

Rheological Characterization of Skim Milk Stabilized with Carrageenan at High Temperatures

A.D. ANDERSON, C.R. DAUBERT, B.E. FARKAS

ABSTRACT: Superpositioning principles were applied twice to model temperature (25 to 125 °C) and concentration (0.005 to 0.040% w/w) effects on skim milk and carrageenan solutions. Samples were analyzed using a controlled stress rheometer equipped with a pressurized sealed cell, permitting measurements well above standard boiling conditions. Individual samples were sheared between 10 and 160 s⁻¹, and predictive equations were developed to predict Newtonian viscosity as a function of temperature and carrageenan concentration. The superpositioning technique coupled with advancements in rheological instrumentation permits high temperature measurements and offers a strategy for viscosity determination for thermal processing unit operations.

Keywords: concentration, temperature, superposition, rheology, carrageenan

Introduction

ADVANCEMENTS IN RHEOLOGICAL INSTRUMENTATION, PERMITTING product assessment at temperatures above sample boiling, present new opportunities for the rheologist to simulate thermal processing conditions using benchtop methodologies. Predictive equations developed from modeling rheological data collected over broader temperature ranges may be applied during process development for calculating product residence times during heating. Better viscosity prediction insures adequate thermal treatment and limits opportunities for product overheating.

Viscosity changes caused by temperature are typically modeled for Newtonian fluids using an Arrhenius relationship (Steffe 1996). In addition to modeling temperature effects, modeling concentration effects is often desirable, especially for predicting viscosity for solutions with varying hydrocolloid content. Davey (1997) and Velez-Ruiz and Barbosa-Canovas (1997) developed predictive equations modeling the effects of temperature and concentration on viscosity by adding terms to the Arrhenius relationship accounting for concentration effects. However, temperatures above standard temperature-pressure (stp) boiling consistent with higher temperature processing have not been modeled, most likely due to instrumental constraints and limitations.

Time-temperature superpositioning (Ferry 1970), a commonly-used empirical technique incorporating shift factors to account for property changes, is a method often used for modeling temperature effects on polymers (Macosko 1994) and reducing the thermal and shear effects to a single master curve. According to the principle behind superpositioning, the effects of time and temperature on a system have equal effects in such a way that a simple shift of the response function superimposes data taken from different temperatures (McNulty and Flynn 1979). This method may be used for modeling viscosity of food products not necessarily adhering to an Arrhenius relationship with increasing temperature or by a simple Newtonian or power law model. For example, locust bean gum solutions were subjected to superpositioning to document the temperature effects on viscoelasticity (Richardson and Norton 1998). Lopes da Silva

and others (1994) collapsed rheological data for pectin dispersions obtained between 5 and 65 °C to a reference temperature of 25 °C. To evaluate the independent effects of concentration and temperature, Partal and others (1997) applied time-temperature and time-concentration superpositioning principles independently to model the flow behavior of stabilized emulsion systems.

The objective of the research is to present a procedure for modeling temperature and concentration effects of skim milk stabilized with a carrageenan blend at processing temperatures up to 125 °C. According to ingredient specifications, the blend selected is typically used to stabilize chocolate milks, and concentrations were selected as representative of typical industrial use levels to accommodate different functional purposes. Carrageenan fulfills many roles when stabilizing food systems, and its functionality depends on the ratio of carrageenan type: kappa, lambda, or iota. Interactions between carrageenan types with dairy ingredients was not a focus of this research. Nevertheless, the blend selected for this study was comprised of greater than 50% κ-carrageenan. Advancements in rheological instrumentation accommodate data collection for low viscosity fluids at high temperature conditions. Superpositioning principles, normally applied once to account for either temperature or concentration effects, are herein performed in combination. Empirical equations derived from variables of the superpositioning process predict viscosity as a function of temperature and carrageenan concentration and may be applied to predict viscosity for high-temperature, processing considerations.

