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High temperature/pressure rheology of carboxymethyl cellulose (CMC)

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Rheological properties of 0·5–2·0% carboxymethyl cellulose (CMC) solutions were evaluated using a computer controlled rotational viscometer under a dynamic upward and downward linear-ramp shearing sequence. Experiments were performed in the temperature range 60–140°C using a high temperature/high pressure sensor system. Rheological parameters were evaluated using different models (power law, Herschel–Bulkley, Casson and linear), while the temperature and time dependency of these parameters were evaluated using Turian and Weltmann models, respectively. All rheological properties were significantly ($p < 0{\cdot}01$) influenced by both temperature and concentration.

Keywords: Carboxymethyl cellulose, rheology, high temperature, carrier fluid, aseptic processing.

NOMENCLATURE

A_w	Weltmann initial stress (Pas)
B_w	Weltmann coefficient of structural breakdown (dimensionless)
C	Concentration (% w/w)
D	Tube diameter (m)
m	Consistency coefficient (Pas^n)
n	Flow behaviour index (dimensionless)
T	Temperature (°C)
u_f	Average fluid velocity (ms^{-1})
η_{ap}	Apparent viscosity (Pas)

INTRODUCTION

Designing of food processing operations (mixing, pumping, heating, cooling) requires accurate data on rheological properties. Flow characteristics of a pumpable food product are dependent on the fluid rheology and density. Calculation of thermal treatment times for aseptic processing of liquid foods containing particulates requires data on the residence time distribution (RTD) of particulates and carrier fluid which are influenced by concentration and type of the carrier fluid, size, shape and density of particles and interactions between particles and fluid as well as other process parameters (time, temperature, pressure, and the system configuration). Data on rheological characteristics, relative velocity between fluid and particles, and fluid to particle heat transfer coefficients are needed for optimizing the heat exchanger and holding tube designs in aseptic processing of liquid foods containing particulates (Dail & Steffe, 1990*a,b*).

Carboxymethyl cellulose (CMC) has been widely used as a pseudoplastic carrier fluid for low acid particulate foods in aseptic processing simulations (McCoy *et al.*, 1987; Alhamdan & Sastry, 1990; Dutta & Sastry, 1990*a,b*; Lee & Singh, 1991; Awuah *et al.*, 1993), but there are little data on its rheological properties and most experimental data on RTD using CMC as carrier fluid have been reported at temperatures below 100°C (Castell-Perez & Steffe, 1990; Abdelrahim *et al.*, 1994). By carrying out experiments at 30°C before and after processing, Rao *et al.* (1981) were able to show that thermal processing has detrimental effects on the structure of CMC.

In aseptic processing operations, the carrier fluid will be subjected to different shear rates in different sections, e.g. low shear rates *m* straight holding tube and high shear rates while passing through pumps and scraped surface heat exchangers. The apparent viscosity in continuous flow situations for most engineering applications

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is generally computed using Equation (1) as described by McCabe *et al.* (1985):

$$\eta_{ap} = [2^{(n-3)}\, m\, \{(3n-1)/4n\}^{n}] / [u_f^{(1-n)} D^{(n-1)}]. \quad (1)$$

The objective of this work was to study the rheology of aqueous CMC as influenced by concentration (0·5–2·0%) in the temperature range 60–140°C; as well as its shear-thinning time-dependent behaviour (thixotropy) at the aseptic processing conditions.

MATERIALS AND METHODS

Four completely dissolved concentrations (0·5, 1·0, 1·5 and 2·0% w/w) of commercial high viscosity CMC sodium salt (0·65–0·85 degree of substitution and 2 × 10^5 molecular weight; Sigma Chemical Co., St. Louis, MO) were prepared by hydrating in distilled water for overnight followed by vigorous hand mixing and standing for 24 h to release air bubbles. Test samples were then gently and carefully mixed before measurements to avoid air entrapment.

Rheological measurements (shear rate–shear stress data) were made using a rotational viscometer (Haake Model RV20; Haake Mess-Technik, Karlsruhe, Germany), equipped with an M-5 OSC measuring head and a D 100/300 sensor system assembly interfaced to a microcomputer for control and data acquisition. The D100/300 rotor assembly sensor system is capable of operation under high temperature/high pressure conditions of aseptic processing as described by Abdelrahim *et al.* (1995).

