

# Rheological Properties of Carboxymethyl Cellulose

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**ABSTRACT:** This work is a complete and comprehensive study of the rheological properties of carboxymethyl cellulose (CMC) solutions. The study was carried out using the computer controlled RheoStress RS100 system of Haake. CMC concentration in the test solutions ranged by weight from 1 to 5%. This range was sufficiently wide to reveal the nearly Newtonian behavior at the lower end of concentrations, and the definitely pseudoplastic, thixotropic, and viscoelastic behaviors of CMC solutions at the higher end of concentrations. The scope of the study included measurements of steady-state parameters, transient shear stress response, and yield stress. In addition, the thixotropic, creep recovery, and dynamic responses of solutions with high concentrations were measured. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 289–301, 1997

**Key words:** carboxymethyl cellulose; viscosity; yield stress; thixotropy; creep recovery; viscoelasticity; oscillating stress

## INTRODUCTION

Carboxymethyl cellulose (CMC) has a very wide range of applications. In detergents and soaps, it acts as a soil-suspending agent. In food products, such as dietetic foods and ice cream, it acts as a water binder, thickener, or as an emulsion stabilizer. CMC is also used in the textile industry as a coating agent. In the pulp and paper industry, CMC is used in the coating colors that improve the surface properties of paper and paper board. Among numerous other applications, CMC is added to drilling mud, resin emulsion paints, adhesives, and printing inks. CMC also enters the formulations of many pharmaceutical and cosmetics products as a suspending agent, tablet excipient, or as a viscosity-increasing agent.

CMC semisynthetic white granules are colorless and odorless and can be classified as a non-toxic water soluble polymer. In them,  $\text{CH}_2\text{COOH}$

groups are substituted on the glucose units of the cellulose chain through an ether linkage with molecular weight ranges from 21,000 to 500,000. Since the reaction occurs in an alkaline medium, the product is the sodium salt of the carboxylic acid  $\text{R}-\text{O}-\text{CH}_2\text{COONa}$ . The presence of metal salts has little effect on the viscosity of CMC solutions. However, viscosity of 1% CMC solution varies from 5 to 2000 mPa s, depending on the extent of etherification. CMC solutions are stable between pH 2 and 10. Below pH 2, precipitation of a solid occurs; above pH 10, viscosity decreases rapidly.<sup>1</sup> For example, 1% CMC has pH 6.5 to 8 and a tensile strength 8000 to 15,000 psi. CMC is insoluble in organic liquids and reacts with heavy metal salts to form films that are insoluble in water, transparent, relatively tough, and unaffected by organic materials.<sup>2</sup>

CMC has been the subject of a number of recent rheological studies.<sup>3–6</sup> McCoy et al.<sup>3</sup> used CMC as a pseudoplastic carrier fluid for low-acid particulate foods in process simulations. Abdelrahim et al.<sup>4</sup> studied the effects of concentration and temperature on the rheological behavior of CMC solu-

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tions. They measured the rheological properties of 0.5 to 2.0% CMC solutions over the temperature range of 30 to 90°C using a computer controlled rotational viscometer in a linearly increasing and decreasing three-cycle shearing sequence. They reported that CMC solutions showed power law flow behavior and that the consistency coefficient and flow behavior index were significantly affected by both temperature and concentration.

Planas et al.<sup>5</sup> carried out a rheological experimental study for microcrystalline sodium carboxymethyl cellulose gels over a concentration range of 1 to 2.5%. They studied the thixotropic behavior of these solutions in terms of agitation time, storage duration time, concentration, and temperature. The results included a semiempirical relationship between the thixotropic area and these variables. Young and Shoemaker<sup>6</sup> used a rotational cone and plate viscometer to measure the intrinsic viscosity of aqueous suspensions of xanthan gum and CMC. They found that the reduced viscosity or hydrodynamic volumes of CMC suspensions increased with dilution and that the intrinsic viscosity of xanthan gum and CMC suspensions decreased with increasing the shear rate.