Materials and Methods

Materials

Pasteurized skim milk, processed at 79 °C for 18 sec, was obtained from the North Carolina State University (Raleigh, N.C., U.S.A.) dairy facility. A commercially available carrageenan blend (SeaKem CM611), specifically developed for use by the dairy industry, was obtained from the FMC Corporation (Philadelphia, Pa., U.S.A.).

Sample Preparation

To add carrageenan, skim milk was heated and stirred at 350 rpm to create a vortex using a Thermolyne stir and heat plate (Barnstead-Thermolyne, Dubuque, Iowa, U.S.A.). Carrageenan was added slowly to the vortex center to avoid clumping at concentrations of 0.005, 0.010, 0.020, and 0.040% (w/w). Solutions were heated to 85 °C for approximately 5 min, allowing the carrageenan to hydrate and solubilize. Next, each sample was cooled to room temperature with no agitation, followed by rheological analyses.

Equipment and Rheological Testing

A StressTech, controlled stress rheometer (Rheologica Instruments AB, Lund, Sweden) was equipped with a pressurized sealed cell to complete rheological measurements, see Figure 1. The rheometer had a minimum stress requirement of 25 mPa, enabling accurate measurements of low viscosities at high temperatures. Compressed air was applied to the sealed cell at 179.270 kPa to prevent sample boiling and excessive moisture loss at all temperatures.

Individual samples were sheared between 10 and 160 s⁻¹ at 25, 65, 85, 105, and 125 °C using a 25.0 mm rotating cylindrical attachment in a 27.5 mm cup. Samples tested above 25 °C were pre-sheared at 50 s⁻¹ while ramping temperature (4 °C/min) to insure adequate heat distribution and limit cooking. All rheological data collected below the rheometer sensitivity (25 mPa) was discarded, and the Taylor number was computed to guard against secondary flows compromising the results. All tests were performed in duplicate the day of sample preparation.

Model Development

Superpositioning principles modeled temperature and concentration effects on apparent viscosity by incorporating calculated shift factors for each condition. To begin model development, shear stress was plotted as a function of rate for each temperature-concentration combination tested (Figure 2). A Newtonian relationship was observed at every combination above 25 °C:

$$\sigma = \mu \dot{\gamma} \quad (1)$$

An 85 °C reference temperature was selected, corresponding to a central temperature tested within the range. The reference viscosity, μ^* , was the Newtonian viscosity at 85 °C for each concentration. For every temperature, shear rate was calculated at 50 mPa using the corresponding Newtonian viscosity, μ . The calcu-

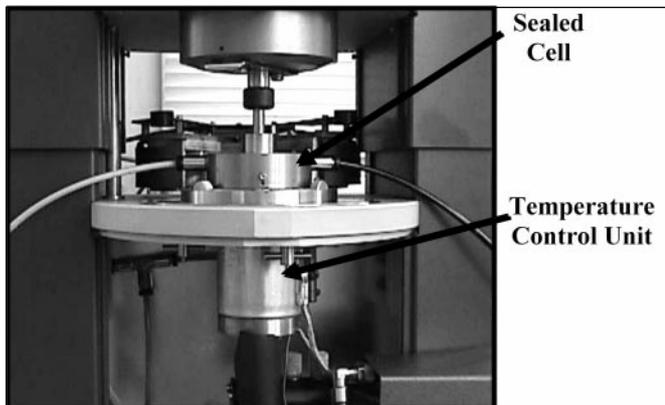


Figure 1—Rheometer pressure cell.

Table 1—Superpositioning Shift Factors.

