

Thermogelation of Methylcellulose from Solution in *N,N*-Dimethylformamide and Characterization of the Transparent Gels

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ABSTRACT: A transparent gel was prepared through the cooling of a methylcellulose (MC) solution in *N,N*-dimethylformamide (DMF) at 80°C to a lower temperature. The temperature at which gelation occurred was dependent on the concentration of the solution. The gel temperature increased with an increase in the concentration of MC. The gelation of MC in DMF was studied by means of optical microscopy (OM), differential scanning calorimetry, and dynamic mechanical analysis (DMA). The OM studies revealed the presence of loosely bound beads of MC with DMF at a lower concentration. These beads

became interconnected to rods, and subsequently, a continuous, thick gel was formed as the concentration increased. From DMA studies, it was observed that the loss modulus of the gel crossed over the storage modulus at two different frequencies. This indicated the presence of two types of network structures generated from the weak and strong associations of MC with the organic solvent DMF. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3031–3037, 2008

Key words: gelation; gels; morphology; rheology

INTRODUCTION

The reversible gelation of aqueous methylcellulose (MC) solutions was first investigated by Heymann.¹ According to Heymann, the gelation is due to the dehydration of hydrated MC molecules. Several mechanisms of thermogelation of aqueous MC solutions have been proposed. The major discussion concerns the nature of the zones in MC, which are responsible for the gelation. Sarkar² postulated that the gelation is due to hydrophobic or micellar interactions. Haque and Morris³ reported the presence of crystalline zones of MC in gels. Koto et al.⁴ remarked that the crosslinking loci of an MC gel consist of crystalline sequences of trimethyl glucopyranose units, and this was confirmed by Khomutov et al.⁵ An MC solution consists of dissolved bundles of partly methylated chains that are cross-linked both by residual cellulose crystallites and by the hydrophobic interactions of densely substituted regions in the cellulose backbone. These hydrophobic regions become solvated by a cagelike water structure around the polymer chain in the temperature range of 30–55°C, but this cagelike solvation shell melts at a higher temperature. If the solvation

shell melts, the MC starts to form a gel, driven by hydrophobic interactions of densely substituted strands.^{3,6–10}

A comparison of MC films made from aqueous and dimethylacetamide solutions was reported by Bocek et al.¹¹ They also tried to explain the mechanism of gelation from an organic solvent (dimethylacetamide). To date, there is no published work on the thermogelation and rheology of MC–*N,N*-dimethylformamide (DMF) gels.

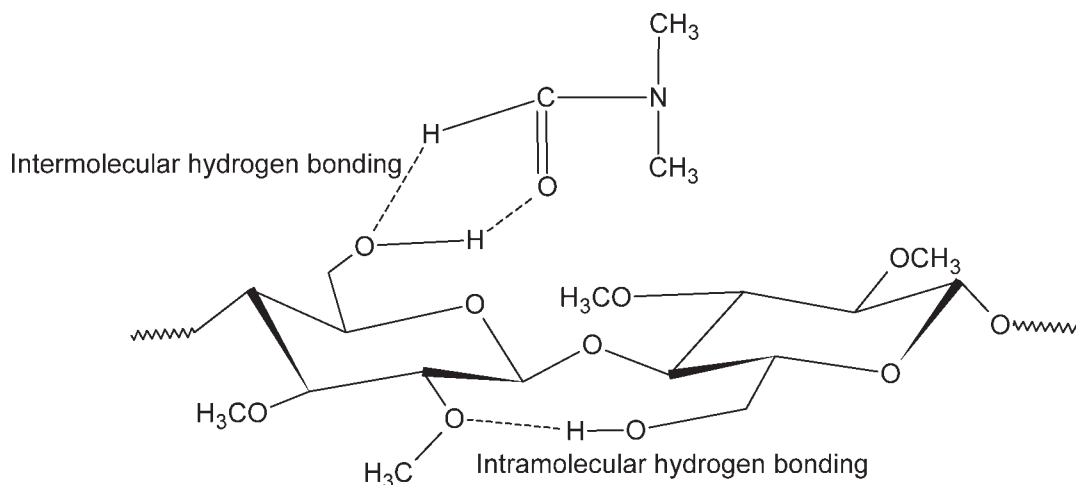
In this work, rheological experiments were carried out for a DMF–MC solution, and the investigation focused on the thermoreversibility of MC in DMF with a detailed study on the gel structure [optical microscopy (OM)], thermoreversibility [differential scanning calorimetry (DSC)], and rheology [dynamic mechanical analysis (DMA)].