Changes in the viscosity of nonNewtonian solutions with shear rate are related to the orientation or deformation of molecule network in the direction of flow. To monitor the non-Newtonian deformation behavior as a function of either shear rate or shear stress, it is necessary to apply a fixed, controlled value of shear rate or shear stress throughout the measurement process. The rotational viscometer with a cone and plate sensor is one of the best candidates for this process. Planas et al.<sup>5</sup> employed a Brookfield Digital DV II rotary cylinder viscometer with eight angular velocities between 0.3 and 60 rpm. Young and Shoemaker<sup>6</sup> carried out their rheological measurements at 25°C with a Carri-Med Weissenberg R20A rheogoniometer of the cone and plate type. The cone angle was 2 degrees, and the diameter was 75 mm. However, Abdelrahim et al.<sup>4</sup> used a Haake Model RV20 rotational viscometer equipped with M5 OSC (oscillation) measuring head and MVI rotor, which interfaced with a microcomputer for control and data acquisition, in their rheological experiment.

The wide range of CMC applications (i.e., food industry, detergents, coating technology, pharmaceuticals, and drilling muds) involves a wide variety of processes, such as storing, mixing, pumping, heating, cooling, separation, etc. The purpose

of this work is to conduct a complete, comprehensive, and accurate study of the rheological measurements of CMC and to depict clear flow behavior characteristics, which are required for the design and operation of these processes. The completeness of the study has been made possible by the use of a Haake RS100 Rheometer, with a cone and plate sensor.

## EXPERIMENTAL

The rheological measurements of this study were carried out using a Haake rheometer RheoStress RS100. This rheometer has several operating test modes. It has a universal controlled rate (CR) mode, a controlled stress (CS) mode, and an oscillation (OSC) test mode. In the CS-mode, shear stress is applied to a test sample by means of extremely low inertia. The drive shaft of the RS100 is centered by an air bearing to ensure an almost frictionless transmission of the applied stress to the test fluid. The resulting deformation of the sample is detected with a digital encoder that processes  $10^6$  impulses per revolution. This resolution makes it possible to measure small yield values, strains, or shear rates. The computer controlled rheometer can be easily switched between both the CS and CR modes, and it can provide oscillating stress inputs and autostrain. A controlled variable lift speed is used to position the cone on the plate. A thermal gap size is controlled to compensate for any of the sensor generated heat. The software package "Haake Windows" controls both test routines and data evaluation. For the completeness of the study, it was important that the RS100 rheometer could test viscoelastic fluids, fluids showing yield points, and shear time effect on their rheological properties. The rheometer is equipped with a cone and plate sensor.

CMC solutions of sodium salt medium viscosity N° C-4888, with Degree of Substitution DS = 0.7, from Sigma Chemical Company, St. Louis, Missouri U.S.A., were prepared by adding a specific weight of CMC to one liter of double distilled water. Depending on the concentration, sufficient time was allowed to achieve complete dissolution without an external source of heat or power to avoid any degradation of the polymer molecules network. This study employed a weight concentration range of 1–5% CMC to cover the whole spectrum of the rheological behavior from a nearly

Newtonian characteristic at 1% concentration of CMC to a viscoelastic thixotropic behavior at 5%. In order to study the many possible phenomena that occur in processes involving the use of CMC solutions, a wide range of tests were carried out at a room temperature of 23°C. The tests conducted were a steady-state flow study, a test of transient shear stress response, yield stress measurements, a thixotropy study, a creep recovery test, and a dynamic test.

## RESULTS AND DISCUSSION

### Steady-state Flow Study

This test describes the flow behavior of CMC solutions in the concentration range of 1–5%. The flow curve or the rheological finger print of any sample provides the correlation between the assigned shear stress and the resulting shear rate in the CS mode, or between the assigned shear rate and the resulting shear stress in the CR mode. On the other hand, viscosity curves show the behavior of viscosity with increasing shear rates or increasing pumping rates through a pipeline. The latter curves provide a very useful view of the rheological properties of the sample. The transformation