Part I Temperature Superposition (5 temperatures)	Part II Concentration Superposition (4 concentrations)
$\bar{a}_{T, 25^\circ\text{C}} = 0.34$	$a_{C, 0.005 \text{ w/w}} = 1.12$
$\bar{a}_{T, 65^\circ\text{C}} = 0.90$	$a_{C, 0.001 \text{ w/w}} = 1.07$
$\bar{a}_{T, 85^\circ\text{C}} = 1.00$	$a_{C, 0.020 \text{ w/w}} = 1.00$
$\bar{a}_{T, 105^\circ\text{C}} = 1.03$	$a_{C, 0.040 \text{ w/w}} = 0.89$
$\bar{a}_{T, 125^\circ\text{C}} = 1.19$	

lated stress (σ) for each temperature was divided by the calculated stress (σ^*) at the reference temperature (85 °C). The subsequent value was the shift factor (a_T) for each temperature

$$a_T = \frac{\sigma}{\sigma^*} \quad (2)$$

Shift factors for a given temperature were averaged considering each concentration to produce \bar{a}_T , provided in Table 1. When shear stress was plotted against shear rate divided by the shift factor, all the data lined up on the reference curve - the curve at 85 °C. The equation for viscosity became:

$$\mu = \frac{\mu^*}{a_T} \quad (3)$$

Since the carrageenan blend was tested at 4 concentrations, 4 reference curves shifted for temperature were produced (Figure 3). The same superposition procedure was applied again to further shift data for concentration effects. The chosen reference concentration was 0.02%, and the variable a_C represented the shift factors for concentration,

$$a_C = \frac{\sigma}{\sigma^*} \quad (4)$$

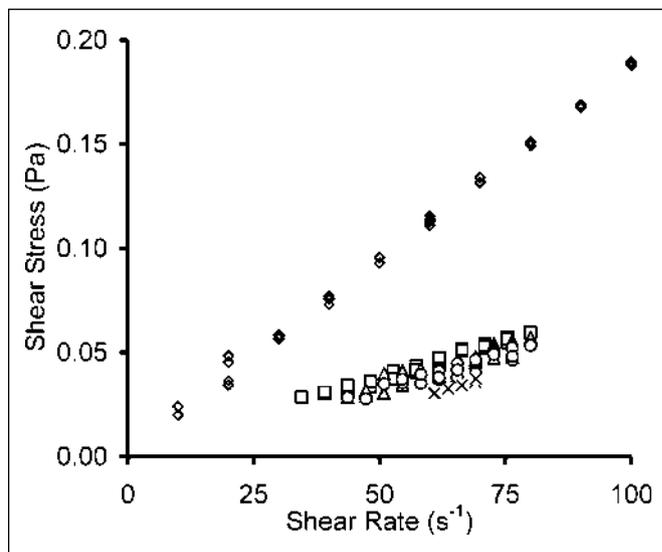


Figure 2—Effects of temperature on the rheology of 0.01% carrageenan in skim milk. Legend: \diamond 25 °C, \square 65 °C, Δ 85 °C, \circ 105 °C, \times 125 °C

also displayed in Table 1. The reference viscosity, μ^* , was modified to be the viscosity at 85 °C at a carrageenan concentration of 0.02%:

$$\mu = \frac{\mu^*}{a_T \cdot a_C} \quad (5)$$

Since a_T and a_C vary with temperature (T) and concentration (C), respectively (see Table 1), the shift factors were modeled using Power Law fits as opposed to Arrhenius fits (Partal and others 1997; Ferry 1970)

$$a_T = bT^d \quad (6)$$

$$a_C = fC^g \quad (7)$$

where b,d and f,g represent empirical power law constants. Substituting equations (6) and (7) into equation (5) gives an empirical model for viscosity:

$$\mu = \frac{\mu^*}{bT^d \cdot fC^g} \quad (8)$$

Collapsing constant values for variables μ^* , b, and f yields an overall constant, A:

$$A = \frac{\mu^*}{b \cdot f} \quad (9)$$

The final equation for Newtonian viscosity becomes:

$$\mu = \frac{A}{T^d \cdot C^g} \quad (10)$$

Results and Discussion

FIGURES 2 THROUGH 4 SHOW THE PROCESS OF SUPERPOSITIONING data for the milk and carrageenan solutions. The first step in

the superpositioning process shifted data based on temperature effects. Figure 2 depicts typical temperature trends for a skim milk and carrageenan solution at a concentration of 0.01% (w/w). For each concentration tested, viscosity typically diminished with increasing temperature as expected. However, results deviated from this trend at certain temperatures, and these discrepancies were attributed to protein denaturation and/or aggregation or sample cooking. Deviant samples were re-evaluated to insure variations were inherent to the sample and not caused by instrumentation errors or inconsistent testing methods. Overall, sample viscosities showed minimal variation at the observed, elevated temperatures.

