Evaluation of Thermal Gelation behavior of different Cellulose Ether Polymers by Rheology

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Abstract

Hydroxypropylmethylcellulose (HPMC) and Methylcellulose (MC) are cellulose ethers which can be dispersed in water and used as thickeners, emulsifiers, binders, film formers, and water-retention agents due to their hydrophilic and hydrophobic characteristics. In this study, various types of HPMCs, in comparison with two types of MCs were examined. The formed gels of the different cellulose ethers showed specific and various structural formation and network properties. The degree of methylation (Meth.) and hydroxypropylation (HyPr.) affected drastically the heat-induced gelation of the examined cellulose ethers.

Keywords: HPMC, MC, structure development and network parameters

INTRODUCTION

Methyl- and hydroxypropylmethyl- derivatives of cellulose have the specific property of forming gels on heating and melting during cooling. There is an extensive literature on gelation of HPMCs and MCs [1-8]. In this study, the gelation properties of HPMCs and MCs with various molecular weights were investigated by rheological steady and oscillatory measurements. structure development rate over the temperature and new parameters of elastifying and liquefying rate were calculated. Moreover, network characteristics of HPMCs and MCs based on the plateue storage modulus and density were determined.

EXPERIMENTAL

Material and sample preparation

The specifications of Food grade MC (E461) including Methocel A4M and A40M, and five types of Food grade HPMCs (E464) including Methocel E19, F4M, K4M and K250M, and one type of Non-food grade HPMC, Methocel J75MS, which were kindly provided by Dow Chemical Company (USA), are presented in Table 1. The samples were prepared by dissolution of HPMC and MC powders in tap water (2% w/w) under stirring at 20°C and then kept for 24h to ensure complete hydration at 6°C.

Table1- Specifications of HPMCs and MCs defined by Company, viscosity (cp) at 2% and 20°C

Type	Viscosity	Meth. in %	HyPr. in %
A4M	4,000	30	-
A40M	40,000	30	-
E19	24	29	8.5
F4M	4,000	28	5.0
K4M	4,000	22	8.1
J75MS*	75,000	18	27
K250M	250,000	22	8.1

Non-food grade

Rheological Measurements

Steady shear and oscillatory measurements were performed on a controlled shear rate rheometer (Physica MCR 301 Anton Paar, Germany) using a concentric measuring cylinder (CC-27/P1). Flow measurements were done at 20° C and shear rate range of 0.1-100/s, 100/s, 100-0.1/s; a satisfactory fitting of the flow behavior data was provided with the Power-law model, as shown below, which fitted to the downward curves in the shear rate range of 5-100/s.

$$\tau = K\dot{\gamma}^n \qquad \text{Pa} \qquad \text{Eq.1}$$

where τ, shear stress (Pa), K, consistency coefficient $Pa.s^n$ and $\dot{\gamma}$ shear rate (s^{-1}) and n flow index. Temperature sweep tests in three intervals (heating run: 20-80°C, holding run: 80°C, 15 min and cooling run: 80-20°C linearly with ($\Delta T/\Delta t$:1K/min) at $\gamma = 0.001$ and f =1Hz) and frequency sweep tests at $\gamma = 0.001$ and f = 0.01-50Hz were carried out. The data reported in the tables are the means of two replications.

Structure formation evaluation

Based on the storage modulus, G', obtained by temperature sweep, the time derivative, the Structure Development Rate, defined as (dG'/dt) was calculated according to Eq.1. Furthermore, the time derivative of loss factor, $\tan\delta$, the rate of elastifying or gelation and rate of liquefying or melting ($d\tan\delta/dt$) were calculated according to Eq.2.

$$\frac{dG'}{dt} = \frac{(G'_i - G'_{i-1})}{(t_i - t_{i-1})} \qquad \text{Pa.min}^{-1} \qquad \text{Eq.1}$$

$$\frac{d(\tan\delta)}{dt} = \frac{(\tan\delta_i - \tan\delta_{i-1})}{(t_i - t_{i-1})} \qquad \text{min}^{-1} \qquad \text{Eq.2}$$