EXPERIMENTAL

Materials and sample preparation

MC, a laboratory reagent in a powdered form, was supplied by Central Drug House (P), Ltd. (New Delhi, India). The viscosity of a 2% aqueous solution at 20°C, as supplied by the manufacturer, was about 4000 cps. The viscosity-average molecular weight of MC was 149,000, and its methoxy value was 26–30%. DMF, a laboratory reagent supplied by Ranbaxy

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Scheme 1 Schematic representation of possible hydrogen bonding in MC in a DMF solution.

Fine Chemical, Ltd. (New Delhi, India), was used as a solvent. A solution of MC was prepared in DMF by the slow addition of MC in hot DMF (80°C) with continuous stirring. The prepared solution was cooled for gelation and was further used for characterization. For controlled cooling of the solution, a Haake (Karlsruhe, Germany) K20 circulator was used. The rate of cooling of a fixed concentration of the MC solution was measured from the time taken for cooling from 80°C to various sink temperatures.

Rheological experiments with the gels were carried out with a PerkinElmer (Waltham, MA) Pyris-7e dynamic mechanical analyzer. The MC gels (3 wt %) were placed in a cone, and the probe was pressed against the gels dynamically with a 110 mN static force and a 110 mN dynamic force. This is the first report of gels dynamically characterized with a dynamic compressive load. The dynamic viscoelastic functions, such as the shear storage modulus (E') and loss modulus (E''), were measured as functions of the to and fro frequency.

Thermal analysis was carried out with a Perkin-Elmer Pyris-7e differential scanning calorimeter. In this work, different heating rates and a fixed cooling rate were used to determine the transitions. The morphology of the gel was studied with a Digital Blue optical microscope at 6000 \times (USA).

RESULTS AND DISCUSSION

Gelation of MC in DMF

A dispersion of MC in DMF starts to form a solution with heating to 80°C. The MC forms a gel upon the cooling of the solution in DMF. On the contrary, the gelation of MC from an aqueous solution requires heating.¹ The gelation from a DMF solution is totally the reverse of the process of gelation from an aque-

ous solution. This indicates that the mechanism of gelation in DMF is different from that in an aqueous MC system. DMF can form two hydrogen bonds with MC and can interact with methoxy groups of the polymer by a dipole-dipole interaction, as shown in Scheme 1.¹¹ Sealed tubes containing equal volumes of hot MC solutions (having different concentrations) at 80°C were placed in a sink at -10°C. Thus, during the cooling of the MC solutions, they gelled at a particular temperature. Because of the fixed terminal temperatures (80 and -10°C), the rate of cooling of a particular solution was constant. Figure 1 shows the variation of the gel temperature against the concentration (wt %) of MC. The gel temperature increased almost linearly with an increase in the concentration of MC. These gels were again heated to 80°C and subsequently cooled. This experiment was repeated (after 24 h) for different

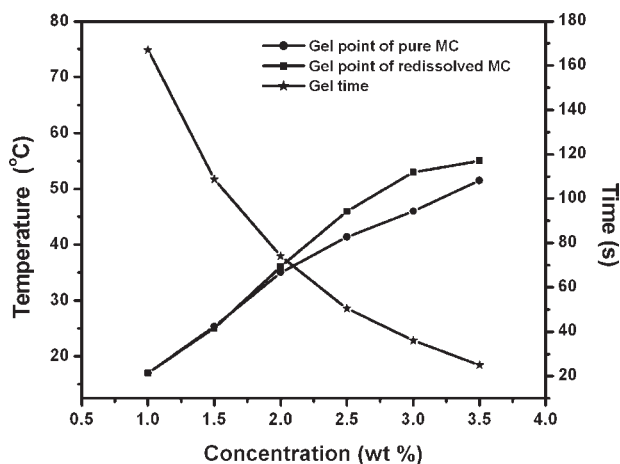


Figure 1 Variation of the gel temperature (°C) with the concentration (wt %) of MC for pure and repeated samples.

