

Effect of Addition of Surfactants on the Rheology of Gels from Methylcellulose in *N,N*-Dimethylformamide

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ABSTRACT: The effect of highly substituted cationic cetyl trimethyl ammonium bromide (CTAB), less substituted cationic hexadodecyl ammonium bromide (HDAB), CTAB- and HDAB-modified montmorillonite (CTABMONT and HDABMONT), and nonionic surfactants on the rheological properties of methylcellulose (MC) *N,N*-dimethylformamide (DMF) gels have been studied. The storage modulus of the MC-DMF gels increases with an increase in frequency. During the frequency scan, the storage and loss modulus of MC-DMF gel crosses over each other at two different frequencies. At the crossover points, the loss tangent is found to be unity. The addition of CTAB- and

HDAB-modified nanofiller increases in the gel strength of MC-DMF gel. The storage modulus of MC-DMF gel in the presence of CTABMONT is found to be higher than that of CTAB-modified MC-DMF gel. Whereas, the storage modulus of MC-DMF gel in the presence of HDABMONT is lower than that of HDAB-modified MC-DMF gel. On the other hand, the addition of nonionic surfactant (Brij78) decreases the gel strength. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1871–1879, 2008

Key words: DMF-methylcellulose gel; rheology; surfactants

INTRODUCTION

The thermoreversible gelation of methylcellulose (MC) from the aqueous solution was first investigated by Heymann.¹ The gelation of MC at higher temperature is believed to be due to the dehydration of hydrated MC molecules. Different mechanisms of thermogelation of MC were proposed. The major discussion concerns the nature of the zones responsible for the gelation. Sarkar² postulated that the gelation was due to hydrophobic or micellar interaction. Koto et al.³ concluded that the crosslinking loci of MC gel consisted of crystalline sequences of trimethyl glucose units. This was further confirmed by Khomutov et al.⁴ MC solution consists of dissolved bundles of partly methylated chains, which are crosslinked, both by residual cellulose crystallites and by the hydrophobic interactions of densely substituted region in the cellulose backbone. These hydrophobic regions become solvated by a cage-like water structure around the polymer chain in the temperature range of 30 to 55°C. This cage-like 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.^{5–10} The variation in the gelation properties

on addition of salts and surfactants was studied by many researchers. The variation of gel temperature with the addition of salts was studied by Touitou et al.¹¹ Hirrien et al.⁷ studied the rheological properties of aqueous MC solution. They proved the presence of hydrophobic interactions. Kundu and Kundu¹² explained that the gelation depended on the ratio of weight percent of surfactants and that of MC present in the aqueous solution (*r*).

Bochek et al.¹³ compared the properties of MC films cast from aqueous and dimethylacetamide (DMAc) solution. Although, they reported the mechanism of the gelation of MC in DMAc, there is no report on the thermoreversibility and rheology of the MC-DMF gels. This work reports the rheological properties of transparent MC-DMF gels in the presence of different surfactants.

EXPERIMENTAL

Materials

Methyl cellulose, laboratory reagent in powdered form was supplied by central Drug House (P) Ltd., New Delhi (India). Viscosity of 2% aqueous solution at 20°C as supplied by the manufacturer is about 4000 cP. The viscosity-average-molecular weight of MC is 149,000 and its methoxy value is 26–30%. As a solvent, we used *N,N*-dimethylformamide (DMF), laboratory reagent (Ranbaxy fine chemical, New

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Delhi, India). Montmorillonite (K-10), cetyl trimethyl ammonium bromide (CTAB), Brij 78, and hexadecyl ammonium bromide (HDAB), purchased from Aldrich Chemical Company (Milwaukee, MI) were used as received.

Modification of montmorillonite

Montmorillonite clays were dispersed in deionized (DI) water by stirring. CTAB and HDAB were added to the dispersion. The whole dispersion was heated at 80°C for 4 h. The exchanged clays were filtered and washed with DI water until it was free from bromide (tested and titrated by silver nitrate). The modified clay was dried at 80°C under vacuum. CEC (cation exchange capacity), calculated from the titer value for CTAB and HDAB is 29.92 and 152.8 mequiv/100 g of clay, respectively.

Sample preparation

Solution of MC in DMF was prepared by slowly adding an weighted amount of MC in 100 mL of hot DMF at 75°C ± 2°C. The whole mass is continuously stirred, followed by the addition of weighted amount (0.5 wt %, if not specified otherwise) of various additives such as sodium chloride, CTAB, HDAB, CTAB-and HDAB-modified montmorillonite (CTABMONT and HDABMONT). The solution is cooled for a gel which was subsequently characterized. Haake K20 circulator is used for cooling the solution.

Rheological characterization of the MC gel in DMF

Rheological characterization of the gels was carried out on a Perkin–Elmer dynamic mechanical analyzer (DMA) Pyris-7e with a 110 mN static force and a 110 mN dynamic force. The MC gels (3 wt % of MC along with the additives) were taken in a cone and the probe was pressed against the gels dynamically with a 110 mN static force and 110mN dynamic force. This is the first report in which the effects of additives on MC-DMF gels were characterized with a dynamic compressed load. The dynamic viscoelastic functions such as the storage modulus E' and loss modulus E'' were measured as a function of angular frequency.