Network Parameters

The density of each sample at 80°C was estimated according to Choi and Okos equations in kg/m^3 [9]. Together with the plateau value of the storage modulus G'_p, the molecular weight between crosslinks, M_c [10], number density of crosslinks, ν [10, 11], the distance between sequential crosslinking points[11], ξ, degree of crosslinking, X_c [12] can be calculated accroding to the following equations:

$$M_c = \frac{\rho\, RT}{G'_p} \qquad \text{kg.mol}^{-1} \qquad \text{Eq.3}$$

$$\nu = \frac{G'_p\, N_A}{RT} \qquad \text{m}^{-3} \qquad \text{Eq.4}$$

$$\xi = \left(\sqrt[3]{\nu}\right)^{-1} \qquad \text{cm}^{-3} \qquad \text{Eq.5}$$

$$X_c = \frac{M}{M_c} \approx \frac{1}{M_c} \qquad - \qquad \text{Eq.6}$$

where ρ density (kg/mole), R gas constant(J/molK), T temperature (Kelvin), G'_p plateue storage modulus, and N_A, Avogadro number (atoms/mole), M_c, molecular weight g/mol.

RESULTS AND DISCUSSION

Flow measurements

Table 2 shows that K250M has the highest consistency, viscosity, hysteresis area and the lowest flow index which is more likely due to its high molecular weight and higher degree of polymerization. Sarkar reported that there is a linear relationship between the logarithm of viscosity and the logarithm of molecular weight for MCs and HPMCs[3]; accordingly, it seems that the order of the molecular weight for the samples could be : K250M > J75MS > A40M > K4M=F4M=A4M>E19

K250M at 20°C showed highest consistency which might be indicative of its highest molecular weight among the examined samples. E19 indicated lowest consisteny, viscosity, hysteresis area and the highest flow index. We could not find any direct or indirect correlation between the degree of methoxylation or hydroxypropylation with the measured value of viscosity. For this reason, it seems to us that the viscosity and flow behavior of the MCs and HPMCs at room temperature might be closely related to the molecular weight rather than the degree and type of substitution.

Frequency sweep

The frequency sweep spectra of the samples at 80°C indicated that MCs solutions formed true and strong gels but HPMCs formed a gel with very weak gel strength. The frequency dependency of the samples was examined by fitting power-law equation for the elastic modulus as shown below:

$$G'(f) = af^b \qquad \text{Pa} \qquad \text{Eq.7}$$

Table 2- Power law model parameters and calculated effective viscosity at shear rate of 50/s for HPMCs and MCs at 20°C

| Samples | K | n | r | s | η_{eff} | A_{hys} |
	Pa.s^n	-	-	Pa	Pa.s	Pa.s^{-1}
K250M	127.3	0.25	0.997	4.6	6.77	1476
J75MS	80.06	0.31	0.996	4.9	5.38	582
K4M	5.950	0.64	0.997	1.2	1.46	28
F4M	4.340	0.71	0.997	2.2	1.40	-114
E19	0.020	0.99	1.000	0.0	0.02	→0
A40M	53.32	0.40	0.996	5.8	5.10	396
A4M	7.670	0.67	0.996	3.2	2.11	47

Obtained parameters including *a*, gel strength, *b*, frequency dependency of G', and r, correlation coefficient are shown in Table 3. Here, the coefficient *a* represents the magnitude of G' at frequency of 1 Hz. *b* value near zero means that G' does not change with frequency; and low *b* values are characteristic for elastic gels. It is also known that for a covalent gel b=0, whereas a physical gel shows b>0 [13]. According to Table 3, the coefficient *b* was zero for A4M which indicated that it was the most stable gel and according to *a* coefficient it was a really strong gel. A40M formed a really strong gel but the gel thermal stability of A40M with b= -0.08 was not as high as A4M with b=0. For HPMCs, the gel strength was considerably low compared to MCs. At 80°C, the very high molecular weight K250M exhibited very lower gel strength compared to low molecular weight A4M and A40M. For this reason, it seems to us that the gel strength of MCs and HPMCs at 80°C might be closely related to the degree and type of substitution rather than the molecular weight. MCs formed gel but HPMCs formed weak gel-like system. It has been reported that during heating presence of large and more polar groups of hydroxypropyl in the backbone of HPMCs inhibits formation of hydrophobic interactions in part[14].