Once each concentration of carrageenan was shifted for temperature, the same process was repeated to shift for concentration effects using the appropriate factor. Figure 3 represents reference curves already shifted for temperature for each concentration of CM carrageenan. Reference viscosity, denoted by the slope of each data set, increased with increasing concentration, as expected.

The final superposition plot (Figure 4) represents data collected at temperatures from 25 to 125 °C at carrageenan concentrations of 0.005% to 0.04%. All data was shifted to a final master curve to account for temperature and concentration effects.

A model equation, based on equation 10, was developed from variables of the superpositioning process to predict viscosity of Newtonian skim milk and carrageenan solutions for the range of temperatures (°C) and concentrations (% w/w) evaluated.

$$\mu = 37.0 \left(\frac{C^{0.11}}{T^{0.75}} \right) \quad (11)$$

The ability of the skim milk and carrageenan equations to accurately predict viscosity is shown in Figure 5. Each temperature-concentration combination produced a viscosity, modeled using the prediction equation for each temperature from 65 to 125 °C (a total of 16 combinations). A correlation between actual measured viscosities and predicted values resulted in a slope of 1.00 and a 0.74 coefficient of determination. Slight scattering of the

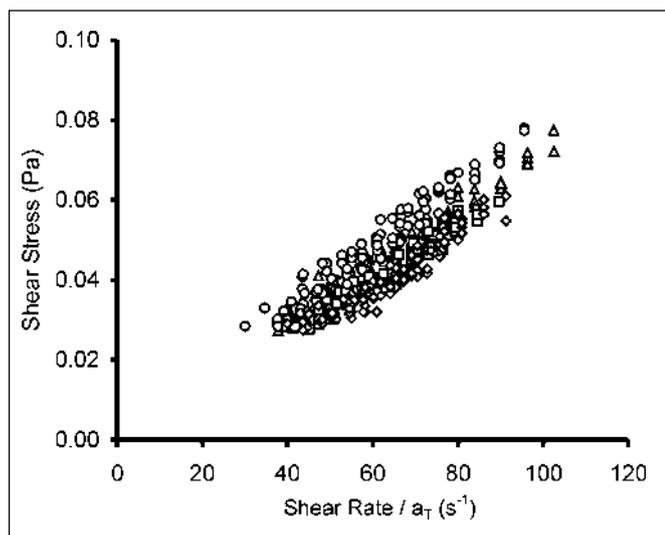


Figure 3—Effects of concentration on the rheology of carrageenan in skim milk. Each concentration represented has already been shifted to account for temperature effects. Legend: \diamond 0.005%, \square 0.01%, \triangle 0.02%, \circ 0.04%