TABLE I
Gelation Data for Various Concentrations of MC in DMF

Concentration (wt %)	Gel point (°C)	Time for gelation (s)
0.3	No gelation	Not applicable
0.5	-6	571
0.6	-6	450
0.7	-6	225
1.0	17	167
1.5	25.33	108.8
2.0	35	74
2.5	41.36	50.5
3.0	46	36
3.5	51.5	25

concentrations and plotted as the gel temperature of the redissolved MC against the concentration. The graph for the repeated sample follows the pattern of the pure MC up to a 2 wt % solution, beyond which it shows a higher gel temperature. This may be due to incomplete reversibility of MC gels at higher concentrations.

The variation of the time required for gelation versus the concentration (wt %) of MC in DMF is also plotted in Figure 1. The time for gelation was noted during the cooling of the solution from 80 to -10°C . The time for gelation decreased with an increase in the concentration of MC. Table I shows that the gel temperature was the same for 0.5, 0.6, and 0.7 wt % solutions of MC, whereas the time for gelation increased with a decrease in the concentration of MC. This is because at a very low concentration (<1 wt %) of MC in DMF, the molecular interactions are very less. At a lower concentration, the availability of MC molecules in the system is less. Therefore, the interactions between MC molecules will be less in comparison with higher concentrations. These interactions between MC chains will cause an increase in the time of agglomeration with an increase in the concentration, leading to the gelation time. The same gelation temperature at -6°C observed for the MC solutions of low concentrations (<1 wt %) is the experimental limitation (the fixed sink temperature of -10°C allows solutions to be cooled not below -6°C). Therefore, the process of gelation is both time- and temperature-dependent (similar behavior was observed in aqueous MC solutions²). Thus, the time for gelation decreases with an increase in the concentration, as reported in Table I. The association of the MC molecules and DMF depends on intermolecular separation. Thus, for a very low concentration of MC, the gel temperature becomes a time-dependent parameter. For the fixed temperature difference between the MC solution at 80°C and the circulating coolant at -10°C , the cooling rate is expected to be constant. The higher concentration

leads to a closer association between DMF and MC, and on the removal of heat, the solution is believed to form beads, which are followed by the formation of rods and a continuous gel (this is well supported by OM studies of the gel). The more the continuous gel structure is formed, the more heat there is that is liberated from the system.

Figure 2 shows the variation of the gel temperature with different cooling rates for 3 wt % MC solutions. The various cooling rates were maintained by the setting of the temperatures to which the MC solutions at 80°C were to be cooled. The calculation of the cooling rate was based on the time required to cool a solution at 80°C to the gel temperature. For a fixed concentration (3 wt %), we expected a single gel temperature to be shown. On the contrary, various gel temperatures were shown, depending on the cooling rate. According to Figure 2, the gel temperature increased with an increase in the rate of cooling. During cooling, such a solution is believed to form beads, which are followed by the formation of rods and a continuous gel (this is well supported by the OM studies of the gel). A higher cooling rate induces liberation of heat from the MC-DMF solution at a faster rate, leading to a reduction of molecular motion and intermolecular separation. Thus, at a higher cooling rate, a continuous gel is formed at a faster rate.

DSC studies

The variation of the heat flow versus the temperature for a gel of MC in DMF is plotted in Figure 3. Thermograms were recorded during both the heating and cooling of the samples. In the cooling cycle, the transition from the sol state to the gel state was

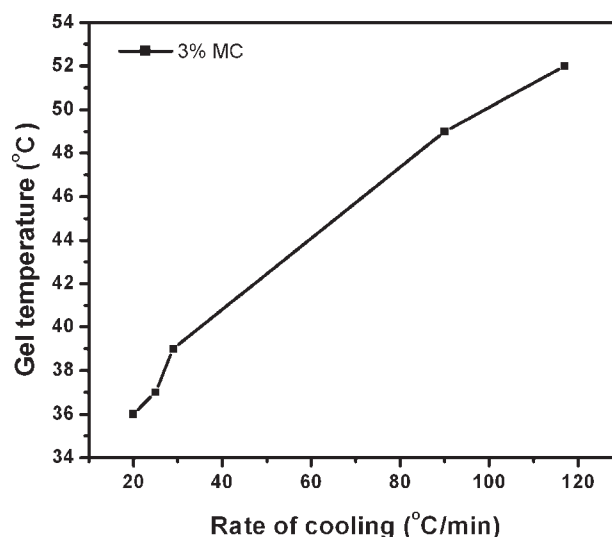


Figure 2 Variation of the gel temperature ($^{\circ}\text{C}$) with the rate of cooling at a constant concentration (3 wt %).

