

Rheological Properties of Methylcellulose Aqueous Gels Under Dynamic Compression: Frequency Sweep and Validity of Scaling Law

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ABSTRACT: The aqueous methylcellulose (MC) gels are characterized with a dynamic mechanical analyzer (DMA) under dynamic vertical compression. During the frequency sweeps of MC gels at different temperatures, the storage modulus is observed to be higher than loss modulus at lower frequencies. Both of the storage and loss modulus increases with frequency, but the rate of increase is higher for loss modulus. This leads to the first crossover between E' and E'' during the frequency scan. For the frequency scan at a high temperature (80°C), a higher rate of increase is observed in storage modulus beyond the first crossover frequency. This leads to the second crossover between storage and loss modulus. Optical microscopy results indicate the presence of core-shell micro-

structure in aqueous MC gels. The first crossover is possibly due to the shell-sol transition, whereas the second crossover is due to the sol-shell-core transition. The validity of scaling laws at and around the first-crossover point (shell-sol transition) is checked. The scaling law is valid at the first-crossover point, but it is invalid around it. Alternate scaling equations based on reduced parameters are also used to check the universality. Irrespective of temperature, scaling laws are valid for reduced parameters. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2436–2443, 2010

Key words: aqueous methylcellulose gel; frequency sweep; dynamic compression; core-shell structure; scaling law

INTRODUCTION

The thermo-reversible gelation of methylcellulose (MC) from the aqueous solution was first investigated by Heymann.¹ MC gels are semisolid materials, which behave like solid materials in respect of dynamic mechanical properties. Thus, irrespective of the temperature or the frequency scan, polymeric gels generally exhibit higher storage modulus. Whereas, any liquid exhibits higher loss (damping or viscous) modulus during dynamic oscillatory shearing.² During the transition from sol to gel or gel to sol state, the damping (E'') and elastic modulus (E') is expected to be equal or in other words, the ratio of E' and E'' would be unity (i.e., $\tan \delta = 1$). As sol-gel transition involves the change from one state to another, it is expected that certain properties, such as, modulus can be scaled universally around this transition point for certain parameters. Winter and Chambon³ developed an equation for the sol-gel transition point at which both E' and E'' scale with frequency, ω or other related parameters.

$$\eta_0 \propto \varepsilon^{-\gamma} \text{ for } p < p_g \quad (1)$$

$$E'(\omega) \sim E''(\omega) \propto \omega^n \text{ at } p_g \quad (2)$$

$$E_e \propto \varepsilon^z \text{ for } p > p_g \quad (3)$$

where $\varepsilon = \frac{|p-p_g|}{p_g}$ is the relative distance of a gelling variable p from the gel-sol transition point p_g , and γ , n , and z are the three indexes used during scaling of zero shear viscosity (η_0), crossover modulus, and equilibrium modulus, respectively. The reported experimental values of γ , n , and z are within the range of 1.3–1.7, 0–0.1, and 2.0–3.0, respectively.^{4,5}

This study aims at assessing the effect of dynamic compressive force on the rheological properties of MC aqueous gels. The earlier reported applicability of scaling law^{4,5} for rheological parameters was under dynamic shearing mode. Thus, the present communication is the first ever report about the applicability of scaling law for dynamically compressed aqueous MC gels.

EXPERIMENTAL

Materials

Central Drug House, New Delhi (India), supplied laboratory grade MC in powdered form. The viscosity of 2% aqueous MC solution at 20°C as supplied