F4M and E19 which are of about 29% methoxyl indicated the lowest frequency dependence among HPMCs. The structural strength of the gels formed by HPMCs was even weaker than that of the sol state.

Network properties

Table 4 lists the network properties of the MCs and HPMCs. The true density of the samples (2%) was estimated to be 980.99 kg.m^{-3}.The molecular weight between crosslinks (M_c) was determined using the equilibrium swelling theory of Flory and Rehner (Eq.3). Netpoint number density, ν, of MCs were significantly higher than that of HPMCs and the average linear distance between two adjacent crosslinks (ξ) for MCs, which characterizes the network and the effective space available for solute diffusion, was much lower than that of HPMCs' network. Degree of crosslinking, X_c, for MCs was

much higher than that of HPMCs. It appears that the higher the methoxy content, the greater the degree of crosslinking and the network number density are. The calculated network parameters were in consistent with the results of frequency sweep. MCs with higher degree of crosslinkings, 70-1500 times higher than that of HPMCs and shorter distance between the crosslinks formed stronger gels.

Temperature sweep

Mechanical spectra of K250M and A4M at three intervals are shown in Fig.1. Accordingly, both G' and G'' for K250M and A4M with increasing the temperature decreases, with reaching a certain temperature in case of A4M, a sudden sharp increase in both moduli particularly G' is observed, but in case of K250M, a sudden sharp decrease in both moduli particularly G'' was observed; this was the same for all HPMCs. Table 5 presents the Incipient Gelation Temperature, IGT, Gelation Temperature, GT, and Incipient Melting Temperature, IMT, and Melting Temperature, MT for all samples according to tanδ curve; tanδ curve was used because for HPMCs, determination of IGT based on G' and G'' is confusing as can be seen in Fig. 1 for K250M determination of IGT can be done based on the initial sharp decrease of G'' and also initial increase of G'.

Since tanδ curve seems to be more straightforward than G' and G'' curves, determination of the IGT, GT, IMT and MT was done according to tanδ curves. Table 5 shows that IGT and GT for MCs with the highest degree of Meth. (30%) are much lower than those of HPMCs. Although E19 and F4M are of about 30% methoxyl, probably due to the presence of the hydroxypropyl in their structure they showed higher IGT. K250M had the highest IGT, GT and IMT which might be due to its high molecular weight and relatively lower degree of Meth. GT for all HPMCs, regardless to the degree of Meth. and HyPr. was 80°C. According to literature [2, 8, 14], HPMC consists of bundles of cellulosic strands (chain). With increasing the temperature, the bundles become less rigid; with more temperature increase at the end of the bundles, the strands are separated and more methyl groups are subjected to water.

Figure 1 – Temperature dependence of G', G' and tanδ ⬜for K250M and A4M

Consequently, the hydrophobic methyl groups strive to reduce their contact with water and aggregate. According to Bodvic et.al, the HPMC chains are more heterogeneous than the MC chains due to presence of hydroxypropyl groups. At IGT the methyl groups escape contact with water, while the hydroxypropyl groups do not. At low temperature the hydroxypropyl groups dominate and the free energy change due to aggregation is positive, whereas at higher temperatures the methyl groups dominate and the aggregation process becomes favorable[8].

Comparison of the tanδ values (Table 6) at the beginning of the heating run with those of the end of the cooling run indicated that HPMCs at the end of the process reverted completely to their original state but

Table 3- Frequency dependence of storage modulus according to $G'(f) = af^b$ at 80°C, $0.1 \leq f \leq 10$ Hz.