RESULTS AND DISCUSSION

Effect of salt and surfactant on gelation of MC in DMF

MC gets solubilized in DMF when it is heated. The hot solution on cooling forms a gel, which is again redissolved on subsequent heating. Figure 1 shows

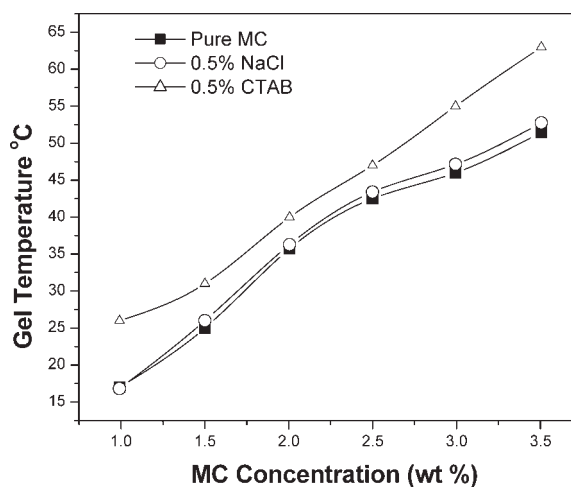


Figure 1 Variation of gel temperature (°C) with concentration (wt %) of methyl cellulose in the presence of 0.5% NaCl and 0.5% of CTAB additives.

the variation of gel temperature against concentration (wt %) of MC in the presence of different additives. It is observed from Figure 1 that the gel temperature increases with an increase in the concentration of MC. However, the gel temperature of MC remains unaltered on the addition of a highly polar salt such as sodium chloride. On the contrary, for the aqueous system, the gel temperature decreases on addition of sodium chloride.¹² It may be explained on the basis of dielectric constant of solvents. The dielectric constant of DMF is 39, whereas, the dielectric constant of water is relatively very high (80). Therefore, the ionization of sodium chloride in DMF is less than that of aqueous system. Hence, there is almost negligible variation in the gel point of MC containing sodium chloride as an additive. On the other hand, Figure 1 indicates that the gel temperature increases on the addition of a cationic surfactant (CTAB). The structure of CTAB (long carbon chain and comparatively less polar than sodium chloride) makes it soluble in an organic solvent, DMF. Therefore, at higher temperature, CTAB competes with MC for the formation of the intermolecular H-bonding with DMF. The long organic tail in CTAB gets solubilized in the hydrocarbon phase of MC. On the other hand, MC can form H-bonds with DMF.¹³ Thus, MC binds itself both to CTAB and DMF. Cooling, helps in early formation of gels, leading to an increase in gel temperature. On the contrary, for aqueous system, the cationic surfactant gets ionized and the cation attracts the water molecules of the system.¹²

Figure 2 shows the variation of gel temperature with concentration (wt %) of MC in the presence of 0.5 and 1 wt % of CTAB. From these plots, it is evident that with an increase in the concentration of MC, the gel temperature increases almost linearly.

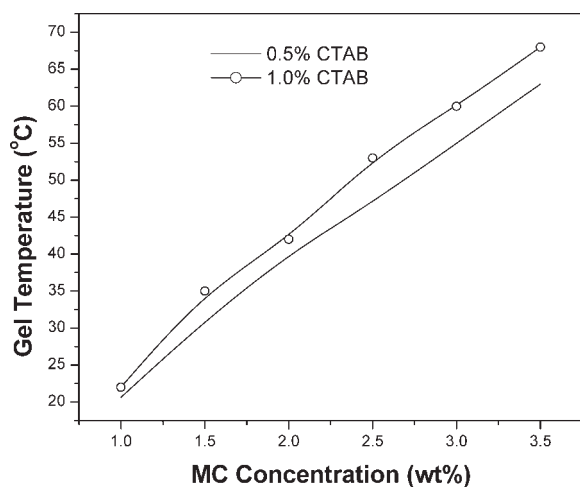


Figure 2 Variation of gel temperature ($^{\circ}\text{C}$) with concentration (wt %) of methyl cellulose in the presence of 0.5 and 1% CTAB additives.

On comparing the gel temperature of MC for two different concentrations of CTAB (0.5 and 1%), higher gel temperature is observed for higher surfactant (CTAB) concentration. From Figure 2, it is evident that the gap in gel temperature between graphs for two CTAB concentrations gets widened with an increase in the concentration of MC. On increasing the concentration of CTAB, the number of molecules of DMF attached to CTAB through MC also increases, leading to an increase in the gel temperature.

Dynamic viscoelastic properties of DMF-MC gels with different surfactants

The rheological properties of MC-DMF gels in the presence of CTAB surfactant are reported in Figure 3. This figure shows the variation of storage modulus (E'), loss modulus (E''), and $\tan \delta$ with angular frequency (ω) at different temperatures [Fig. 3(a–c) for 25, 50, and 75 $^{\circ}\text{C}$, respectively]. With an increase in frequency, both of E' and E'' is found to increase. But, the rate of increase in E' and E'' is different at different zones of frequency, causing crossover of E' and E'' at two different values of frequencies. The first crossover is at lower frequency (9.4 Hz) and the second one is at relatively higher frequency (26.6 Hz). The storage modulus at the first crossover point is found to be 27.81 KPa, which increases to 76.38 KPa at the second crossover. It is reported elsewhere that the aqueous MC-gels at 45 $^{\circ}\text{C}$ also exhibits the double crossover between E' and E'' at two different frequencies.¹³ It is also reported that with an increase in frequency, the storage modulus of aqueous MC gels increases.¹⁰ The reasons behind the double crossover observed in aqueous MC-gels are