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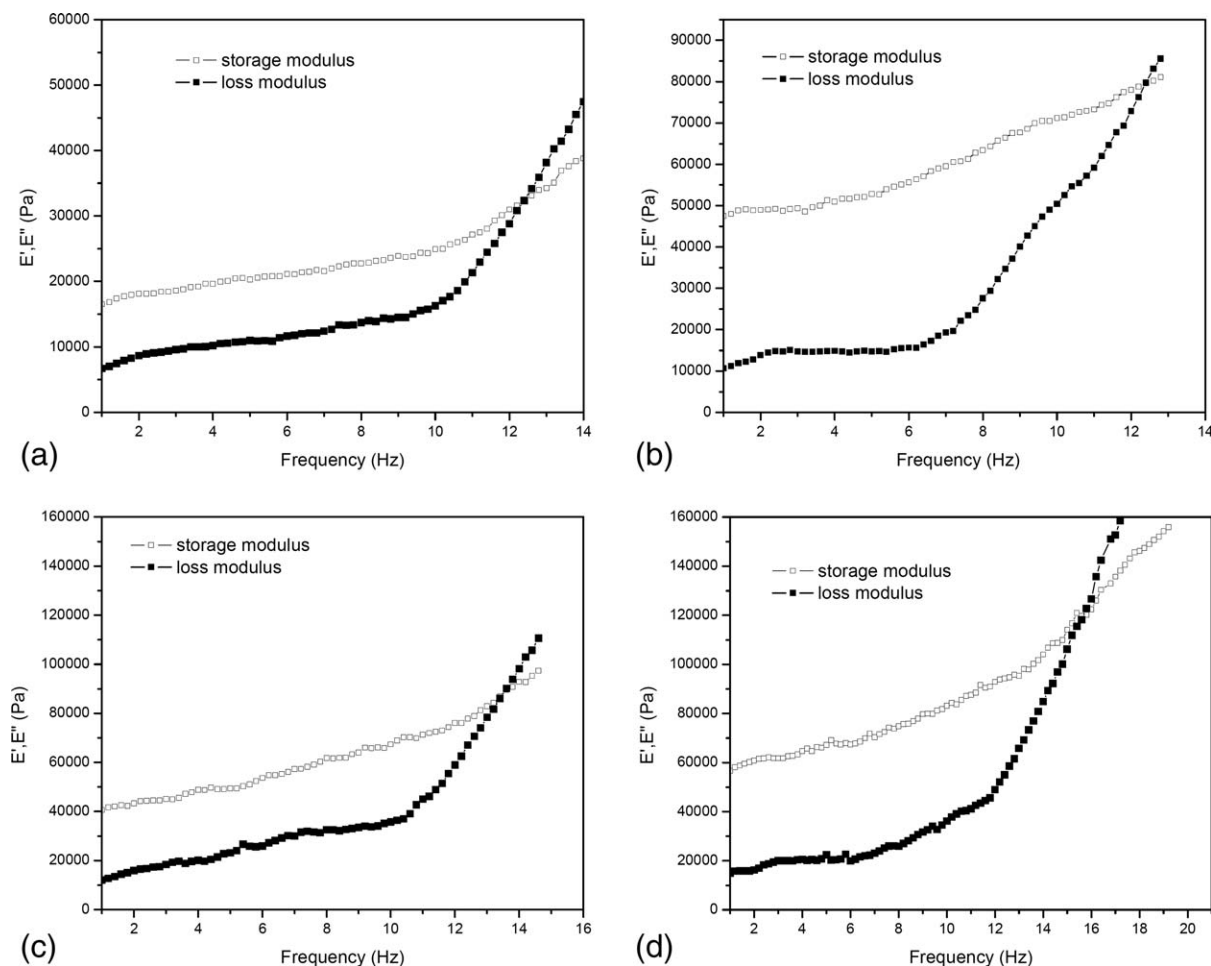


Figure 1 (a) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 50°C) as a function of frequency, ω at 50°C. (b) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 55°C) as a function of frequency, ω at 55°C. (c) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 60°C) as a function of frequency, ω at 60°C. (d) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 65°C) as a function of frequency, ω at 65°C. (e) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 70°C) as a function of frequency, ω at 70°C. (f) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 75°C) as a function of frequency, ω at 75°C. (g) Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (for 10 min preheating at 80°C) as a function of frequency, ω at 80°C.

by the manufacturer was about 4000 cP. The viscosity average molecular weight of MC was 149,000 and its methoxy value was 26–30%.

Sample preparation

Solution of MC was prepared in deionized (DI) water by slowly adding MC in warm water (42°C) with continuous stirring. The solution was cooled for 12 h to get a clear solution. A Haake K20 circulator was used to cool the solution.

Morphology

The morphology of the gel was studied under an optical microscope (Digital blue) at 6000 \times .

Rheological characterization of the aqueous MC gel

A Perkin-Elmer dynamic mechanical analyzer (DMA) Pyris-7e with a 110 mN static force and a 110 mN dynamic force was used to carry out rheological experiments of the gels. Aqueous MC solutions (3 wt %) were taken in the dynamic test kit (a conical container). The dynamic testing was programmed in such a way that a sufficient preheating of the MC solution at a preset temperature of 50–80°C for a prefixed time was allowed. The time of preheating was usually 10 min. Other preheating times such as 3, 7, 15, and 25 min were also used. The preheating causes gelation of MC in the dynamic test kit. Thereafter, the test probe was pressed against the gels (at the preheating