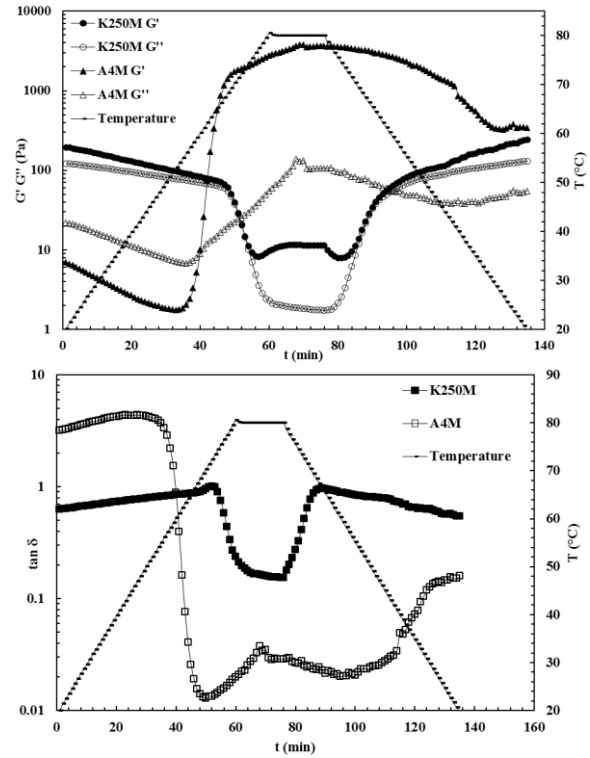| Samples	a $(Pa.s^b)$	b -	r -	behavior
K250M	23.7	0.11	0.999	Gel-like
K4M	3.7	0.24	0.999	Gel-like
F4M	18.11	0.02	0.975	Gel-like
J75MS	4.35	0.07	0.986	Gel-like
E19	1.04	0.06	0.832	Gel-like
A40M	1888	-0.08	0.995	Gel
A4M	1768	0.00	0.175	True gel

Table 4- Network Parameters of the samples at 80 °C

Sample	M_c kg/mol	ν m^{-3}	ξ cm	X_c mol/kg
K250M	120515	4.9E+21	5.9E-06	8.3E-06
K4M	770135	7.7E+20	1.1E-05	1.3E-06
F4M	158085	3.7E+21	6.4E-06	6.3E-06
J75MS	663664	8.9E+20	1.0E-05	1.5E-06
E19	2691872	2.2E+20	1.7E-05	3.7E-07
A40M	1524	3.9E+23	1.4E-06	65E-05
A4M	1627	3.6E+23	1.4E-06	61E-05

MCs did not reach their original state which is not in agreement with other studies which had all indicated that MCs revert totally to the original state during cooling [4, 8]. The gel-sol transition for MC seems to be dependent on thermal history of the gelling process. In our study, probably fifteen minutes holding time at 80°C made some irreversible changes in the structure of MCs; such irreversible changes on holding run, in the structure of HPMCs did not occur. Apparently, Hydroxypropyl groups contribute against such irreversible changes. tanδ values at GT for MCs are drastically lower than those of HPMCs.

Structure formation evaluation

In order to have a profound insight into the structural changes, dG'/dt was calculated. Diagrams of dG'/dt vs. T for two samples has been presented in Fig. 2. Many fluctuations are observed in Fig. 2 which makes it difficult to estimate the accurate initial gelation temperature and gelation point. For MCs and HPMCs, many fluctuations on the diagrams of dG'/dt vs. T were observed, although this method has been previously used well for studying pectin gelation[15, 16]. Since in the evaluation of the structural development rate only G' values or rigidity was considered, it was not possible to estimate exactly the gelation temperature, the temperature at which the gelation or solidifying rate is maximum as well as the temperature at which the melting or liquefying rate is the highest.

For this reason, we decided to determine the rate of the changes based on tanδ values the, *dtanδ/dt,* according to Eq.2. In Fig. 3and 4, the *d(tanδ)/dt vs. T* are plotted for all of the samples. Compared to *dG'/dt vs. T,* the plots of the *dtanδ/dt vs. T* provided us with sharper and clearer peaks. Accordingly, new parameters of Temperature of Initial elastifying or Gelation, T_{IG}, Temperature of maximal gelation rate, $T_{MGR,}$ and Temperature of Maximal Melting or Liquefying rate T_{MMR} were clearly elucidated and summarized in Table 7. The negative values of (*dtanδ/dt)* is indicative of solidifying or elastifying or in this case gelation and positive values of that can be indicative of liquefying or melting.

Table 5- Incipient Gelation Temperature (IGT), Gelation Temperature (GT), Incipient Melting Temperature (IMT) and Melting Temperature (MT) in °C based on tanδ curves.