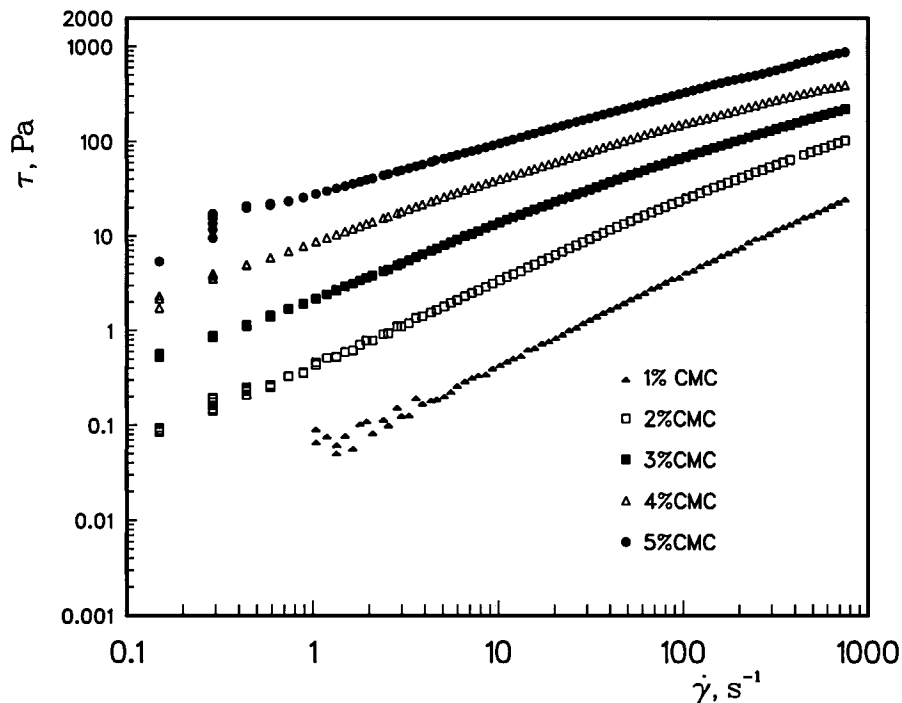
of flow curves to viscosity curves was accomplished using computer software.

Figure 1 shows the flow curves in terms of shear stress–shear rate relationships for 1–5% CMC concentrations. These curves are plotted over a log–log scale that includes four cycles of shear rate from 0.1 to 1000 s<sup>-1</sup>. A consistent nearly linear pattern is recorded for all the CMC solutions from 1 to 5%. The results show some scatter for 1% concentration of CMC in the range of shear rates 1.0–4 s<sup>-1</sup>. This is due to the relatively low concentration of this solution that corresponds to rather low values of shear stress in this range of shear rates. Rotational rheometers such as the RS100 Haake tend to have lower sensitivity in measurements of low shear stresses at low shear rates.

When flow and viscosity curves plotted in double logarithmic scales give straight lines, it is a good indication that the Ostwald-de-Waele Equation is a suitable model for the measurements. This can be written as

$$\tau = k\dot{\gamma}^n \quad (1)$$

where  $\tau$  (Pa) is shear stress,  $\dot{\gamma}$  (s<sup>-1</sup>) is shear rate,  $k$  (Pa s<sup>n</sup>) is the consistency index, and  $n$  is the flow



**Figure 1** Shear stress–shear rate behavior of different concentrations of CMC.

**Table I** Regression Coefficients

CMC (%)	$k$	$n$	$r$
1	0.05	0.95	0.99
2	0.45	0.85	0.99
3	2.30	0.73	0.99
4	8.30	0.61	0.99
5	28.0	0.53	0.99