Experimental procedure

Test samples of CMC (0·5–2·0% w/w) were filled into the sample cup and loaded on to the jacketed chamber through a cylindrical spindle. The sample was allowed to rest in the test chamber for 20 min to equilibrate to the desired temperature preset in the circulating bath. Test samples were treated in a similar way to starch solutions as described by Abdelrahim *et al.* (1995). Temperature effects at the different concentrations were evaluated in the range 60–140°C (20°C increments) with three replicates. The flow curves (rheograms) were evaluated using the power law, Herschel–Bulkley, Casson and Bingham linear models (Abdelrahim *et al.*, 1994).

Effect of temperature

Turian (1964) approach was employed to evaluate the temperature sensitivity of the rheological parameters, m and n. A combined model for CMC solution was developed for $\log_{10}(m)$ and n with temperature and concentration using multiple regression analyses based on the Turian approach.

Thixotropic behaviour of CMC was evaluated using a modified Weltmann (1943) logarithmic model as detailed by Ramaswamy and Basak (1991).

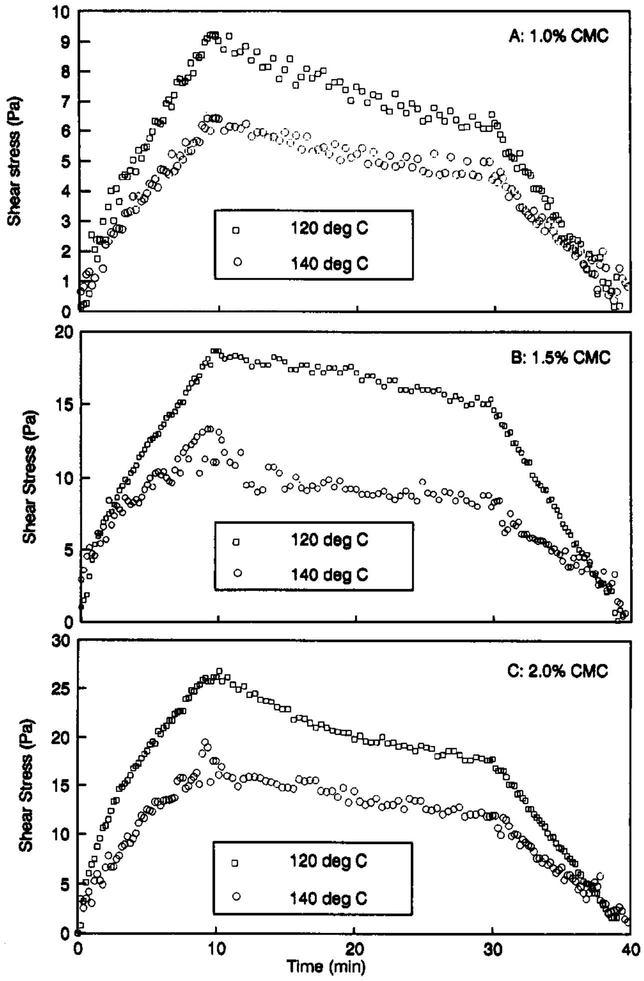

Fig. 1. Shear stress–shear rate curves for CMC solutions during a programmed 40 min run under dynamic and constant shearing (A: 1·0%, B: 1·5%, C 2·0% w/w) using the D100/300 sensor system.

RESULTS AND DISCUSSION

Characterization of the flow curves

Typical flow curves for the different concentrations of CMC (1·0, 1·5 and 2·0% w/w) at high temperatures (120 and 140°C) are presented in Figure 1 (A, B, C). Higher concentrations of CMC were associated with higher viscosities as indicated by the higher shear stress values at a given shear rate (at 500 s^{-1} the shear stress was ~9, 19 and 29 Pa for 1·0, 1·5 and 2·0% w/w CMC concentrations at 120°C; respectively), while increasing the temperature from 120 to 140°C decreased the shear stresses (lower viscosities). Structural breakdown was observed with CMC solutions under all temperatures, as they were sheared at a constant rate of 500 s^{-1} for 20

Table 1. The power law model parameters of CMC solutions as influenced by concentration and temperature determined using the D100/300 sensor system