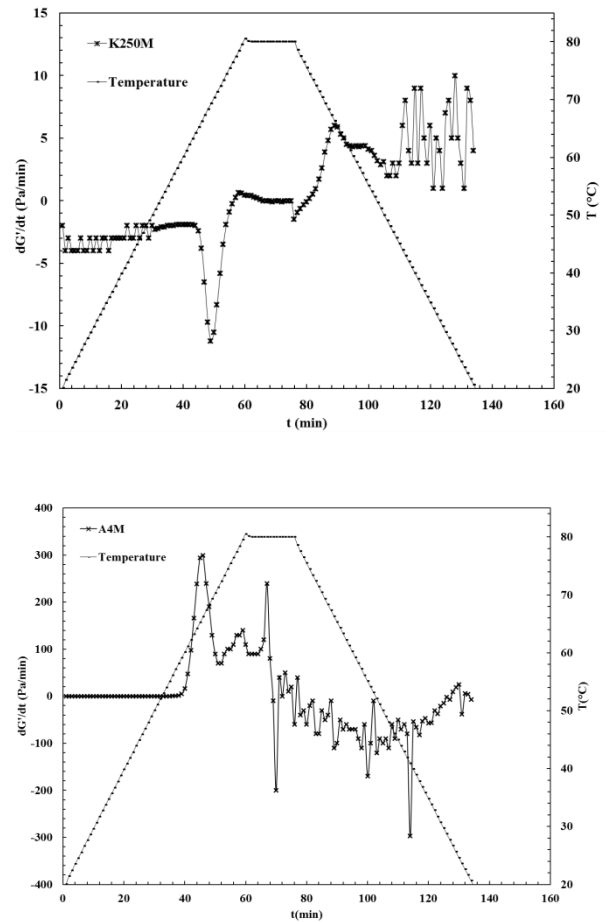| Sample	IGT	GT	IMT	MT
K250M	74.4	80.0	78.6	66
K4M	67.3	80.0	72	44
F4M	62.1	80.0	53	31
J75MS	63.2	80.0	71	57
E19	70.3	80.0	51	50
A40M	51.0	73.4	38	29
A4M	56.0	70.3	35	-

Figure 2 – Structure development rate of the K250M and A4M as a function of temperature

The T_{MGR} and T_{MMR} are shown in Fig.3 and 4 with arrows.

Table 7 shows that T_{IG} for HPMCs was much higher than that of MCs. A4M compared to A40M started to gelation at lower temperature (48 vs. 50°C). A4M and A40M both have 30% methoxy groups. The molecular weight of the A40M is higher than that of A4M. According to frequency sweep tests, we found out that A4M forms a more stable and rigid gel compared to A40M. There could be probably an omtimized or more appropriate degree of Meth. for each MC with its

Table 6- tanδ values at the start, gelation and end point

Sample	tanδ		
	20°C Start	GT	20°C End
K250M	0.63	0.150	0.54
K4M	2.40	0.320	2.48
F4M	3.70	0.084	4.04
J75MS	0.88	0.090	0.88
E19	→∞	0.170	→∞
A40M	1.18	0.015	0.23
A4M	3.18	0.013	0.16

specific molecular weight. 30% Meth. seems not to be the appropriate degree of Meth. for A40M in terms of forming true gel.

Comparison of the Table 5 and 7 indicates that the values of T_{IG} for all of the samples except A4M are close to the values of IGT estimated by original tanδ curve.

As can be seen in Table 5, the GT for all HPMCs was about 80°C. With first deviation of the tanδ, Temperature of maximal gelation rate, $T_{MGR,}$ was obtained. If we may consider this point as the gelation point, we observe that the gelation temperature of HPMC varies with its grades which have different degree of polymerization different degree and type of substitution (compare Table 5 and Table 7). T_{MGR} for HPMCs was in the range of 63-75 °C, depended on the grade. These values appeared to us more logically than the obtained GT by original tanδ curves.