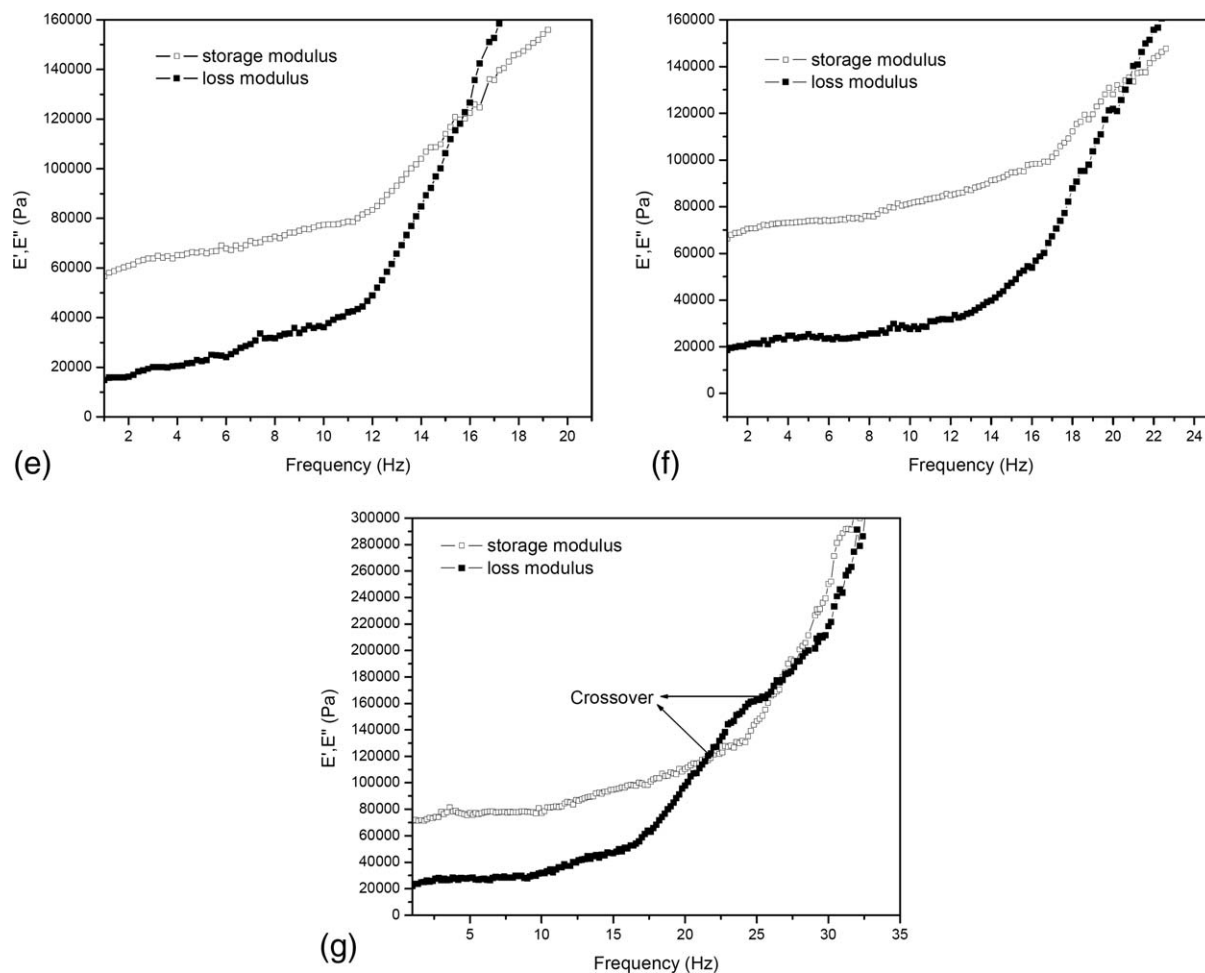


Figure 1 (Continued from the previous page)

temperature) with a 110 mN static force and 110 mN dynamic force, followed by dynamic compression of the gel in accordance to the predesigned program through a PC. For frequency scan, the sample was dynamically compressed isothermally (at the preset temperature) with various frequencies and the change in dynamic properties such E' , E'' , and $\tan \delta$ were recorded against frequency.

RESULTS AND DISCUSSIONS

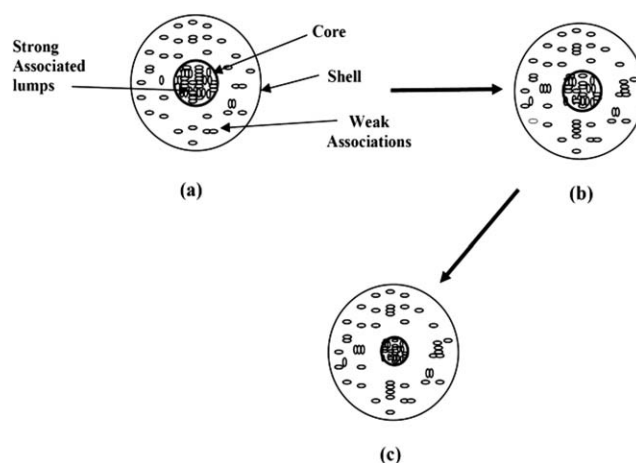
Figure 1 shows the variation of storage (E') and loss (E'') modulus with frequency at various temperatures [50, 55, 58, 62, 66, 76, and 80°C in Fig. 1(a–g), respectively]. With an increase in frequency, both E' and E'' increase almost linearly up to a certain frequency, beyond which a steep increase in loss modulus is observed. Both for polymer solutions and gels, the increase in modulus with frequency is also reported by Desbrieres et al.² With the application of a dynamic compressive force, it is expected that the gels will also respond with an equal and opposite force. When the frequency is low enough, the gel gets sufficient time to relax. Thus, no change in