Conc. (%)	Temp. (°C)	Upward flow curve $m^{*\dagger}$	Upward flow curve $n^{*\dagger}$	Downward flow curve m	Downward flow curve n
0·5	60	0·252 ± 0·033	0·681 ± 0·026	0·073 ± 0·002	0·904 ± 0·028
0·5	80	0·170 ± 0·010	0·802 ± 0·043	0·062 ± 0·001	0·982 ± 0·026
0·5	100	0·084 ± 0·012	0·874 ± 0·029	0·029 ± 0·005	1·041 ± 0·059
0·5	120	0·054 ± 0·007	1·036 ± 0·029	0·012 ± 0·001	1·043 ± 0·043
0·5	140	0·024 ± 0·007	1·215 ± 0·076	0·006 ± 0·003	1·168 ± 0·044
1·0	60	1·191 ± 0·101	0·560 ± 0·029	1·032 ± 0·077	0·560 ± 0·018
1·0	80	0·364 ± 0·049	0·673 ± 0·030	0·320 ± 0·041	0·681 ± 0·021
1·0	100	0·129 ± 0·032	0·924 ± 0·067	0·078 ± 0·060	0·820 ± 0·009
1·0	120	0·105 ± 0·022	0·991 ± 0·005	0·046 ± 0·002	1·159 ± 0·043
1·0	140	0·044 ± 0·007	1·010 ± 0·002	0·045 ± 0·004	1·189 ± 0·056
1·5	60	3·559 ± 0·123	0·481 ± 0·028	2·581 ± 0·111	0·564 ± 0·012
1·5	80	1·443 ± 0·053	0·565 ± 0·002	1·336 ± 0·144	0·653 ± 0·015
1·5	100	1·045 ± 0·045	0·750 ± 0·014	0·635 ± 0·049	0·779 ± 0·010
1·5	120	0·619 ± 0·025	0·787 ± 0·025	0·234 ± 0·018	1·020 ± 0·023
1·5	140	0·255 ± 0·019	0·867 ± 0·054	0·130 ± 0·007	1·062 ± 0·075
2·0	60	15·55 ± 0·554	0·412 ± 0·032	13·65 ± 0·781	0·445 ± 0·016
2·0	80	6·767 ± 0·354	0·498 ± 0·016	6·784 ± 1·212	0·553 ± 0·018
2·0	100	1·990 ± 0·236	0·607 ± 0·013	1·948 ± 0·141	0·686 ± 0·018
2·0	120	1·134 ± 0·081	0·695 ± 0·018	0·878 ± 0·101	0·861 ± 0·045
2·0	140	0·642 ± 0·068	0·744 ± 0·018	0·490 ± 0·025	0·882 ± 0·015

*$\sigma = m\,\dot{\gamma}^n$

†Results are means ± standard deviations of triplicates.

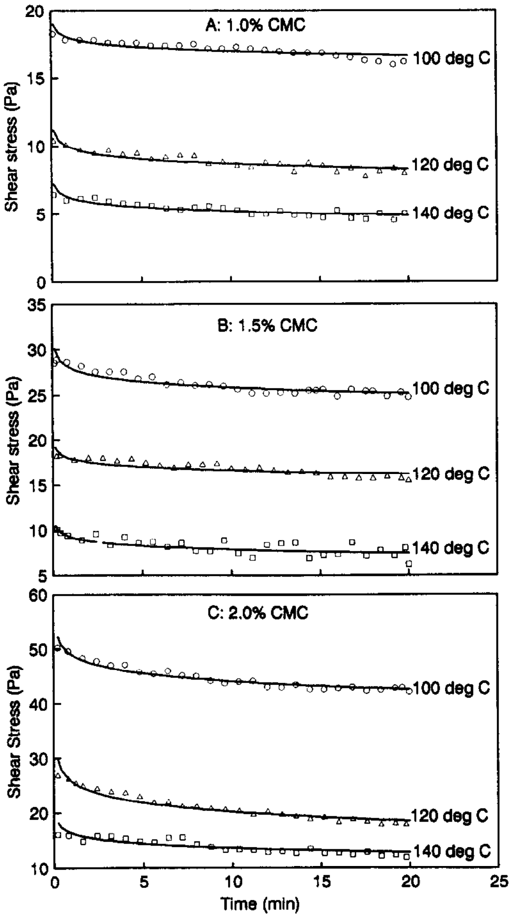

Fig. 2. Time dependency plots for 1·0–2·0% CMC solutions during a programmed 20 min constant shearing (500 s^{-1}) at 100, 120 and 140°C (A: 1·0%, B: 1·5%, C: 2·0%).

min (Figures 1 and 2). Further discussion of the thixotropic behaviour of CMC is given below.