For MCs, T_{MGR} values was much higher than GT. However, it seems that T_{MGR} values are more reliable because it corresponds to the crossover point of original G' and G" curves. The crossover point of original G' and G" curves for MCs was clear and distinctive but it was not so clear for all HPMCs. According to original tanδ curve, Initial Melting Temperature, IMT for HPMCs and MCs was estimated based on the re-increase of tanδ which was relatively close to the T_{IMR} values.

The temperature at which $d(tan\delta)/dt$ became greater than zero at cooling run was assumed to be the T_{IM}. Estimation of T_{IM} was easier than that of IMT. As can be seen in Fig. 3 and 4, one can simply read the T_{IM} with a quick look; however estimation of IMT based on the original tanδ curve was not so easy, because there was a range of temperature which could be considered as IMT.

T_{MMR} was also estimated which might be considered as a melting temperature. T_{MMR} for MCs and HPMCs can be easily obtained (Fig. 3 and 4). T_{MMR} for A4M was not observed. It seems that the true gel of A4M begins to melt at 35 °C however a real melting does not occurred. A4M showed much more stability against cooling compared to A40M and HPMCs. HPMCs with reaching T_{MMR} revert to the initial sol state.

Table7- Critical temperatures of the diagrams of ($dtan\delta/dt$) vs. T for all samples in °C

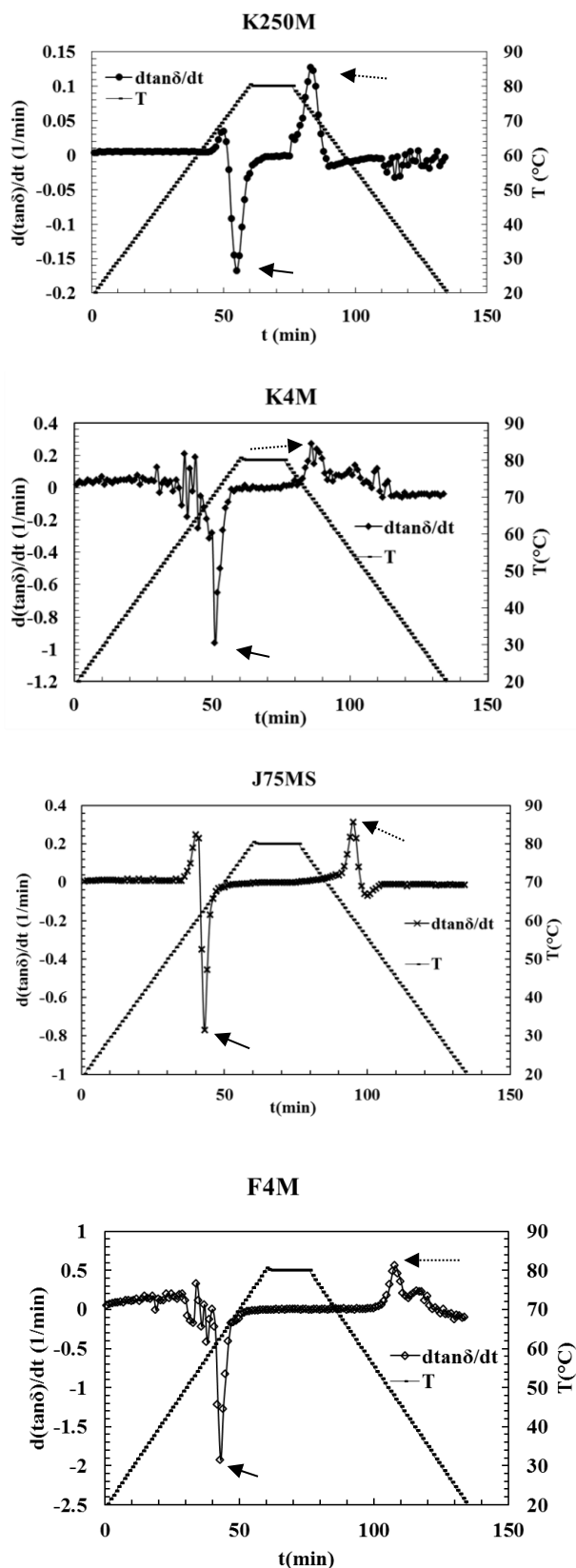| Sample	T_{IG}	T_{MGR}	T_{IM}	T_{MMR}
K250M	71	75	78.6	72
K4M	66	71	75.5	69
F4M	61	63	52.0	47
J75MS	62	63	66.3	60
E19	-	70	-	-
A40M	50	56	40.0	38
A4M	48	57	-	-