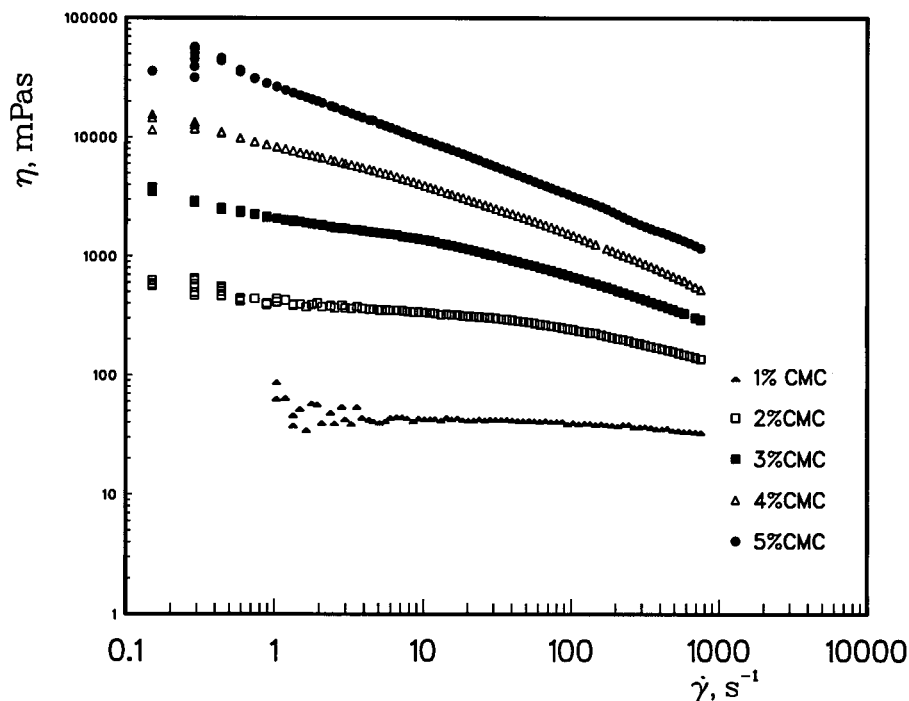
behavior index. The regression coefficient Table I shows that the power law model is a suitable fit for the experimental data of all the examined CMC solutions. The flow behavior index for 1% CMC shows that the flow is very close to Newtonian ( $n = 0.95$ ). However, increasing the solution concentration from 2 to 5% leads to a sharp drop in the flow behavior index from 0.85 to 0.53. This corresponds to a strong shear thinning behavior for the higher range of concentrations. This conclusion can be clearly seen in Figure 2, which shows viscosity in mPa over four log cycles of shear rate  $s^{-1}$ .

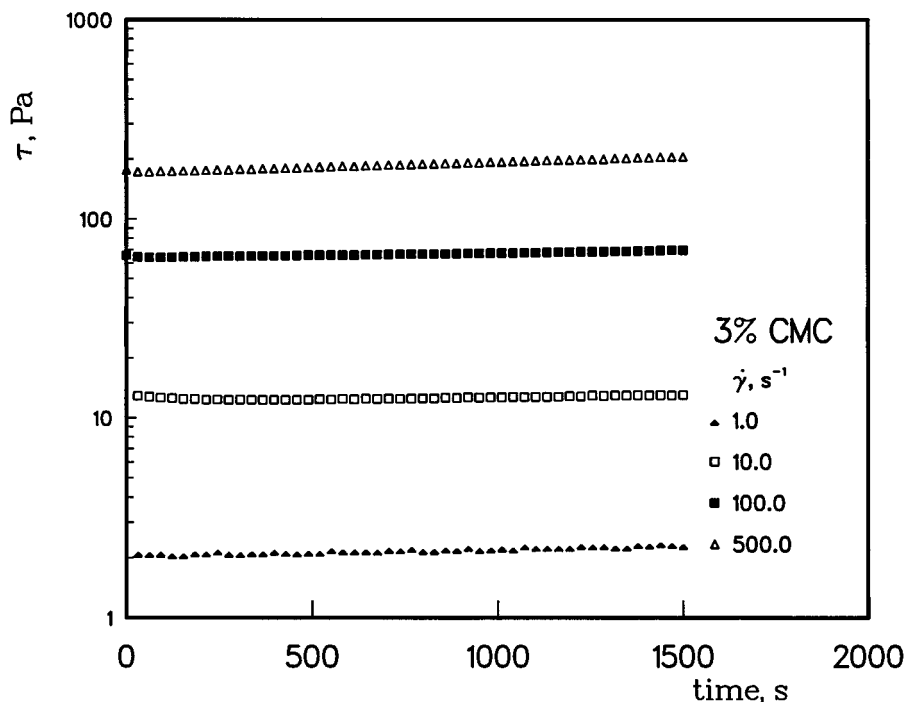
By increasing the concentration of CMC, the viscosity of each solution drops from a high value at shear rate of  $0.15 s^{-1}$  to a lower viscosity at