modulus is observed with an increase in frequency. The results reported by Li et al.⁴ at low level of frequency are in expected line. They termed this frequency as quasi-equilibrium frequency. Unfortunately, due to machine limitation, we are unable to employ a low frequency (<1 Hz) and we have observed only an increase in modulus during frequency scan. On increasing the frequency, the polymers or gels do not get sufficient time to relax, causing an increase in the modulus.² The smooth increase in modulus with an increase in frequency will be continued up to the load bearing capability of the material. As MC is of heterogeneous structure, hydrophobic associations in solutions or gels are formed.^{6–10} These associations start to disintegrate at higher frequency,^{2–4} leading to a sudden increase in loss modulus. At the higher region of frequency, the storage modulus is expected to fall due to the disintegration of structure. Thus, in higher frequency region, two opposing factors, namely disintegration of structure as well as insufficient relaxation of dynamic force are playing against each other. Thus, a less steep increase in storage modulus (E') compared with loss modulus (E'') is observed.

Eventually, with an increase in frequency, a point is reached where E'' crosses over E' at a certain frequency. From Figure 1, the value of E' is found to be higher than E'' up to the crossover point, beyond which E'' is found to be higher.

If one passes from the frequency sweeps for the samples with a low (50°C) to a high (80°C) preheating temperature [Fig. 1(a–g)], it is observed that the modulus values at a low frequency (1 Hz) are increasing with an increase in temperature. The increase in preheating temperature for a fixed time period (10 min) allows an increase in the number of junction joints¹¹ in the gels and hence leads to an increase in the gel strengths and E' values.

On increasing the preheating temperature from a low to a high value [Fig. 1(a–f)], it is observed that the crossover point shifts to a higher frequency and modulus. The gel network formed during preheating gets distorted by dynamic compressive force at a sufficiently higher frequency. This is due to insufficient relaxation of the compressive force. Also, the higher the temperature, the stronger will be the gel network. Therefore, more force is required for destroying the gel network. As the gels are compressed dynamically with the same force, the higher force will be generated at a higher frequency due to an insufficient relaxation. Thus, an increase in crossover frequency as well as modulus is observed with an increase in the preheating temperatures. But, at very high preheating temperature of 80°C, the sample during frequency scan exhibits a double crossover in E' and E'' [Fig. 1(g)]. However, the double crossover was also observed for aqueous MC gels at 45°C.² However, these double crossovers in aqueous MC gels were not properly explained. Probably, the gel strength explains these double crossovers of aqueous MC gels. The strength of the gel is derived from two different types of gel structures. The first type of structure of gel consists of the weakly associated molecules of MC separated apart and the second type is composed of the highly associated lumps of MC.^{12,13} In Figure 1(g), a small increase in E' is initially observed, followed by the steep increase. In case of loss modulus, the increase is steep at around the first crossover, followed by an plateau at around the second crossover. In the frequency range between first and second crossover, the loss modulus is higher than the storage modulus. This unusual rheological behavior of MC aqueous gels can be explained by using the core–shell structure of gels as depicted in Scheme 1. The core (inner part) consists of highly associated aqueous MC gel (more hydrophobic), surrounded by the weakly associated MC aqueous shell (less hydrophobic). The assumption of this type of structure is originated from the heterogeneous structure of methylcellulose.⁶ The major part of the gel structure consists of the shell at low preheating tem-



Scheme 1 The core–shell structure of gels.

perature and the core possibly grows to a bigger size at the expense of the shell at a higher temperature. At very high temperature (80°C), the core grows to such a big size that the majority of the gel structure consists of the core. The presence of core–shell structure in gels is further verified from the optical microscopy of the gels (Fig. 2). The presence of small beads (core structure) at a low temperature (30°C) is due to hydrophobic association of MC [Fig. 2(a)]. The small core grows to a bigger size at higher temperature of 80°C [Fig. 2(b)]. Thus, the increase in loss modulus at the first-crossover point in Figure 1(a–g) is due to the destruction of the majority structure (weak shell) of the gels. In Figure 1(g), after the first-crossover point, the majority structure (core) has the capability of withstanding higher compressive forces originated due to insufficient relaxation at a higher frequency. Thus, after the first-crossover point, the storage modulus (E') starts to increase steeply with an increase in frequency, leading to the second-crossover point. At the crossover points, the values of $\tan \delta$ are observed to be unity, which symbolizes with the equality of elastic and viscous response of the MC aqueous gels.