Rheological models of CMC

The suitability of different rheological models was tested for fitting the shear stress/shear data of CMC. The power law model gave a better fit especially at lower temperatures (60 and 80°C) for all CMC concentrations. The Bingham linear model showed the best fit at temperatures exceeding 100°C and at the lower concentrations (0·5 and 1·0%) particularly for the downward flow curve. However, the power law model was chosen for the subsequent analysis and discussion of the data in this study because of its overall good fit (based on the determination coefficient, r^2, among the different models at all test conditions) and its inherent compatibility for engineering calculations (Lalonde *et al.*, 1991).

Effect of temperature and concentration

The mean values and standard deviations of m and n using the D100/300 sensor system for various concentrations of CMC at different temperatures are presented in Table 1. From this Table, the consistency coefficient (m) increased with concentration and decreased with temperature, while the opposite trend was observed with the flow behaviour index (n). It is worthwhile noting that at temperatures above 80°C (0·5 and 1·0% CMC) and above 100°C (1·5% CMC), the flow behaviour index was >1·0 indicating a dilatant flow behaviour. Insufficient instrument sensitivity to record shear stresses below 100 s^{-1} was the reason for

Table 2. Analysis of variance of the CMC consistency coefficient (*m*) and flow behaviour index (*n*) as influenced by concentration and temperature

Factor	Treatment	D.F.	Upward curve MS	Upward curve %SS	Downward curve MS	Downward curve %SS
m	Main effects	7	64·02*	60·00	52·06*	59·73
	Concentration	3	83·63*	33·59	72·06*	35·43
	Temperature	4	49·32*	26·41	37·06*	28·30
	Interaction	12	22·90*	36·79	18·92*	33·21
	Residual	40	0·60	3·21	0·47	3·06
n	Main effects	7	0·34*	93·55	0·39*	88·98
	Concentration	3	0·32*	37·55	0·30*	29·73
	Temperature	4	0·36*	56·00	0·45*	59·25
	Interaction	12	0·008†	3·79	0·02*	8·64
	Residual	40	0·002	2·66	0·002	2·38

*†Significant at $P \leq 0{\cdot}001$ and $P \leq 0{\cdot}01$ respectively.
^{ns}Not significant, $P > 0{\cdot}05$.

this obviously incorrect behaviour as previously reported by Abdelrahim *et al.* (1994). This can be accounted for by setting n equal to 1·0 and taking m as viscosity (which is the slope of the Bingham linear model) of the sample (the Herschel–Bulkley model transforming to Bingham linear). The restriction is that this relationship is applicable only for shear rates above 100 s^{-1}, below which no measurable shear stress was recorded (Abdelrahim *et al.*, 1994).

Analysis of variance showed that m and n of CMC were significantly influenced ($p < 0{\cdot}001$) by temperature, concentration and their interaction (Table 2). Concentration was the major contributor to the variability of m for both the upward and downward flow curves with 33·6 and 35·4% of the total variability; respectively, while the contribution of temperature was ~26 (upward) and 28% (downward). The differences between the two flow curves may be attributed to the differences in the shear history for the downward flow curve of CMC samples following the steady shear at 500 s^{-1} for 20 min. Flow behaviour index (n) was mainly influenced by temperature with 56 and 59% of the variability of upward and downward flow curves; respectively, while concentration was responsible for ~38 and 30% of the variability. Interaction have only little effect (~4 and 9% of total variability of up and down flow curves, respectively) despite the fact it was significant (Table 2).