shear rate of  $1000 s^{-1}$ . Figure 2 shows a strong pseudoplastic behavior for all CMC concentrations from 2 to 5%. In practice, this means that the flow encounters less resistance at higher shear rates. CMC solutions contain long entangled and looping molecular chains, which have irregular internal order that forms high resistance against flow (higher value of viscosity). With increasing shear rates, chain type molecules in CMC solutions are disentangled, stretched, and reoriented parallel to the driving force. Molecular aligning allows molecules to slip past each other more easily and reduce the viscosity of the CMC solution.

### Transient Shear Stress Response

CMC solutions have complex rheological behavior. In an effort to reveal the transient characteristics of these solutions, transient tests were conducted for the concentrations 1 to 5%. The tests were performed for 25 min each, for a number of constant value shear rates over a range of  $0.2$  to  $500 s^{-1}$ . CMC solutions with 1, 2, and 3% concentrations showed no transient effects. Figure 3 illustrates this conclusion for the 3% solution. Solutions of 4 and 5% concentrations revealed some

**Figure 2** Viscosity–shear rate of aqueous solutions of CMC.



**Figure 3** Transient shear stress response as a function of shear rate for 3% CMC.

interesting pattern. For the lower range of shear rates 0.2 to 1.0  $\text{s}^{-1}$ , tests showed (Figs. 4 and 5) that shear stress increases rapidly over less than 100 s to a constant value for each shear rate applied.

Time dependence of shear stress is called rheopexy.<sup>7</sup> At shear rates higher than 10  $\text{s}^{-1}$ , CMC solutions did not exhibit rheopexy. Rheopexy is a characteristic behavior of viscoelastic liquids and liquids of a thixotropic structure. These rheological patterns will be discussed later in this article. Such complex rheopexy behavior is believed to be due to a limited structure breakdown at lower shear rates. The gradual increase or decrease in the resulting shear stress is attributed to structure recovery.

#### Yield Stress Measurements

The yield stress, or yield point, can be defined as a limiting stress below which a sample behaves as a solid. A lower stress causes an elastic deformation that elastically disappears when the applied stress is released. The elastic deformation is linearly proportional to the applied stress. Above the yield point, the applied stress causes unlimited deformation, and the sample starts to

flow. Under flow conditions, the applied stress is correlated to the rate of deformation with viscosity as the correlating factor.

Yield stress test was carried out for all the examined solutions of the range 1–5% CMC. This test employed controlled stress mode to ramp stress until the assigned stress surpasses the yield value and the sample starts to flow. In the first segment, the assigned stress ramped from 0.09 to 100 Pa to establish the up curve. Then, the assigned stress was instantaneously reduced from 100 to 0.09 Pa to develop the down curve. Figures 6–7 show the up and down curves for all the CMC solutions. Higher concentration of CMC produces higher cycles of up and down curves and, consequently, causes higher resistance to flow. However, none of the solutions showed any yield stress. The measurements showed, on the other hand, that the 4 and 5% solutions exhibit time-dependent rheological behavior.