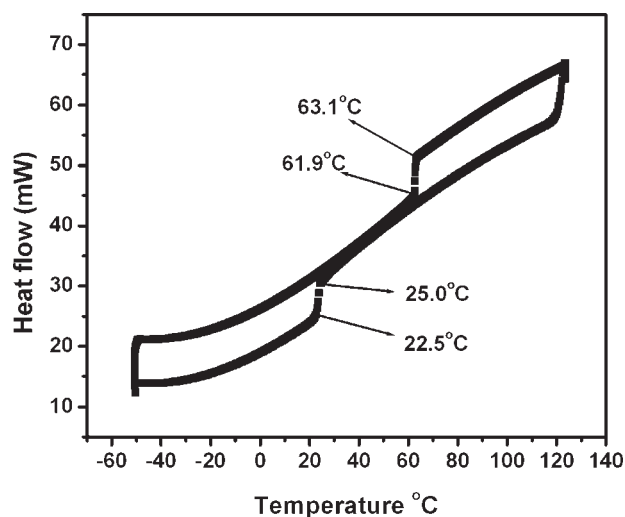


Figure 3 Calorimetric thermograms of a 0.5 wt % MC-DMF gel during a thermal cycle from heating to cooling. The heating rate was 0.7°C/min, and the cooling rate was 20.0°C/min. The numerals in the figure indicate the transition or characteristic temperature.

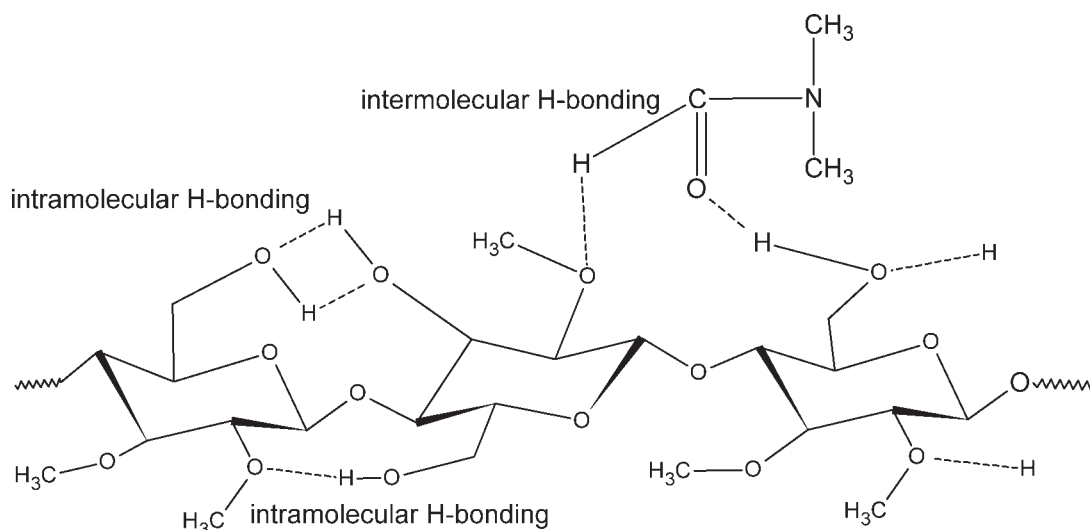
observed between 25.0 and 22.5°C; it was reported earlier that this sol-gel transition for an aqueous system in a DSC thermogram was observed during the heating process.¹⁰ The association of MC molecules in DMF is considered to be a thermodynamic process. The association in solution occurs only when ΔG is negative in eq. (1):

$$\Delta G = \Delta H - T\Delta S < 0 \quad (1)$$

where ΔG is free energy change, ΔH and ΔS are the enthalpy and entropy changes, respectively, and T is temperature. For the gelation process to be spontaneous, change in free energy during sol-gel transition ($\Delta G_{\text{sol-gel}}$) must be a negative quantity. MC