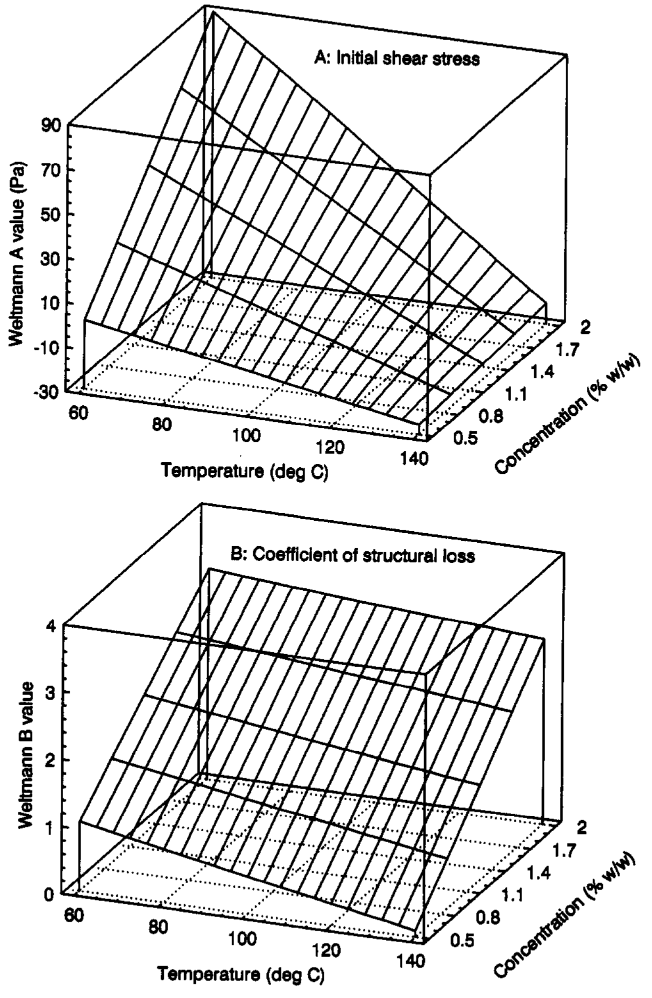

Fig. 3. Multiple regression generated response surface plots for the A and B values of the Weltmann model for CMC solutions sheared at 500 s^{-1}.

The time dependency (thixotropy)

Thixotropic behaviour of CMC solutions was examined using the modified Weltmann logarithmic model and a good fit was obtained as presented in Figure 2 for 1·0, 1·5 and 2·0% w/w at 100, 120 and 140°C. The Weltmann A value (A_w), which is the measure of initial resistance to shearing force was significantly affected by concentration, temperature and their interaction ($P < 0{\cdot}001$). A_w value increased with concentration and decreased with temperature which has a more dominant effect than concentration. The susceptibility of CMC solutions to structural breakdown with shearing time was measured by the Weltmann B value (B_w coefficient of thixotropic structural loss). The B_w value