For further investigation about the double crossovers in aqueous MC gels, we studied the rheological properties of the gels formed by preheating at 80°C for a very brief period of 3 min (Fig. 3). At low frequency (1 Hz), the modulus value in Figure 3 is less than that observed in Figure 1. The less preheating time (3 min) for the sample in Figure 3 allows forming less junction points (less dense core structure of the proposed gel structure in Scheme 1) in comparison with the sample with more preheating time (10 min) in Figure 1(a–g). The preheating time of 3 min is so low that the gel strength is lower than the sample preheated for 10 min at 50°C. Thus, the sample in Figure 3 shows minimum modulus compared to the samples preheated for 10 min at much

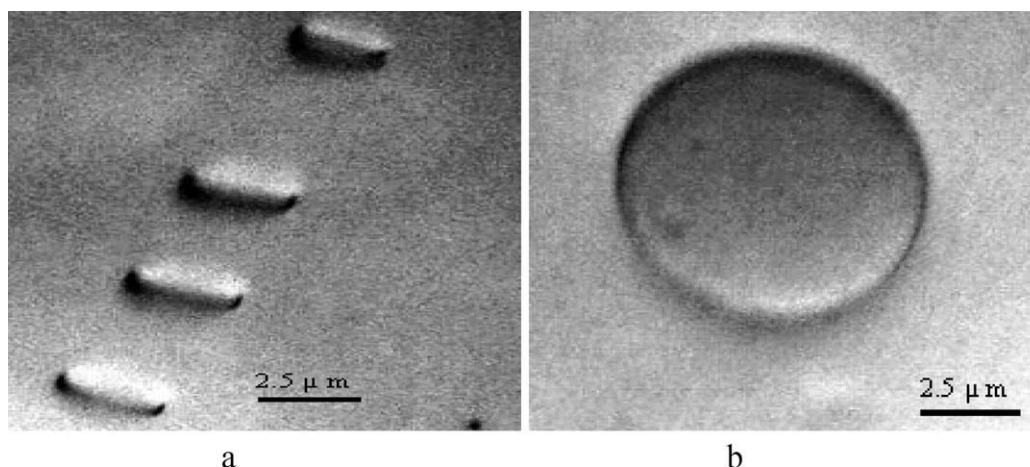


Figure 2 Morphology of (3% wt) aqueous methylcellulose under optical microscope at 6000 \times . (a) Small-sized core (beads) and large-sized shell in methylcellulose solution at 30 $^{\circ}$ C. (b) Large-sized core and small-sized shell in methylcellulose gel at 80 $^{\circ}$ C.

lower temperatures (50 $^{\circ}$ C). The first-crossover point in Figure 3 is at 8.2 Hz and 28.67 kPa, whereas the second crossover is at 50 Hz and 769.43 kPa. The first crossover frequency and modulus in Figure 3 is lower than that for any sample in Figure 1(a–g). As the allowed time for gelation is very low (only 3 min), the majority of the gel structure possibly consists of the weakly associated shell structure (Scheme 1). The shell structure dissociates on increasing the frequency due to insufficient relaxation of the dynamic force, causing steep rise in loss modulus. Thus, the sample in Figure 3 exhibits lower modulus and frequency in comparison with any sample with higher preheating time of 10 min [Fig. 1(a–g)]. The gap between the first- and second-crossover points in Figure 3 is wider than the sample in Figure 1(g). Moreover, the second-crossover frequency and modulus in Figure 3 is lower than those in Figure 1(g). Although both the samples in Figures 1(g) and 3 are preheated at the same temperature (80 $^{\circ}$ C), the allowed time for gelation (preheating time) is very low (3 min) for the sample in Figure 3 in comparison with the sample in Figure 1(g) (10 min). During the process of frequency scan at 80 $^{\circ}$ C of the sample in Figure 3, the weakly associated shell structure starts to augment the core structure. With the passage of more time during frequency scan, the gels find sufficient time to associate themselves strongly, leading to the dominance of the core structure in gels. This causes the widening of gap between the first and second crossover. The lower gelation or preheating time in Figure 3 causes lowering in modulus and frequency at the second crossover.

To check the time dependence of gelation process, the storage modulus is measured at 8 Hz for the samples preheated at 80 $^{\circ}$ C for various time intervals. From the plot of storage modulus against preheating

time in Figure 4, it is observed that the storage modulus initially increases with time and reaches a maxima (at 10 min), followed by a decrease. The increase in the value of storage modulus indicates the increase in the gel strength. The unusual behavior for the samples after preheating for 10 min may be due to the melting of gel.⁹

To examine the validity of frequency independence, the values of E' and E'' from Figure 1 are used to compute $\tan \delta$ values at various frequencies (selected randomly). The results are shown in Figure 5. The plots of $\tan \delta$ versus temperature at various frequencies are nonlinear and the plots are not following any specific pattern. Thus, the $\tan \delta$ plots in Figure 5 are not frequency independent over the

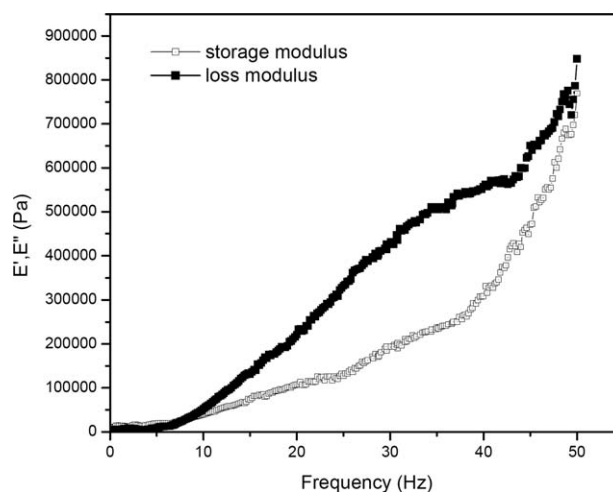


Figure 3 Storage modulus and loss modulus of 3 wt % aqueous methylcellulose gel (7 min preheating at 80 $^{\circ}$ C) as a function of frequency ω at 80 $^{\circ}$ C.