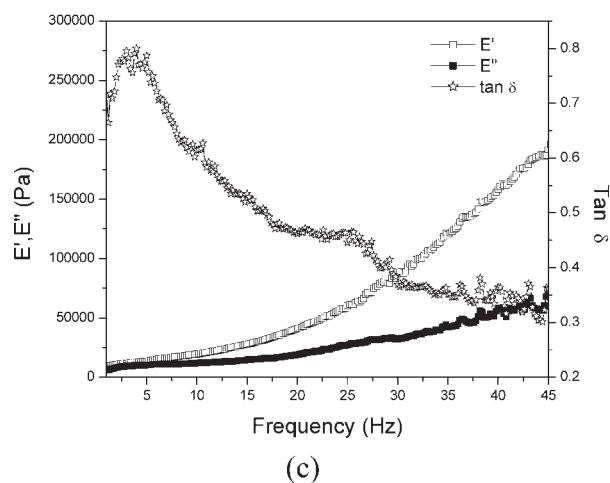
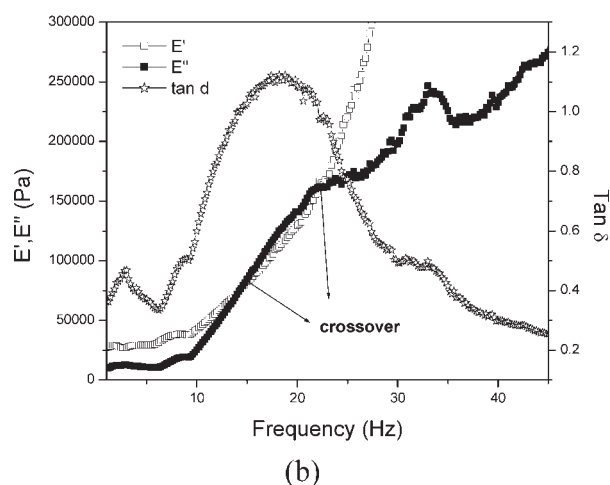
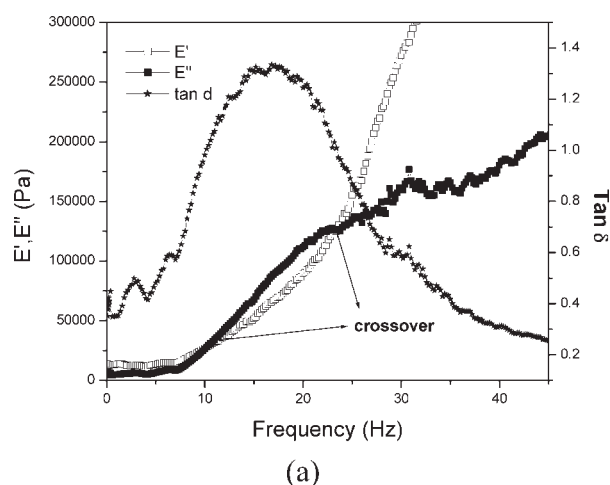
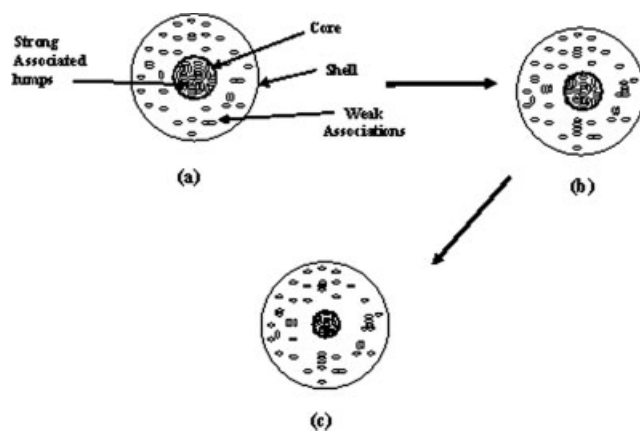


Figure 3 (a) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 25 $^{\circ}\text{C}$. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTAB. (b) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 50 $^{\circ}\text{C}$. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTAB. (c) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 75 $^{\circ}\text{C}$. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTAB.

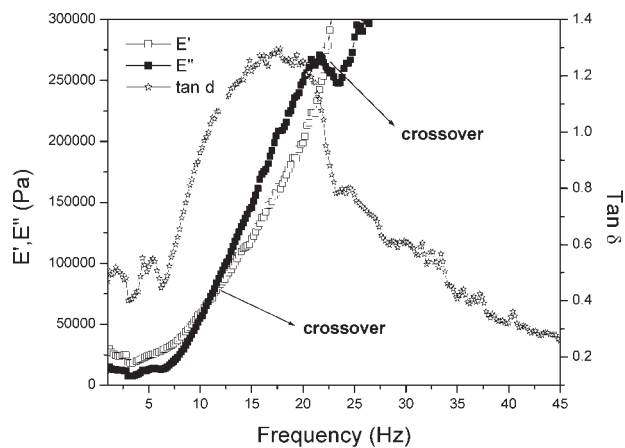


Scheme 1 Schematic representation of core-shell system of MC-DMF gel at different temperatures. (a) 25°C, (b) 50°C, and (c) 75°C.