chains are in association with DMF through intermolecular hydrogen bonding to form a solution (Scheme 1). On cooling, the dissociation of intermolecular hydrogen bonding between DMF and MC and the formation of intramolecular hydrogen bonding between MC molecules lead to the formation of aggregates or clusters (Scheme 2). This cluster formation is further enhanced by a decrease in temperature, resulting in gelation. With a decrease in the temperature of the solution, ΔS or the degree of randomness of the solution also decreases, and this results in a restriction of molecular motion of MC molecules. This will enhance cluster formation and subsequent gelation. Therefore, $T\Delta S$ makes a small and positive contribution toward $\Delta G_{\text{sol-gel}}$. In the cooling process, the change in the ΔH value is always negative. The presence of hydrogen bonding further reduces the ΔH value, and this leads to a negative contribution to $\Delta G_{\text{sol-gel}}$. As $T\Delta S$ is much lower than ΔH , $\Delta G_{\text{sol-gel}}$ will be a negative quantity. Thus, the sol-gel transition is thermodynamically favorable during the cooling cycle. As observed from Scheme 2, the presence of both intermolecular and intramolecular hydrogen bonding prevents phase separation, leading to a gel.

In the heating cycle of DSC thermograms, the gel-sol transition can be observed from 61.9 to 63.1°C. This process is also based on the thermodynamics of the gel-sol transitions. For the transition from the gel state to the sol state to be a spontaneous process, $\Delta G_{\text{gel-sol}}$ should be a negative quantity [eq. (1)]. When the temperature increases, ΔS of the system increases, providing a very high negative contribution to $\Delta G_{\text{gel-sol}}$. With an increase in the energy of the system, the self-association between polymer chains breaks and enhances the formation of intermolecular hydrogen bonding between MC and DMF. Thus, ΔH



Scheme 2 Schematic representation of possible hydrogen bonding in MC in a DMF gel.

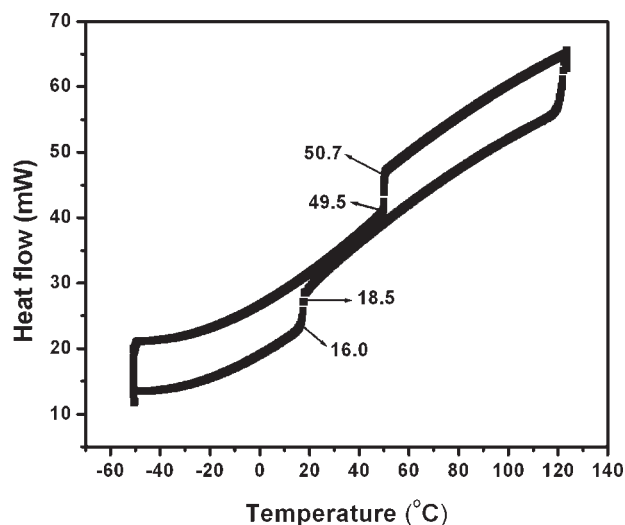


Figure 4 Repeated calorimetric thermograms of a 0.5 wt % MC-DMF gel during a thermal cycle from heating to cooling. The heating rate was 0.7°C/min, and the cooling rate was 20.0°C/min. The numerals in the figure indicate the transition or characteristic temperature.

makes a positive contribution to $\Delta G_{\text{gel-sol}}$. As $T\Delta S$ is much higher than ΔH , $\Delta G_{\text{gel-sol}}$ will be a negative quantity. Thus, the gel-sol transition is thermodynamically favorable during the heating cycle.

To check the thermoreversibility of the system, the DSC thermograms were repeated cyclically with

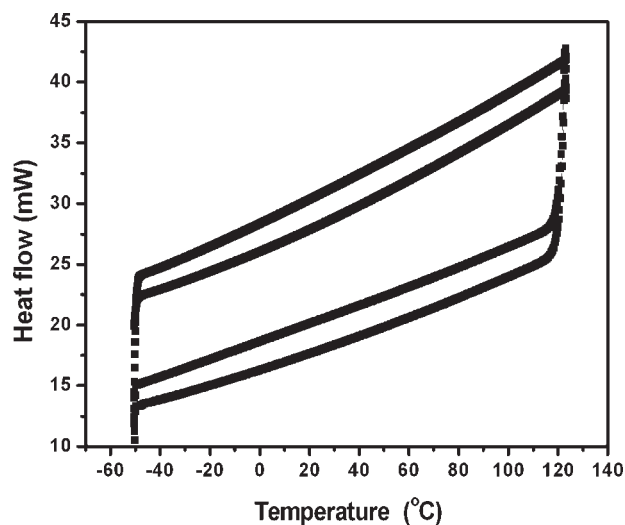


Figure 5 Calorimetric thermograms of a 0.5 wt % MC-DMF gel during a thermal cycle from heating to cooling. The heating rate was 1.0°C/min, and the cooling rate was 20.0°C/min. The numerals in the figure indicate the transition or characteristic temperature.

