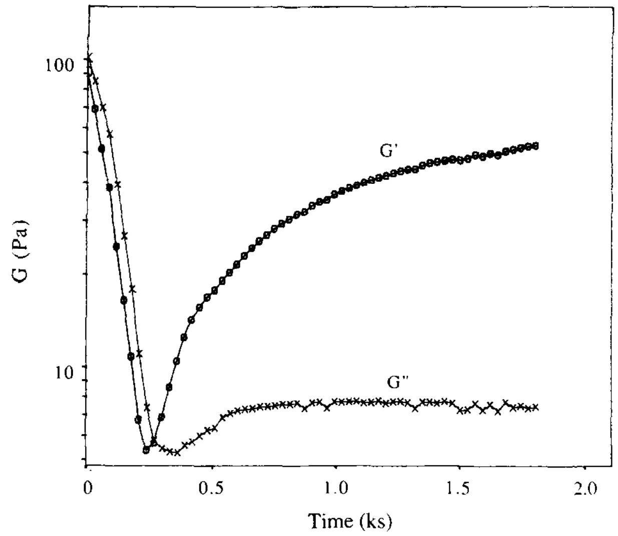

**Fig. 15.** $G'$ and $G''$ values for 4% solution of a 4000 mPa viscosity grade HPMC polymer with DS of 1·85 and MS of 0·16 as function of time at 1 Hz and 8·5% amplitude when suddenly heated to reach a final temperature of 65°C.

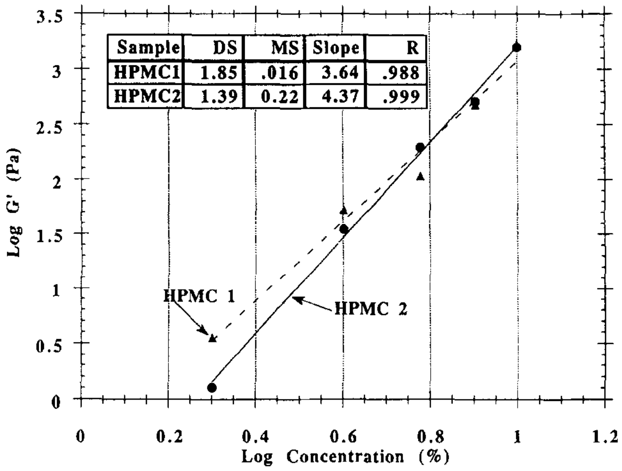

**Fig. 16.** $G'$ values after 30 min of heating at 65°C ($G'_f$) as a function of concentration for solutions of two ~30,000 mPa viscosity grade HPMC samples.

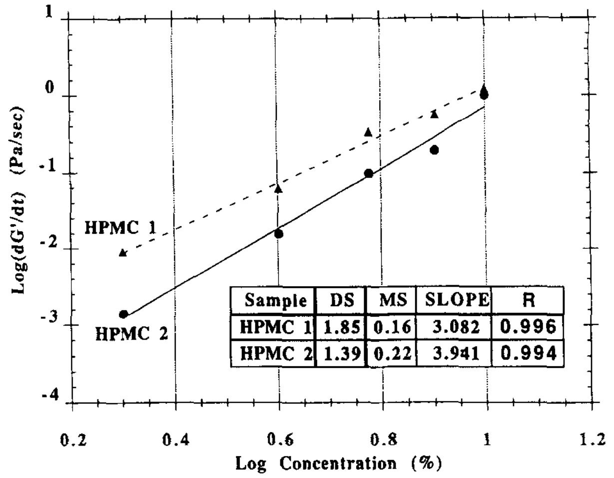

**Fig. 17.** Maximum values of $dG'/dt$ as a function of concentration for solutions of two ~30,000 mPa viscosity grade HPMC samples heated to reach a final temperature of 65°C.

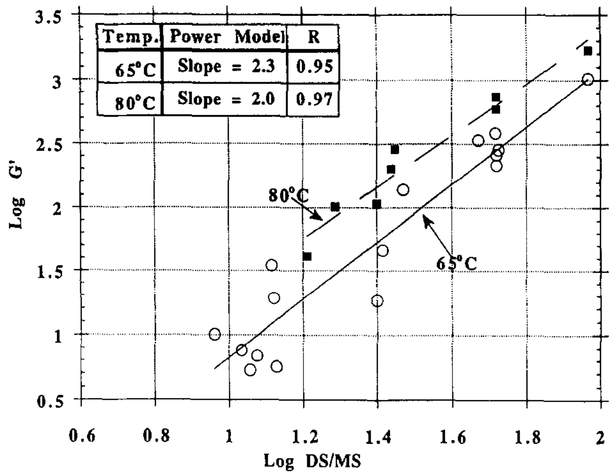

**Fig. 18.** $G'$ values after heating for 30 min at two different temperatures ($G'_f$) as a function of the ratio DS/MS for 2% solutions of HPMC samples with viscosity of ~30,000 mPa at 20°C.

values of $dG'/dt$, respectively, for solutions of two HPMC samples, indicating approximately a third power relationship with respect to concentration. This is again similar to what is found for MC solution as well as for many other polymers reported in the literature. As was previously reported (Sarkar, 1979), gel strengths of HPMC solutions increase with the increase in methoxyl DS and the decrease in MS. We plotted $G'_f$ and the maximum values of $dG'/dt$ as a function of the DS/MS ratio, as shown in Figs 18 and 19, at two different temperatures. It is seen that there is approximately a second power relationship of $G'_f$ and maximum $dG'/dt$ with respect to the DS/MS ratio. Data also show that both $G'_f$ and maximum $dG'/dt$ increase considerably as a function of temperature. As is the case with MC polymers, $G'_f$ and maximum $dG'/dt$ values of HPMC polymers will then be related to different variables according to the following models:

$$dG'/dt = KC^3\,(DS/MS)^2 \ldots \quad (8)$$

$$G'_f = KC^3\,(DS/MS)^2 \ldots \quad (9)$$

We expect the relationships with molecular weight to be similar to MC samples.

In conclusion, a new method has been developed based on oscillatory shear rheometry to measure gel strength and the rate of gelation of aqueous solutions of methylcellulose and hydroxypropylmethylcellulose. The initial rates of gelation of MC and HPMC solutions are

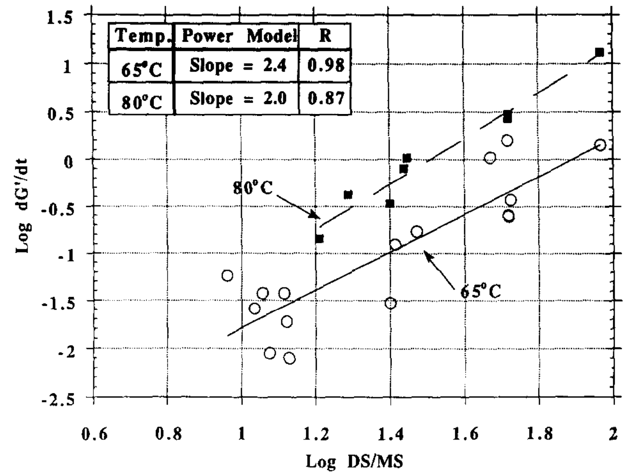

**Fig. 19.** Maximum values of d$G'$/d$t$ vs DS/MS for 2% solutions of HPMC samples with viscosity of ~30,000 mPa at 20°C.

quite fast followed by a slow annealing process. The rates of gelation and gel strengths of MC and HPMC solutions have been found to follow a power law relationship with concentration, temperature, substitution and molecular weight.

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