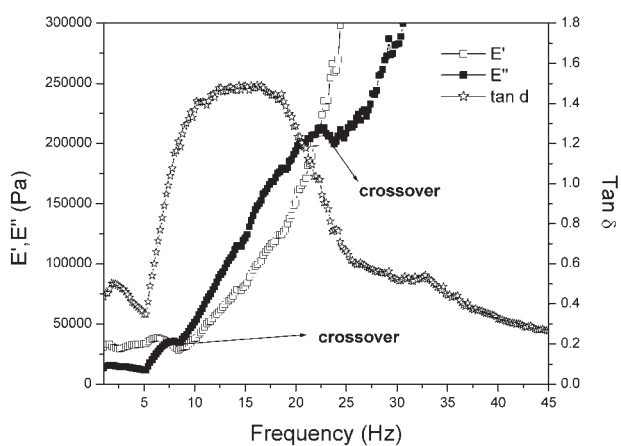
not mentioned in the literature. Whereas for MC-DMF gels (Fig. 3), a small increase in E' is initially observed, followed by a steep increase. In case of loss modulus, the increase is steep at around the first crossover between E' and E'' , followed by almost plateau behavior at around second crossover. In the frequency range between first and second crossover, the loss modulus is higher than the storage modulus, indicating liquid-like behavior. Probably, the double crossovers for aqueous as well as DMF MC-gels can be explained on the basis of the gel strength. The strength of the gel is assumed to be derived from two different types of structures of gels. This unusual rheological behavior of MC-DMF gels may be explained by the core-shell structure of gels as depicted in Scheme 1. The core (inner part) consists of highly associated DMF-MC gel, surrounded by the weakly associated MC-DMF shell. The gel strength of weakly associated shell is always less than that of highly associated core. For the aqueous system, this type of structure of gel consisting of the weakly associated molecules and the highly associated lumps of MC is already reported.¹⁴ At the first crossover, the loss modulus is equal to storage modulus, indicating the shell-sol transitions. The core part of the gel behaves like a spring, which absorbs more energy than shell part during dynamic compression testing. As a result, with an increase in frequency, the rebounding tendency of core increases due to insufficient relaxation. This causes an increase in storage modulus at a much higher rate than that of loss modulus, leading to second crossover. At the crossover points, the values of $\tan \delta$ are observed to be unity that symbolizes with the equality of elastic and viscous response of the MC-DMF system. It is interesting to note that crossover points come closer to each other with an increase in temperature [Fig. 3(a–c)]. Also, the closer the crossover points, the

sharper are the $\tan \delta$ peaks. With an increase in temperature, the first crossover frequency increases, whereas the second crossover frequency is found to be decreasing. However, no crossover is observed at higher temperature of 75°C [Fig. 3(c)]. The increase in first crossover frequency may be due to the intermixing of two different shell and core structures present in gels. On increasing the temperature, core part of DMF-MC gel starts to dissociate (diffuse) into the shell structure of gels. Thus, the size of the core part decreases with an increase in temperature [Scheme 1(a–c)]. Therefore, the gel strength of the shell in gel increases at the expenses of core structure. At higher temperature of 75°C, a peak in loss tangent is observed at a low frequency of 2.5 Hz, indicating low strength of MC gel. Probably, this peak is associated with the disintegration of core structure of DMF-MC gel. The peak value in $\tan \delta$ is 0.798. This transition is possibly due to a core-shell transition.

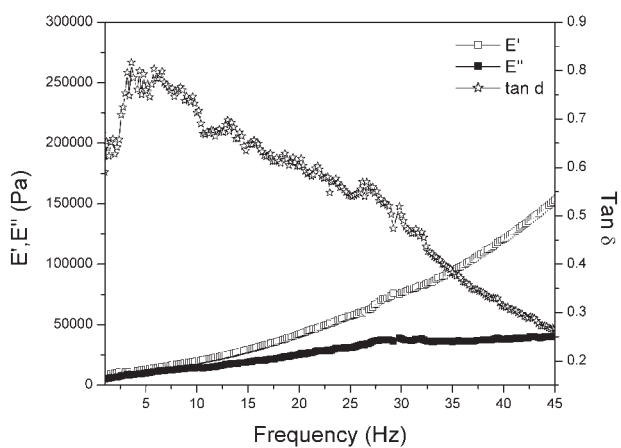
The rheological properties of MC-DMF gels in the presence of CTABMONT are reported in Figure 4. This figure shows the variation of E' , E'' , and $\tan \delta$ with angular frequency at different temperatures [Fig. 4(a–c) for 25, 50 and 75°C, respectively]. At lower temperatures (25 and 50°C), E' and E'' increases sharply with an increase in frequency. Whereas, at higher temperature of 75°C, the increase in E' and E'' is not so sharp (it is rather gradual). When compared with CTAB surfactant at 25°C [Fig. 3(a), Table I], it is observed that the first crossover point is shifted toward a higher frequency and modulus (10.2 Hz for CTAB and 11.0 Hz for CTABMONT), whereas the second crossover point shifts toward a lower frequency (23.4 Hz for CTAB and 22.0 Hz for CTABMONT). On the other hand, the storage modulus at the first crossover point is found to be low for CTAB (27.81 KPa) in comparison to CTABMONT (68 KPa). It may be explained on the basis of reinforcing effect of CTABMONT (nanofiller) into the DMF-MC gel. The surfactant (CTAB)-modified nanofiller can penetrate into the gel through pendent organic surfactant. Therefore, the first crossover point is shifted to higher frequency indicating the higher strength of the CTANMONT filled MC-DMF gel. On the other hand, the CTABMONT may reduce the elastic response of the core part of the gel. The nanofiller, which has high modulus, can induce the rigidity in the core part of DMF-MC gel. Thus, the inclusion of nanofiller in MC-DMF gel causes reduction in elastic response. Therefore, a decrease in second crossover frequency is observed. At 50°C, the crossover points between E' and E'' for CTAB and CTABMONT exhibit opposite trend in comparison to the properties at 25°C. In this case, the first crossover decreases (14.4 Hz for CTAB and 7.6 Hz for CTABMONT) and the second crossover



(a)



(b)



(c)

Figure 4 (a) Variation of storage modulus, loss modulus, and tan δ of gels as a function of angular frequency ω at 25°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTABMONT. (b) Variation of storage modulus, loss modulus, and tan δ of gels as a function of angular frequency ω at 50°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTABMONT. (c) Variation of storage modulus, loss modulus, and tan δ of gels as a function of angular frequency ω at 75°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% CTABMONT.