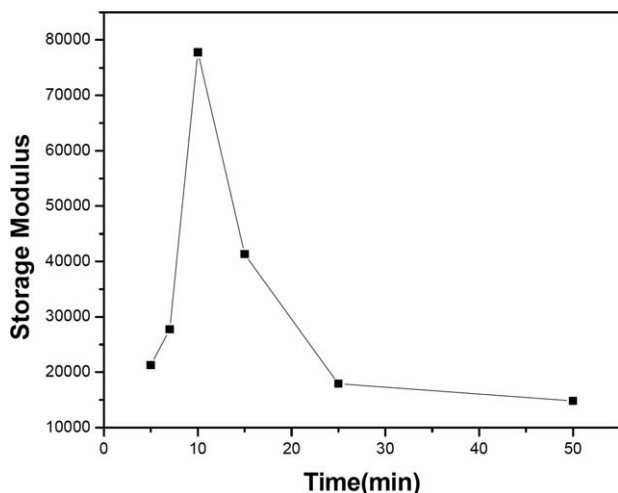


Figure 4 Storage modulus of 3 wt % aqueous methylcellulose gel at 8 Hz frequency as a function of time.

whole temperature range of 50 to 80°C. This frequency dependence of $\tan \delta$ is similar to the observation of Li et al.⁴

In all of the frequency sweep [Figs. 1(a–g) and 3], it is observed that the storage modulus (E') and loss modulus (E'') crosses over at a certain frequency. The crossover of E' and E'' during the temperature scan has been defined as the gel point by Desbrieres et al.² Thus, keeping in view of the above definition of gel point, one can define the crossover between E' and E'' during isothermal frequency scan as the transition point between gel to sol. If this would have been the transition from gel to sol, then the storage modulus during frequency scans (Figs. 1 and 3) would not continue to rise after this transition. Moreover, during the transition from a gel to a sol, the sample on dynamic testing would not have suffi-

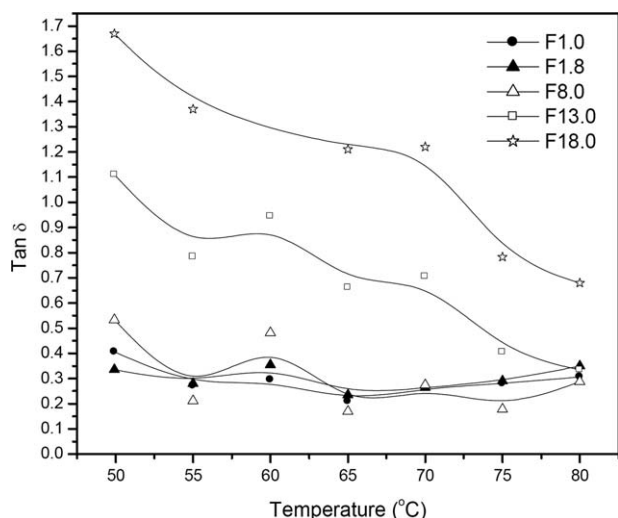


Figure 5 Loss tangent ($\tan \delta$) as a function of temperature for a 3 wt % methylcellulose gel at various frequencies (1.0, 1.8, 8, 13, and 18 Hz).

cient strength to resist the penetration of the testing probe into the metallic cone (container of sample), leading to erratic results. This prompts us to postulate a different kind of gel structure, namely core and shell structure. This hypothesis of core–shell microstructure of gels is also verified experimentally from the optical microscopy (Fig. 2). In all of the above discussions [Figs. 1(a–g) and 3], the crossover points are well explained by the hypothesized core–shell structure of the gel. The first-crossover point between E' and E'' involves the destruction of shell structure of the gel, causing a shell–sol transition. As universality exists at the crossover point (sol–gel transition),^{4,5} one may try to find the possible universality at the first-crossover point during the shell–sol transition. Thus, we have tried to find a universality of the first crossover by applying scaling law.