Figure 3. Diagramms of $d(tan\delta/dt$ vs. T for HPMCs. The T_{MGR} and T_{MMR} are shown with full and dotted arrows repectively
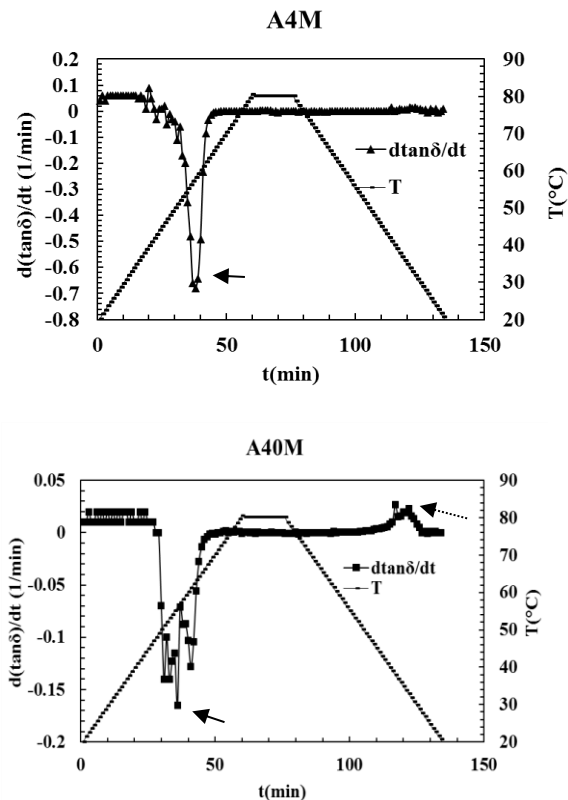
A4M

A40M

Figure 4. Diagramms of $d(tan\delta/dt$ vs. T for MCs. The T_{MGR} and T_{MMR} are shown with full and dotted arrows repectively.

CONCLUSION

i-The shear measurements at 20°C showed that K250M had the highest consistency coefficient and lowest flow index among all samples which might be indicative of its highest molecular weight.

ii- the temperature sweep measurements indicated sol to gel like transition for HPMC and sol to gel transitionduring heating and gel-like to sol transition for HPMCs during cooling process. upon cooling, true gels of MCs did revert to sol state. MCs compared to HPMCs started to gelation at lower temperatures which might be attributed to their higher degree of methoxylation. During the cooling run HPMCs reverted totally to their original state but MCs did not. Probably 15min holding time at 80°C led to irreversible changes in the structure of MCs.

iii- frequency sweep spectra indicated that the gel strength and gel stability of the MCs were greater than those of HPMCs. The structural strength of their formed gels at 80°C were even lower than their structural strength at 20°C. MCs formed true and firm gels but HPMCs formed very weak and soft gels which can be due to higher hydrophobicity of MCs in comparison with HPMCs. The degree of cross linking of MCs was about 70-1500 times higher than that of HPMCs, depended on the type of HPMCs. The

network number densities of MCs were about 70-500times higher than that of HPMCs, depended on the type of HPMCs.

iv- based on the G' values obtained by temperature sweep, the first time derivative, (*dG'/dt*), were calculated. Although this method had been previously used well for studying pectin gelation, the diagrams of (*dG'/dt*)-T did not indicated clearly the mentioned critical temperatures for MCs and HPMCs. Seemingly, the problem was ignoring the role of G" modulus in structural changes analysis of MCs and HPMCs. Alternatively, for the first time in this study (to the best of our knowledge), the values of (*d(tanδ)/dt)* were determined. Diagram of *d(tanδ)/dt* vs. T provided us with clearer and sharper peaks that helped us to estimate the critical transion temperature more accuarately and easier. Despite the fact that this method is in part assumptions, yet, and have to be confirmed by further studies, it could be considered complementary to other methods that are used for monitoring structural changes of HPMCs and MCs during gelation and melting process.

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