TABLE I
The Crossover Frequencies of Methylcellulose-DMF Gels

Temperature °C	CTAB		Nano-CTAB		HDAB		Nano-HDAB		Brij*	
	First crossover frequency (Hz)	Second crossover frequency (Hz)	First crossover frequency (Hz)	Second crossover frequency (Hz)	First crossover frequency (Hz)	Second crossover frequency (Hz)	First crossover frequency (Hz)	Second crossover frequency (Hz)	First crossover frequency (Hz)	Second crossover frequency (Hz)
25	10.2	23.4	11.0	22.0	10.4	22.2	13.2	21.0	9.2	23.0
50	14.4	21.8	7.6	22.4	12.0	22.4	Overlapped	Overlapped	—	—

TABLE II
The Peak $\tan \delta$ Values of Methylcellulose-DMF Gels

Temperature (°C)	Tan δ Peak Height (Ctab)	Tan δ Peak Height (Ctab-nano)	Tan δ Peak Height (Hdab)	Tan δ Peak Height (Hdab-nano)
25	1.334	1.29	1.27	1.15
50	1.122	1.49	1.21	1.01
75	0.799	0.81	0.92	1.00

increases (21.8 Hz for CTAB and 22.4 Hz for CTAB-MONT). On increasing the temperature from 25 to 50°C, the internal energy of the system increases, leading to an increase in entropy of the system. Therefore, the solubility of the filler increases in the core part of the microstructure of DMF-MC gel. Hence, the second crossover increases. Possibly, this soluble part has no compatibility to the small sized shell part of the gel. Therefore, it is predicted that the reduction in first crossover is only a temperature-induced phenomenon.

In Figures 3 and 4, it is observed that with an increase in frequency, $\tan \delta$ initially increases, reaches a maxima (peak), followed by a decrease. The peak $\tan \delta$ value for CTAB and CTABMNOT at different temperatures are reported in Table II. It is observed that the peak $\tan \delta$ value decreases with an increase in the temperature. It is interesting to note that the peak $\tan \delta$ for CTABMONT decreases at 25 and 75°C, whereas an increase is observed at 50°C. This anomalous behavior can be explained on the basis of compatibility of CTABMONT with MC-DMF gel at 50°C. Although at a higher temperature (75°C), the solubility of filler is much higher than that at 50°C, but the effect of temperature is so dominating that filler effect can be neglected.

The rheological properties of MC-DMF gels in the presence of hexadecylamine bromide (HDAB) surfactant are reported in Figure 5. This figure shows the variation of storage modulus (E'), loss modulus (E''), and $\tan \delta$ with angular frequency (ω) at different temperatures [Fig. 5(a-c) for 25, 50, and 75°C, respectively]. With an increase in frequency, loss tangent initially increases, reaches a maxima, followed by a decrease. At 25°C, the crossover between E' and E'' is observed at 10.4 Hz and 22.2 Hz. The storage and loss modulus follows the similar increasing trend with frequency as discussed earlier in the case of CTAB. On comparing the graphs of CTAB [Fig. 3(a)] with HDAB [Fig. 5(a)] at 25°C, it is observed that both crossover points shifts toward a higher frequency and modulus, but, the $\tan \delta$ peak is reduced for HDAB-modified DMF-MC gel. This may be due to the less bulky structure of HDAB. Although, the number of carbon atoms in HDAB is equal to that of CTAB, the bulkiness of nitrogen ion in trisubstituted

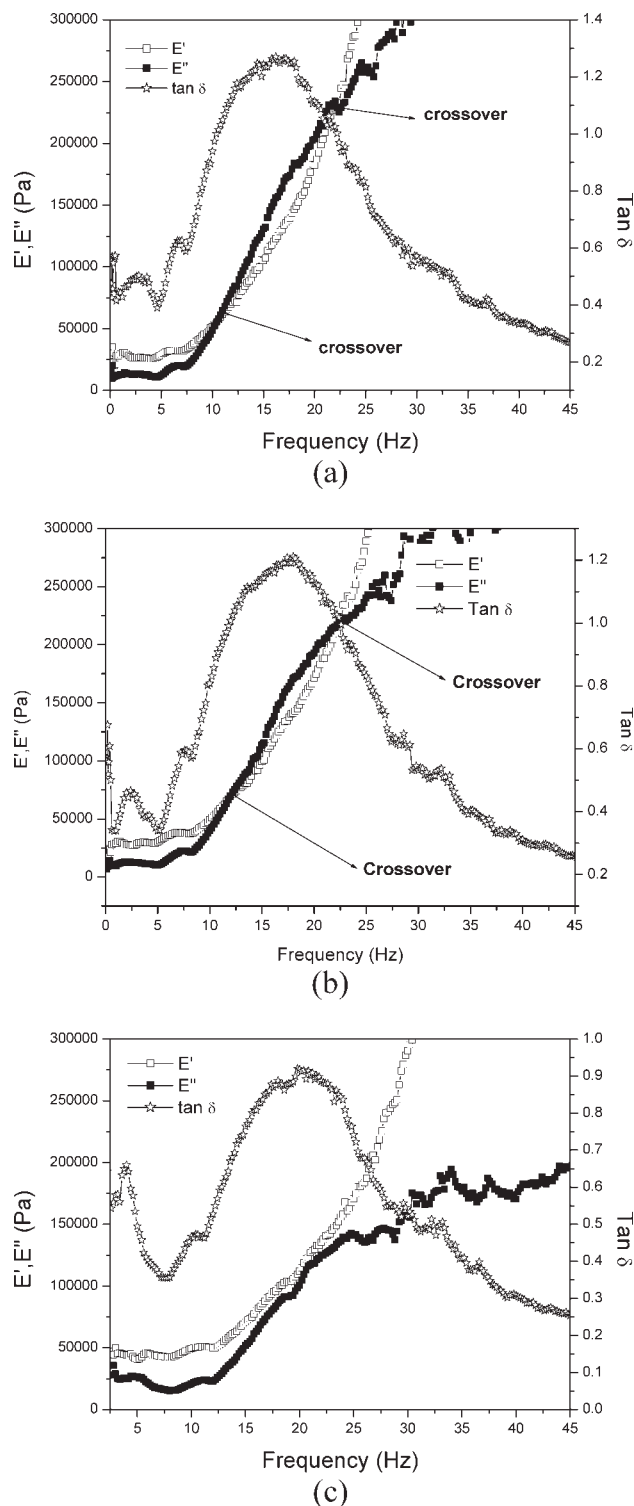
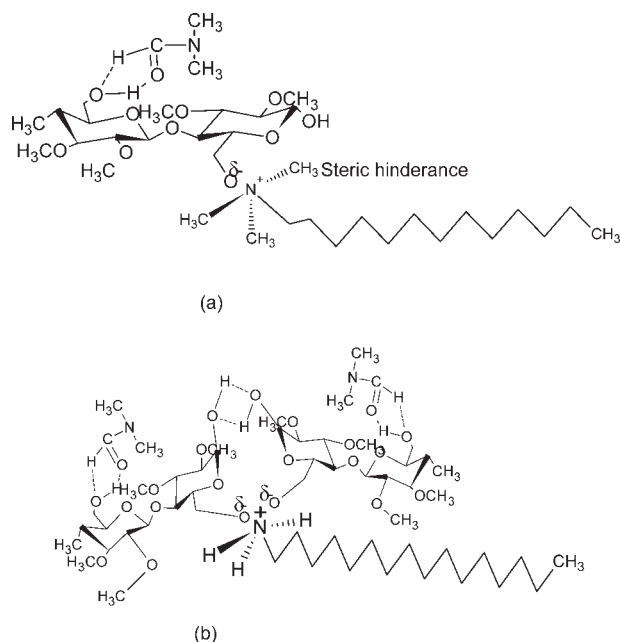