heating and cooling (Fig. 4). The transition pattern for the heating and cooling cycles, shown in Figure 3, remains the same for the repeated cycles in Figure 4. Although the same pattern of transitions is observed, there is a shift in the transitions for the repeated cycles. The transitions for the heating and

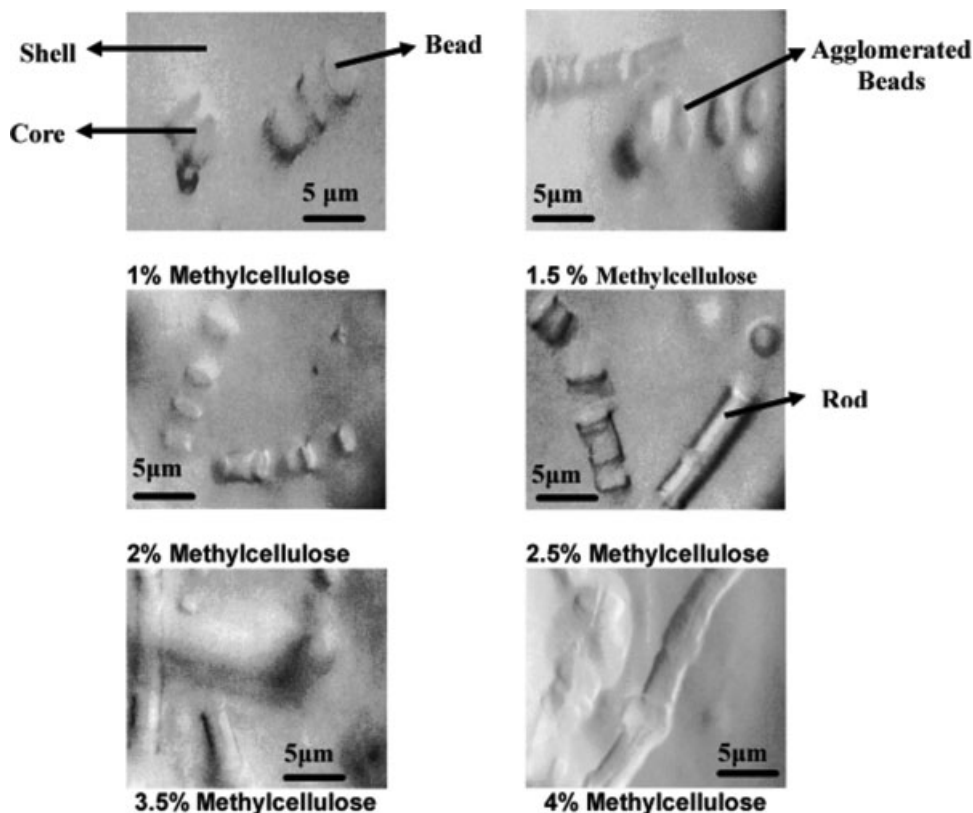


Figure 6 Morphology of MC gels at different concentrations.