The three scaling laws for gels as reported in eqs. (1)–(3) were first tried to apply in our studies. In stead of eqs. (1)–(3), the following modified equations are used:

$$\eta' \propto \varepsilon^{-\gamma} \quad \text{for } \omega < \omega_c \quad (4)$$

$$E'(\omega) \sim E''(\omega) \propto \omega^n \quad \text{at } \omega_c \quad (5)$$

$$E' \propto \varepsilon^Z \quad \text{for } \omega > \omega_c \quad (6)$$

where $\eta' = E''/\omega$ and $\varepsilon = \frac{|\omega - \omega_c|}{\omega_c}$ is the relative distance of a crossover (between E' and E'') variable, ω from the first-crossover point, ω_c . The log–log plots of η' and E' versus ε and E' versus ω at the crossover point for the samples with various preheating temperatures are reported in Figures 6–8. It is observed that no linear correlation exists between η' versus ε and E' versus ε . Thus, the scaling laws as in eqs. (4) and (6) are not valid. On the other hand, log–log plots of crossover modulus (E') against crossover frequency (ω) at various preheating

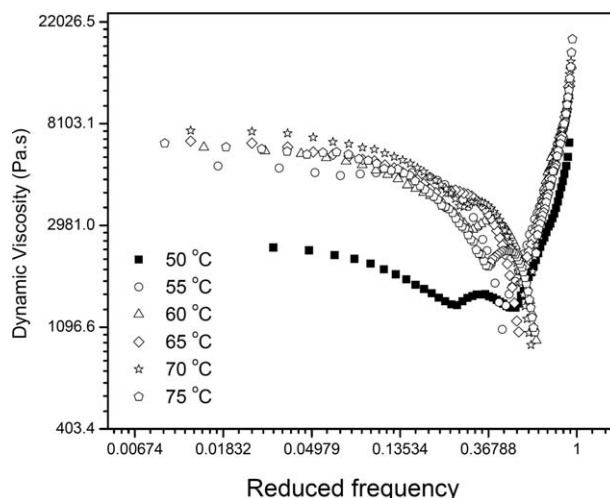


Figure 6 Log–log plot of dynamic viscosity (η') versus reduced frequency (ε) at different temperatures.

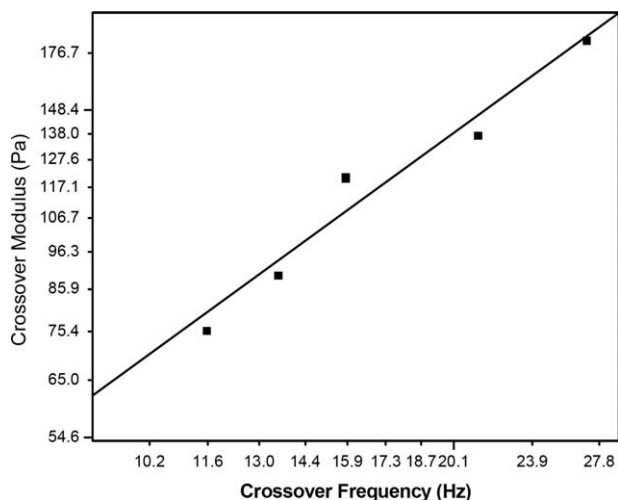


Figure 7 Log-log plot of crossover modulus (E_c) versus crossover frequency (Hz) at different temperatures.

temperatures are found to be linear (Fig. 7). In fact, all the points at different temperatures except for lower temperatures (50°C) can be linearly fitted. This indicates the validity of scaling law at the crossover point and follows the eq. (5) (the proportionality constant in eq. (5) is 6.89 and the index, n is 1).^{14–20} As scaling law prevails at the first-crossover point, it is expected that this should also prevail around this point. So, the invalidity of the scaling law around the first-crossover point indicates certain inherent flaws of the eqs. (4) and (6). The term on the right-hand side of eqs. (4) and (6) have a parameter, ϵ , which may be defined as relative frequency. Instead of a relative term on the left-hand side of eqs. (4) and (6), an absolute term is used. From mathematical point of view, two relative terms can be better correlated and scaled for universality of the parameters. Thus, instead of eqs. (4) and (6), the following two equations are generated:

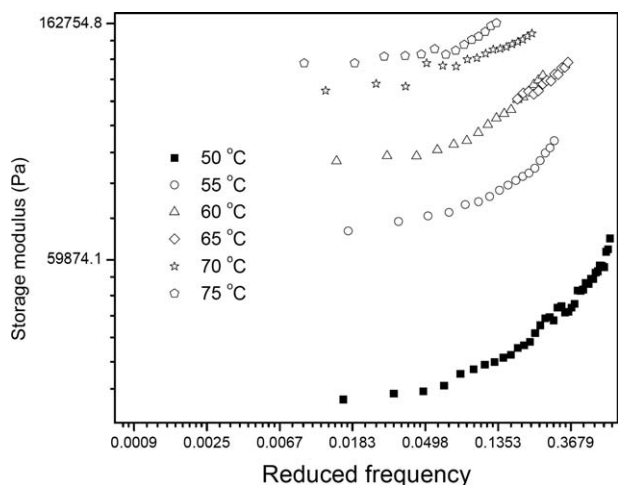


Figure 8 Log-log plot of storage modulus (E') versus reduced frequency (ϵ) at different temperatures.