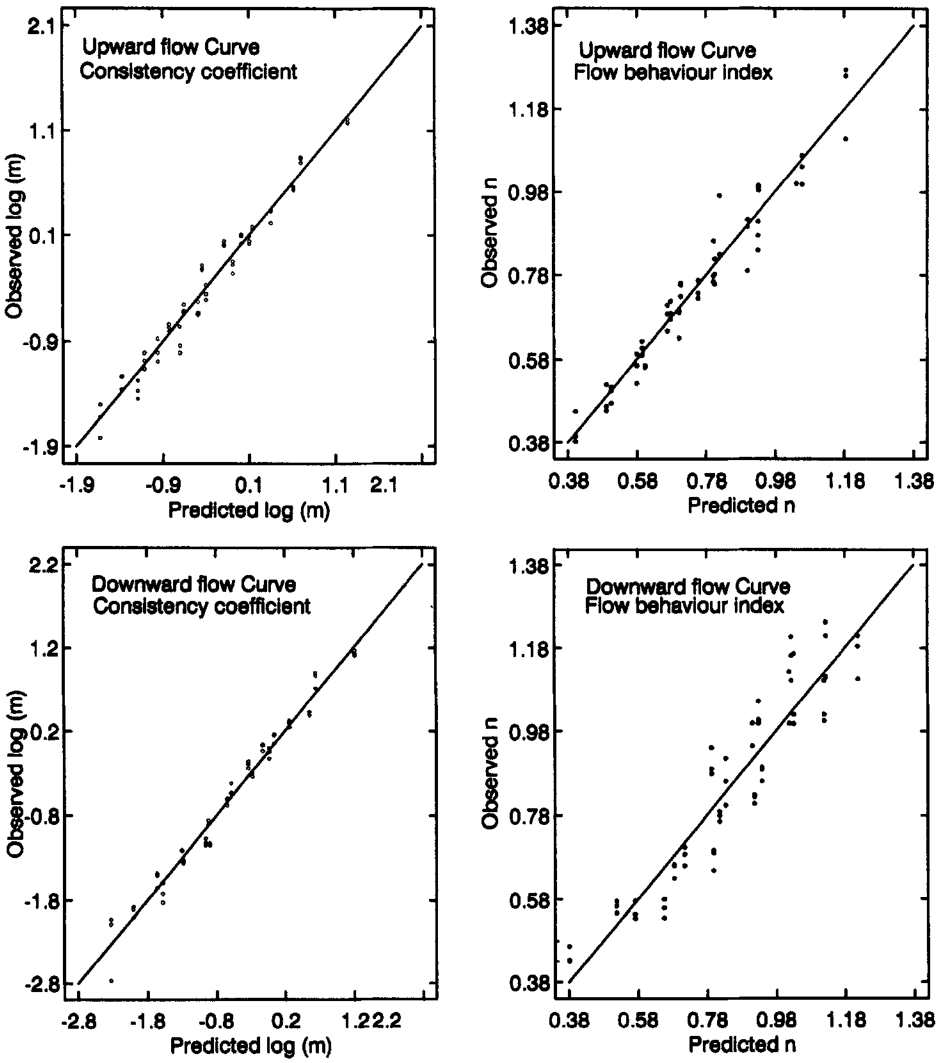

Fig. 4. Experimental vs multiple regression generated data for consistency coefficient (m) and flow behaviour index (n) of CMC solutions under the influence of concentration and temperature for the upward and downward flow curves.

was significantly ($P < 0{\cdot}001$) influenced by concentration and temperature and their interactions. The B_w value also increased with concentration and decreased with temperature, but the effect of concentration was more dominant. Multiple regression equations for both A_w and B_w values are given below:

$$A_w = -29{\cdot}77 + 101{\cdot}42\ C + T\ \{0{\cdot}216 - 0{\cdot}703\ C\}(R^2 = 0{\cdot}88) \qquad (2)$$

$$B_w = 1{\cdot}191 + 1{\cdot}139\ C + T\ \{0{\cdot}005 - 0{\cdot}014\ C\}(R^2 = 0{\cdot}96). \qquad (3)$$

Both A_w and B_w increased with concentration and decreased with temperature, but the effects of concentration and temperature were more pronounced with A_w as presented in response surface plots (Figure 3).

Regression coefficients for CMC rheological parameters

A modified Turian model was used to accommodate the effects of concentration and temperature on CMC rheological parameters using multiple regression analyses. The predictive equations for $\log_{10}(m)$ and n employing various functions of temperature and concentration are given below for the upward flow curve:

$$\log_{10}(m) = -0{\cdot}66 - 0{\cdot}013\ T + 0{\cdot}159\ /\ C + 0{\cdot}005\ TC + 59{\cdot}5\ C/T(R^2 = 0{\cdot}97) \qquad (4)$$

$$n = 0{\cdot}329 + 0{\cdot}007\ T - 0{\cdot}002\ TC - 4{\cdot}088\ C/T(R^2 = 0{\cdot}94) \qquad (5)$$

and similarly for the downward flow curves:

$$\log_{10}(m) = -0{\cdot}195 - 0{\cdot}018\ T + 0{\cdot}133\ /\ C + 0{\cdot}006\ TC + 54{\cdot}5\ C/T(R^2 = 0{\cdot}97) \qquad (6)$$

$$n = 0{\cdot}647 + 0{\cdot}005\ T - 0{\cdot}001\ TC - 14{\cdot}32\ C/T(R^2 = 0{\cdot}87). \qquad (7)$$

The pooled data for experimental m and n *vs* those predicted by the above regression relationships are presented in Figure 4 which shows an overall uniform good distribution (as indicated by the R^2 values of 0·87–0·97) of data points along the perfect diagonal line.

CONCLUSIONS

The flow behaviour of CMC can be adequately described by the power law model using high temperature viscometry. The physical isolation of rotor and sensor (D100/300) assembly with the coupling achieved through a magnetic clutch permits evaluating the rheological properties at the temperature conditions of aseptic processing. Both *m* and *n* of CMC were sensitive to changes in concentration and temperature. A modified Turian approach was used to describe the combined influence of temperature and concentration which can be conveniently incorporated in the power law model for different engineering calculations (Awuah *et al.*, 1993). The Weltmann model adequately described the CMC time dependency.

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