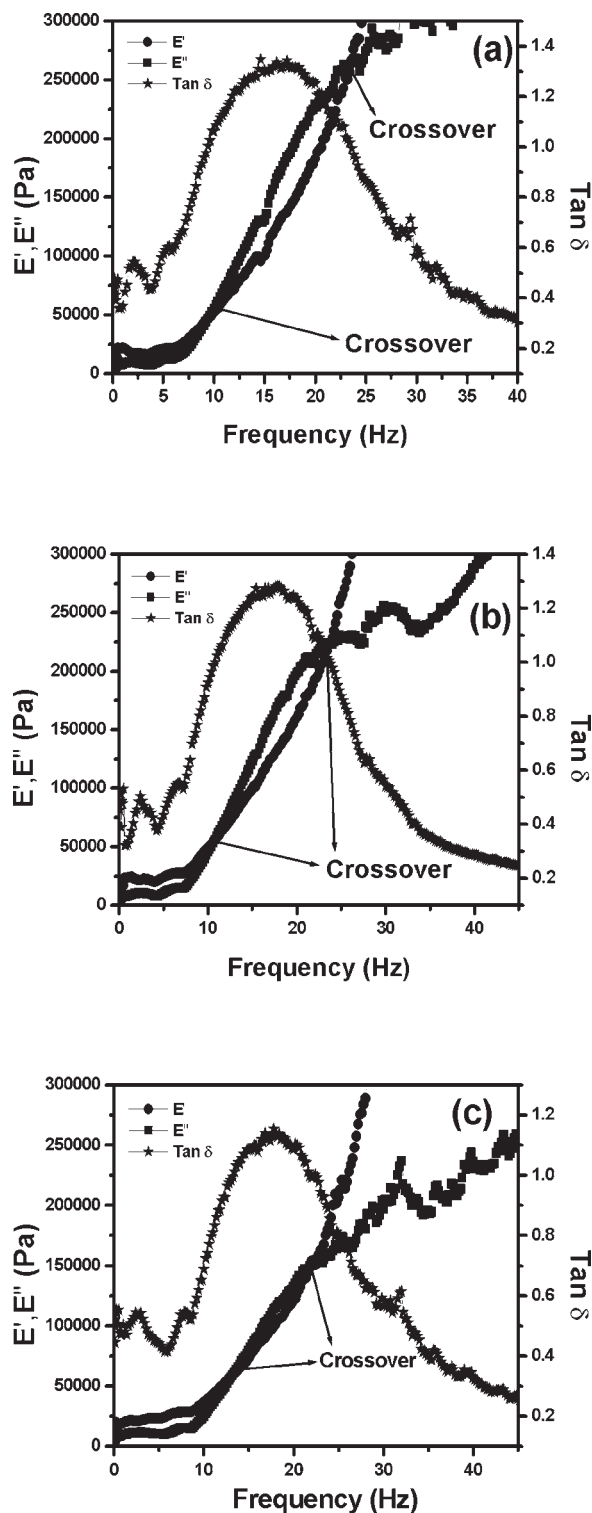


Figure 7 E' , E'' , and $\tan \delta$ of a 3 wt % MC-DMF gel as a function of the to and fro frequency at (a) 25, (b) 50, and (c) 60°C.

cooling cycles, as shown in Figure 4, range from 49.5 to 50.3°C and from 16.0 to 18.5°C, respectively. Thus, in comparison with Figure 3, the transitions for the repeated cycles are shifted to a lower temperature.

This shift can be explained on the basis of a disruption in the structure of the MC gel, which results in a decrease in the gel strength.

Figure 5 presents DSC thermograms at higher heating (1°C/min) and cooling (40°C/min) rates. No transition can be observed during heating and cooling at higher rates. During the transition process, sufficient relaxation time should be allowed to set in the transition. At higher rates, the allowed transition time is too short, and this results in the disappearance of the transition.

Morphology of the MC gels

Figure 6 shows the morphology of MC gels at room temperature and different concentrations (1, 1.5, 2, 2.5, 3.5, and 4 wt %). As shown in Figure 6, the association of the core part of the gel increases with an increase in the concentration of MC. At a lower concentration (1 wt %), fewer molecules are associated, and hence less core can be observed.¹² When the concentration increases from 1 to 2.5 wt %, these molecules agglomerate to form a cluster, which can be observed as a beadlike structure. On a further increase in the concentration (3.5 and 4 wt %), these beads further associate into a rodlike structure. Thus, increasing the MC concentration leads to higher gel strength.

DMA

The variations of E' , E'' , and $\tan \delta$ at different temperatures (25, 50, and 60°C) are plotted as a function of frequency in Figure 7(a–c), respectively. Both E' and E'' values increase with an increase in frequency. With an increase in frequency, $\tan \delta$ increases, reaches a maximum, and then decreases. Thus, a $\tan \delta$ peak is generated with an increase in the frequency. It can be observed from the $\tan \delta$ peak in Figure 7(a–c) that the broadness of 31 Hz (3.6–34.6 Hz) decreases to a lower value of 29.2 (4.2–33.4 Hz) and 28.6 Hz (5.8–34.4 Hz), whereas the peak maxima of 1.340 at 25°C decreases to 1.281 and 1.154 with an increase in the temperature to 50 and 60°C, respectively.