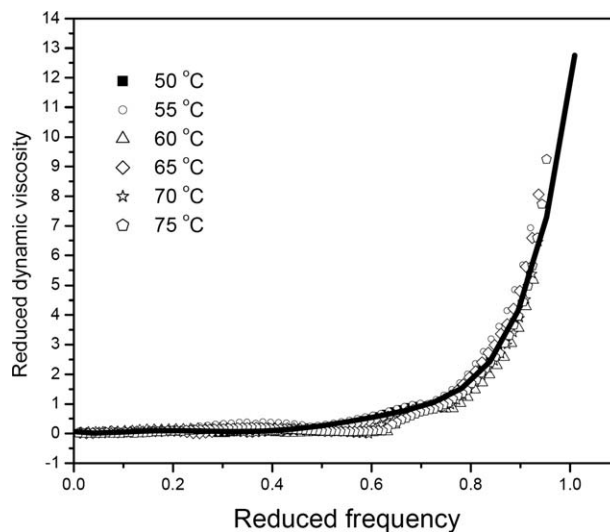


Figure 9 Plot of reduced dynamic viscosity (η'_r) versus reduced frequency (ϵ) at different temperatures.

$$\eta'_r \propto \epsilon^{-\gamma} \quad \text{for } \omega < \omega_c \quad (7)$$

$$E'_r \propto \epsilon^Z \quad \text{for } \omega > \omega_c \quad (8)$$

where $\eta'_r = \frac{E'' - (E''_c)}{(E''_c)}$ and $E'_r = \frac{E' - E'_c}{E'_c}$ are the relative viscosity and the relative modulus. To check the validity of eqs. (7) and (8), the relative viscosity and modulus are plotted against the relative frequency in Figures 9 and 10, respectively. From the plots in Figure 9, it is observed that all data points at different temperatures fall in the same region. Thus, one can have a polynomial fit of the data points. So, instead of eq. (7), the scaled polynomial equation is as follows:

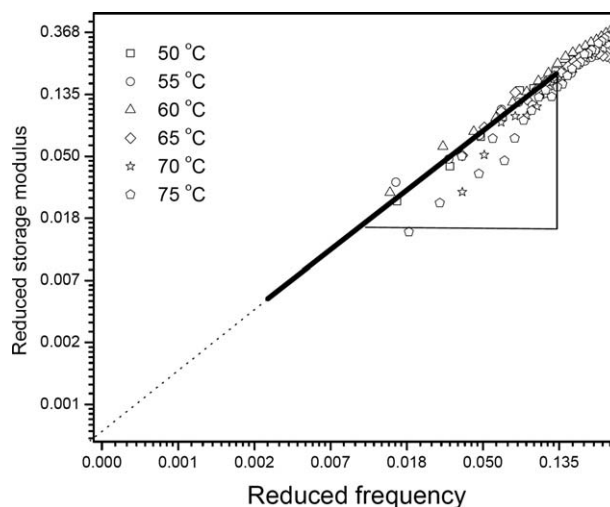


Figure 10 Log-log plot of reduced storage modulus (E'_r) versus reduced frequency (ϵ) at different temperatures.

$$\eta'_r = A + B_1\varepsilon + B_2\varepsilon^2 + B_3\varepsilon^3 + B_4\varepsilon^4 + B_5\varepsilon^5 + B_6\varepsilon^6 \quad \text{for } \omega < \omega_c \quad (9)$$

where the values of A , B_1 , B_2 , B_3 , B_4 , B_5 , and B_6 are 0.04669, -1.96192 , 37.43563 , -222.53228 , 574.40199 , -664.03602 , and 288.26831 , respectively. From Figure 10, it is observed that the data points at different temperatures lie in the same region. Thus, the scaling law is valid for E'_r and the scaled equation is as follows:

$$E'_r = \varepsilon^{1.423} \quad \text{for } \omega > \omega_c \quad (10)$$

CONCLUSIONS

During dynamic rheological characterization (frequency sweeps) of MC gels at different temperatures, the storage modulus is observed to be higher than the loss modulus at lower frequencies. With an increase in frequency, both of the storage and loss modulus increases, but the rate of increase in loss modulus is higher, leading to the first crossover between E' and E'' . At high temperature (80°C), with further increase in frequency (beyond the first crossover frequency), the rate of increase in E' is much higher than that of E'' , leading to the second crossover of E' and E'' . All these rheological properties can be explained by the concept of core-shell microstructure of the MC gels. The presence of core-shell microstructure in MC gel is experimentally observed under optical microscope. The first crossover is possibly due to the shell-sol transition, whereas the second crossover is due to the sol-shell-core transition.

The earlier efforts by other scientists^{4,5} of finding universality at and around the crossover point through scaling laws prompts us to find universality at and around the first-crossover point (shell-sol transition). The scaling law is valid at the first-crossover point, but it is not valid around the first-crossover point. We have tried to find alternate scaling equations by using reduced parameters and found that irrespective of temperatures, scaling law is valid for reduced parameters.

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