Figure 5 (a) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 25°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDAB. (b) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 50°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDAB. (c) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 75°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDAB.



Scheme 2 Schematic representation of possible interaction of MC-DMF gel with cationic surfactants. (a) The interaction of CTAB with MC-DMF gel, (b) The interaction of HDAB with MC-DMF gel.

CTAB makes it comparatively less compatible with DMF-MC gel. Therefore, the strength of HDAB-modified DMF-MC gel is greater than that of CTAB-modified DMF-MC gel. Whereas, at higher temperature (50°C), the first crossover frequency of CTAB-modified DMF-MC gel is higher than that of HDAB-modified DMF-MC gel. This unexpected variation in first crossover frequency is not explainable right now. On the other hand, for lower temperature (25°C), the second crossover frequency of CTAB-modified DMF-MC gel is greater than that of HDAB-modified DMF-MC gel. It is because of less bulky structure of HDAB, which is compatible with the core part of the gel [Scheme 2(a,b)]. Therefore, the rigidity in the core is enhanced, leading to reduction in elasticity. On further increasing the temperature to 75°C , apparently no crossover between E' and E'' is observed. In spite of this, the $\tan \delta$ exhibits a peak ($E' \approx E''$) at a higher frequency in comparison to CTAB-modified system at 75°C . The crossover modulus for HDAB-modified gels [Fig. 5(c)] is observed to be higher than that for CTAB-modified system [Fig. 3(c)]. This may be due to the high strength of the core microstructure of the gel. At higher temperature (75°C), it is assumed that the solubility of the HDAB in MC-DMF gel is higher than that of the tri-substituted CTAB. This will improve the shell strength at the expense of core microstructure. Thus, higher frequency is required to disrupt the core microstructure of HDAB-modified gels.