As shown in Figure 7(a–c), E'' shows a lower value than E' , and E'' crosses over E' at two different frequencies.^{12,13} Between these crossover frequencies, the values of E'' are higher than those of E' . The first crossover is at a lower frequency (10 Hz for 25°C, 11.2 Hz for 50°C, and 13.6 Hz for 60°C), and the second one is at a higher frequency (23.8 Hz for 25°C, 23.6 Hz for 50°C, and 22.4 Hz for 60°C). These crossovers can be explained on the basis of the gel strength and core-shell structure of the gels.¹² The gel strength is assumed to be derived from two components of the gel. The first component is the

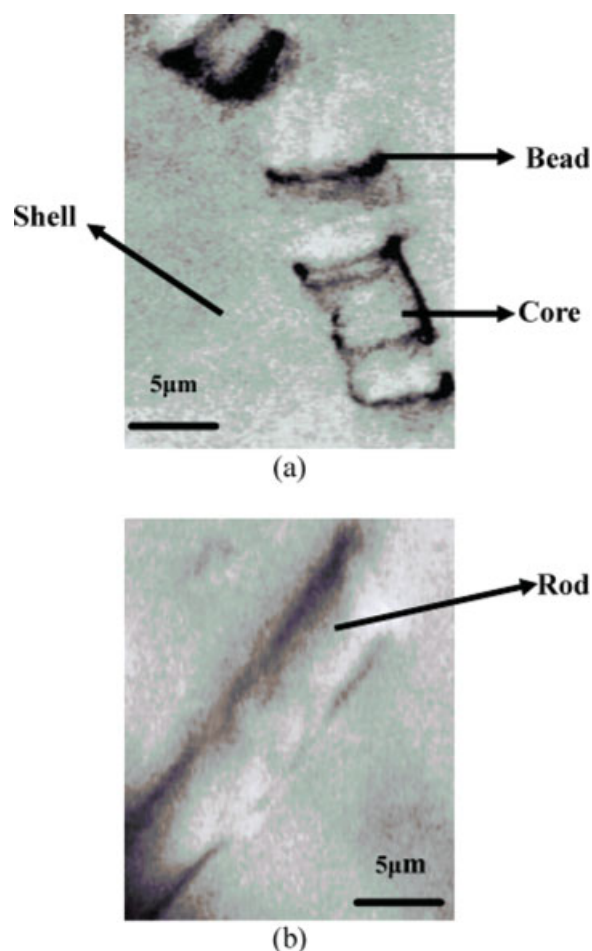


Figure 8 Morphology of (a) a weakly associated MC gel and (b) a strongly associated MC gel. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

beadlike structure [from Fig. 8(a)], which consists of weakly associated molecules of MC that are separated. The second component is composed of highly associated lumps of MC (rodlike structure and core part), as shown in Figure 8(b). The lower frequency is sufficient to break the loosely associated beads of MC, and this results in the first crossover between E' and E'' . The second crossover at a higher frequency indicates the breaking of all associations, including the rodlike structure of MC molecules. As shown in Figure 7, with an increase in temperature, the first crossover frequency increases, whereas the second crossover frequency decreases. The increase in the first crossover frequency is not explainable right now, but the decrease in the second crossover fre-

quency can be explained on the basis of the gel strength, which decreases with an increase in the temperature. At the crossover points, the values of $\tan \delta$ are unity, and this symbolizes the equality of elastic and viscous responses of the MC-DMF system. It is interesting that the crossover points come closer to each other with an increase in the temperature. Also, the closer the crossover points are, the sharper the $\tan \delta$ peaks are.

CONCLUSIONS

During the cooling of an MC solution in DMF, a transparent gel is formed. The gelation temperature is dependent on the concentration of the solution, and the gel temperature increases with an increase in the concentration of MC. The gels observed under OM revealed the presence of loosely bound beads of MC with DMF at a lower concentration. These beads become interconnected to rods, and subsequently, a continuous, thick gel is formed as the concentration increases. Thus, the presence of dual strength in MC-DMF gels is confirmed by OM. DMA studies show that E'' of the gel crosses over E' at two different frequencies. In DSC studies, a transition was observed in both processes, heating and cooling. Thus, the process of gelation is thermoreversible. On the other hand, at higher rates, the allowed transition time is too short, and this results in the disappearance of the transition.

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