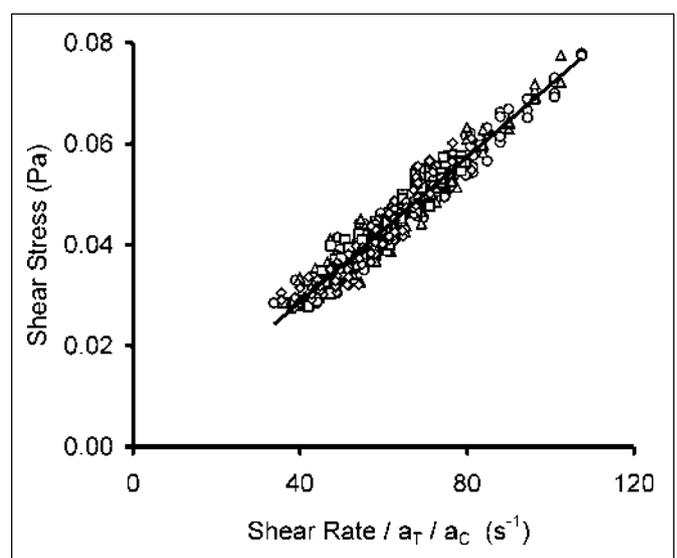


Figure 4—Reference curve showing combined temperature and concentration effects for carrageenan in skim milk. Legend: \diamond 0.005%, \square 0.01%, \triangle 0.02%, \circ 0.04%

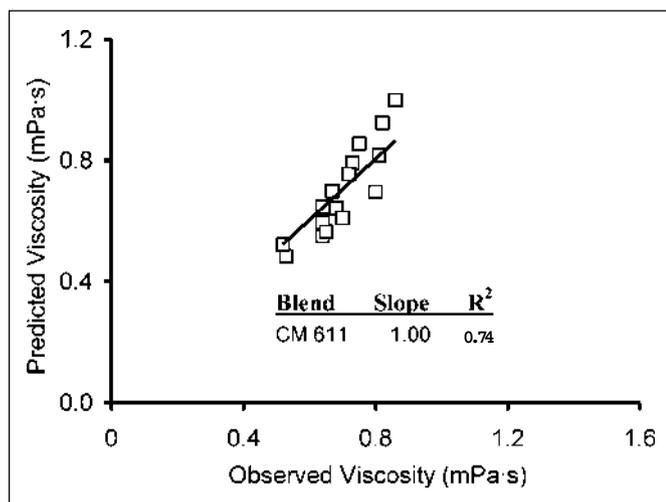


Figure 5—Correlation between observed viscosity and predicted viscosity for skim milk and carrageenan solutions.

data reduced the correlation, attributed to the narrower range of viscosities produced at the conditions. Overall variability between measured viscosity and predicted viscosity was less than 0.1 mPa·s.

In order for superpositioning to be effective, molecular relaxation mechanisms are assumed to be similarly influenced by equivalent temperature changes (Lopes da Silva and others 1994). This consideration is valid for solutions above a critical temperature where the carrageenan undergoes transition from a helix (ordered) to a coiled (disordered) formation (Schorsch and others 2000; Langendorff and others 2000). At 25 °C, carrageenan solutions have gelled and display helix formation, frequently leading to non-Newtonian rheological flows. This deviation from ideal Newtonian behavior may complicate superpositioning. This situation was not experienced for the described experimental design, but should be considered at elevated concentrations, alternative carrageenan selection, or lower temperatures in general.

The pressure cell attachment allowed the measurement of rheological properties at all experimental temperatures. At high temperatures, low viscosities did challenge rheometer sensitivity, and data collection was in fact limited to a narrower shear rate range. By considering sensitivity constraints and Taylor flow complications, the data described is accurate. A close inspection of Figure 5 reveals the viscosity was below 1.2 mPa·s for each con-

dition above 65 °C. For the food engineer designing a thermal process, this value is important for design considerations.

Conclusions

SUPERPOSITIONING PRINCIPLES DEVELOPED AN EMPIRICAL EQUATION to predict viscosity of skim milk and carrageenan solutions as a function of temperature (°C) and carrageenan concentration (% w/w). The equation is applicable only within the ranges of experimental conditions tested. Viscosities at temperatures of 65 °C and above were below 1.2 mPa·s for all concentrations considered, and overall variability between measured viscosity and predicted viscosity was less than 0.1 mPa·s. The superpositioning technique presented, coupled with advancements in rheological instrumentation to permit high temperature measurements, offers a method for viscosity prediction at thermal processing conditions.

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Authors are with the North Carolina State University, Department of Food Science, Box 7624, Raleigh, N.C. 27695. Please address correspondence to author Daubert, e-mail: chris_daubert@ncsu.edu