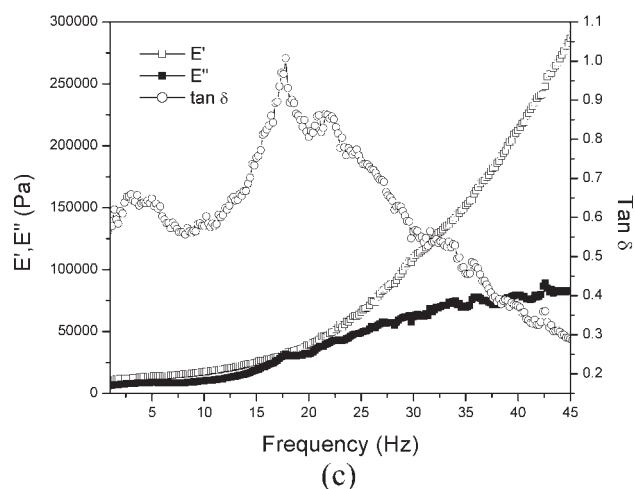
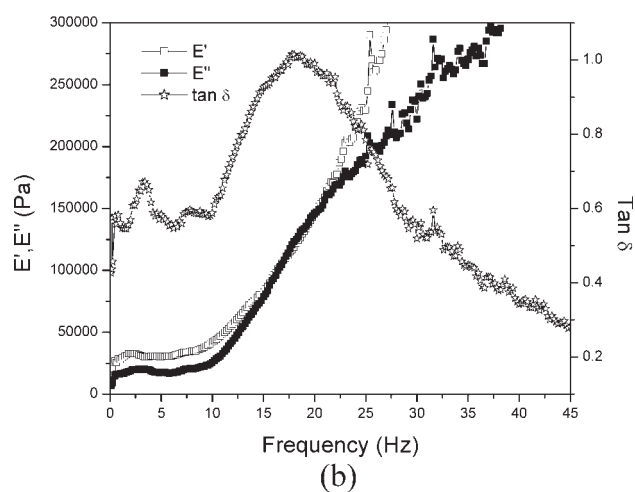
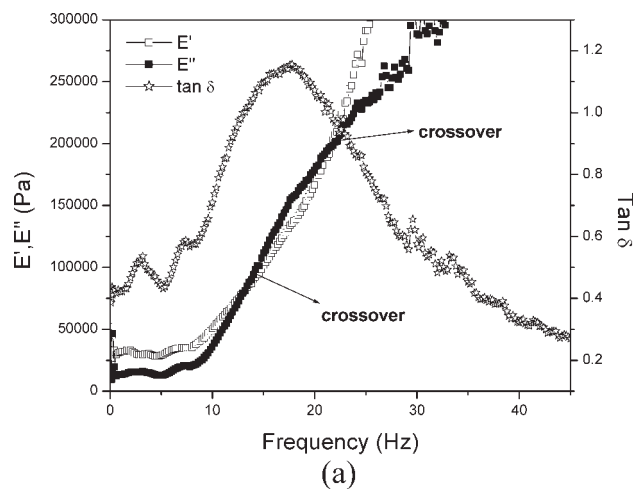
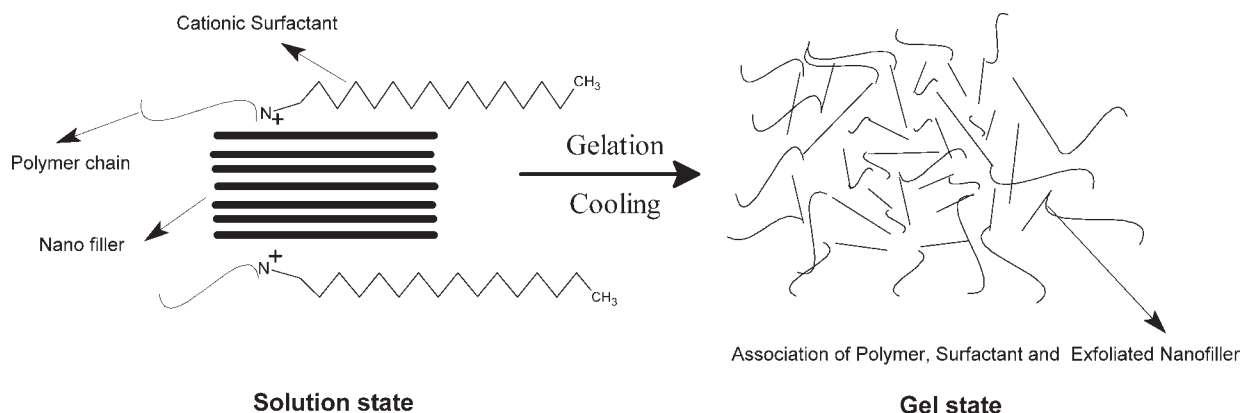


Figure 6 (a) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 25°C . The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDABMONT. (b) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 50°C . The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDABMONT. (c) Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 75°C . The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% HDABMONT.



Scheme 3 The possible mechanism of interactions of surfactant-modified nanofiller with MC-DMF gel.

The rheological properties of MC-DMF gels in the presence of HDABMONT are reported in Figure 6. This figure shows the variation of E' , E'' , and $\tan \delta$ with angular frequency at different temperatures [Fig. 6(a–c) for 25, 50, and 75°C, respectively]. When compared with HDAB surfactant at 25°C [Fig. 5(a), Table I], it is observed that the first crossover point between E' and E'' is shifted toward a higher frequency (10.4 Hz for HDAB and 13.2 Hz for HDABMONT), whereas the second crossover point shifts toward a lower frequency (22.2 Hz for HDAB and 21.0 Hz for HDABMONT). When the crossover modulus of HDAB is compared with HDABMONT, it is observed that the HDABMONT exhibits a high first crossover modulus (55.62 KPa for HDAB and 81.38 KPa for HDABMONT) and a low second crossover modulus (228.89 KPa for HDAB and 196.65 for HDABMONT). The surfactant (HDAB)-modified nanofiller can penetrate into the gel through pendent organic surfactant (Scheme 3). Thus, the reinforcing effect of HDABMONT (nanofiller) into the DMF-MC gel is dominating over the surfactant effect of HDAB, pendent on the nanofiller. Therefore, the first crossover point is shifted to higher frequency indicating the higher strength of the HDABMONT filled MC-DMF gel. The nanofiller (HDABMONT) can penetrate into the gel through the pendent surfactant, hence gel strength of shell and core increases. The HDABMONT is compatible with the micro associated part of gel (weak association or shell) and leads to an increase in the gel strength. On the other hand, the reduction in second crossover frequency with respect to HDAB-modified gels at 25°C may be explained on the basis of elastic response of the core part of the gel. The nanofiller (HDABMONT), which has high modulus, can induce the rigidity in the core part of DMF-MC gel. Thus, the inclusion of nanofiller in MC-DMF gel causes reduction in elastic response. Therefore, a decrease in second crossover frequency is observed.

At higher temperatures, the crossover points between E' and E'' are so close to each other that they are overlapped. On further increasing the temperature (75°C) no crossover between E' and E'' is observed. But, the $\tan \delta$ shows a peak indicating the shell-sol transition. In comparison the storage modulus of nano-CTAB MC-DMF gel is higher than that of CTAB MC-DMF gel. Whereas, the storage modulus of nano-HDAB MC-DMF gel is lower than that of HDAB MC-DMF gel.

The rheological properties of MC-DMF gels in the presence of a nonionic surfactant (polyethylene lauryl ether, Brij 78) are reported in Figure 7. This figure shows the variation of E' , E'' , and $\tan \delta$ with angular frequency at 25°C. Two crossover points between E' and E'' is observed at two different frequencies. The crossover frequencies at 9.8 Hz and 23.2 Hz for Brij are slightly less than that of unmodified MC¹⁴ (10 Hz and 23.4 Hz). At 25°C, the first

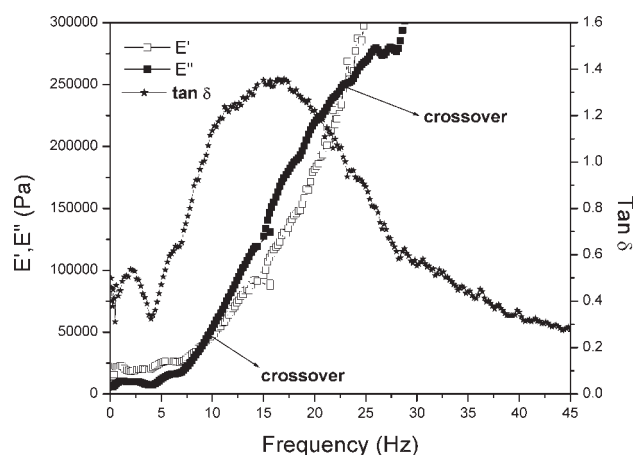


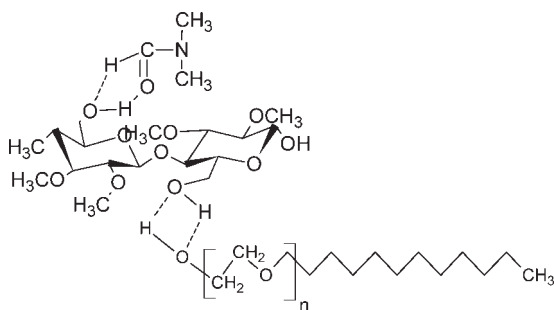
Figure 7 Variation of storage modulus, loss modulus, and $\tan \delta$ of gels as a function of angular frequency ω at 25°C. The gel obtained from 3 wt % methylcellulose in DMF in the presence of 0.5% polyoxyethylene lauryl ether (Brij 78).

crossover modulus of Brij-modified MC-DMF gel is found to be higher (41.41 KPa) than that of CTAB-modified MC-gel (27.81 KPa). On the other hand, the second crossover of Brij is higher (250.01 KPa) than that of CTAB-modified MC-DMF gel (76.38 KPa). Although Brij is nonionic ether, it may form H-bond with MC molecules through the ether linkages as shown in Scheme 4. The H-bonding between the Brij and MC molecules is stable even in the gel state. Therefore, the decrease in the crossover frequency is noticed, indicating the decrease in the gel strength.

Figure 8 shows the variation of storage modulus for different additives with temperature at three fixed sets of frequencies. The modulus data were chosen at three different temperatures of 25, 50, and 75°C. The three chosen frequencies are before the first crossover point, in between the two crossover points and after the second crossover point between E' and E'' . It is observed from the Figure 8 that the storage modulus decreases with an increase in temperature for all sets of frequencies and additives excluding CTAB. In case of CTAB-modified MC-DMF gel, the storage modulus first increases and then decreases. This type of behavior is unexplainable. The linear decrease in the storage modulus is noticed only in case of HDAB modified MC, indicating the independency on temperature. In the presence of surfactant-modified nanofillers (CTABMONT and HDABMONT), the storage modulus decreases with temperature and the decrease is comparatively sharp above 50°C.

CONCLUSIONS

The gel temperature observed during gelation of MC in DMF is found to be increasing due to the presence of a surfactant. From DMA studies, it is observed that the storage modulus increases with an increase in frequency. This is true for all of the additives. During the frequency scan, the loss modulus



Scheme 4 Schematic representation of possible hydrogen bonding between methylcellulose and polyoxethylene lauryl ether (Brij 78) in MC-DMF gel.

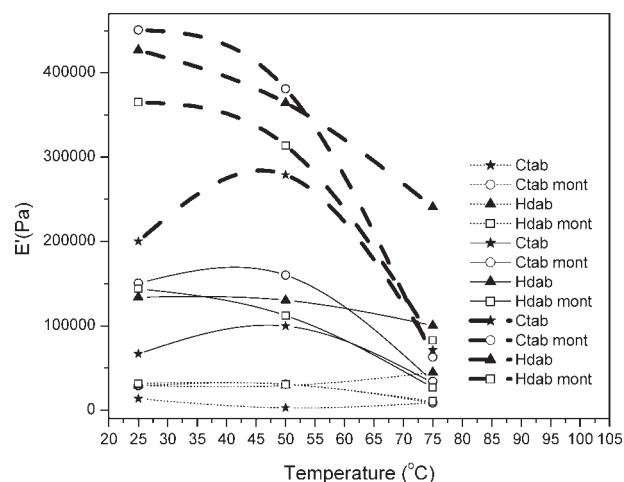


Figure 8 Variation of storage modulus (Pa) at different frequencies (1, 17, and 27 Hz) as a function of temperature (°C).

of MC-DMF gel crossovers the storage modulus at two different frequencies. The higher storage modulus in comparison to the loss modulus of the MC-DMF gels indicates the three dimensional gel networks. The addition of CTAB- and HDAB-modified nanofiller induces an increase in the gel strength. The storage modulus of MC-DMF gel in the presence of CTABMONT is found to be higher than that of CTAB-modified MC-DMF gel. Whereas, the storage modulus of MC-DMF gel in the presence of HDABMONT is lower than that of HDAB-modified MC-DMF gel. On the other hand, the addition of non-ionic surfactant (Brij78) decreases the gel strength.

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