#### Thixotropy

Our measurements of thixotropy were conducted under the controlled-rate CR mode. The apparatus was programmed to gradually increase the assigned shear rate from a given initial value to

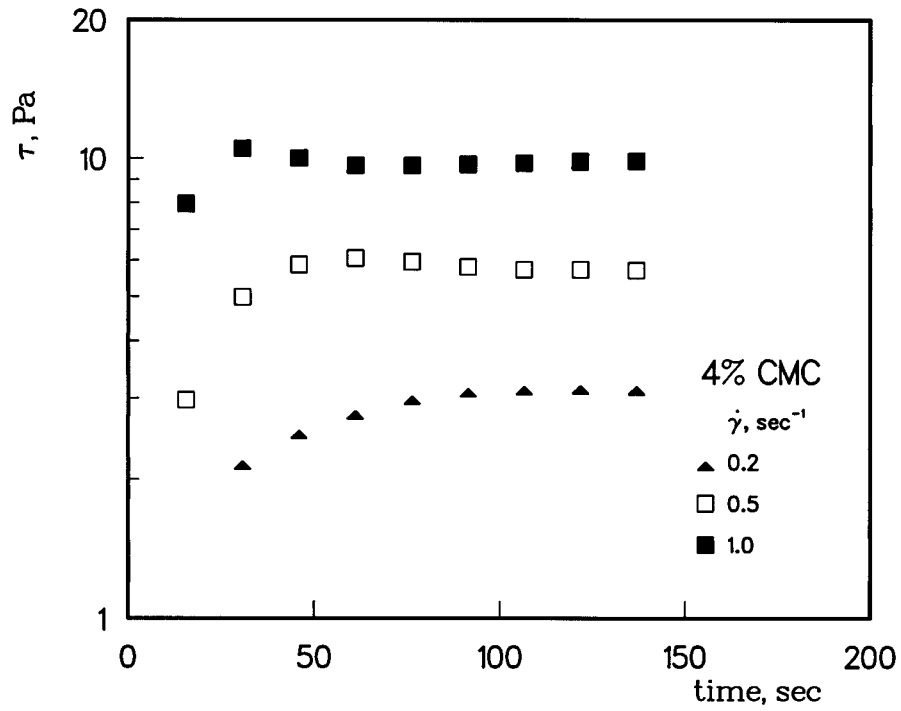


Figure 4 Transient shear stress response as a function of shear rate for 4% CMC.

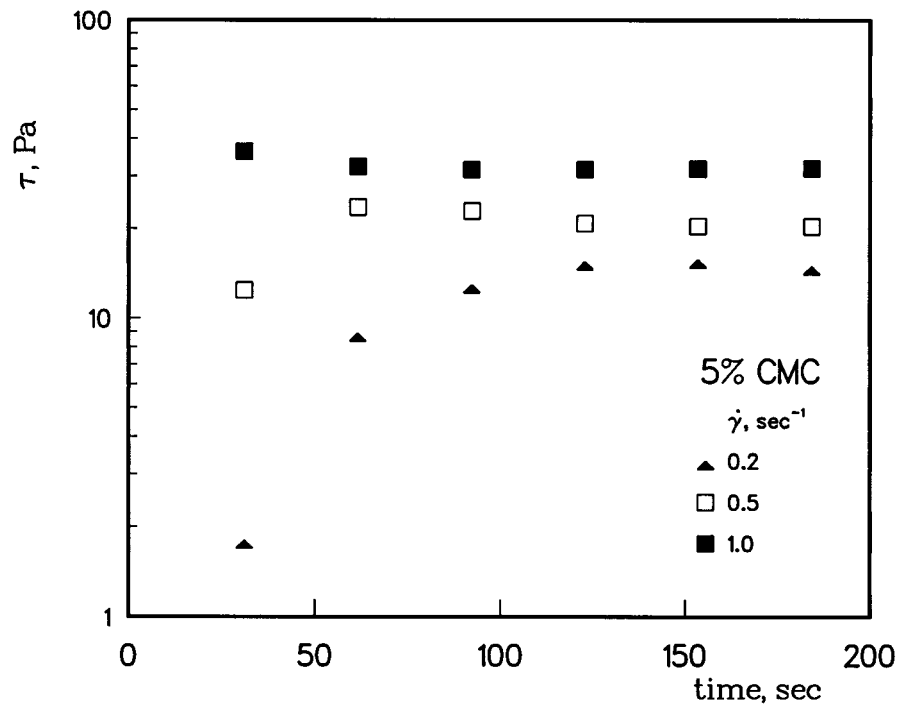


Figure 5 Transient shear stress response as a function of shear rate for 5% CMC.

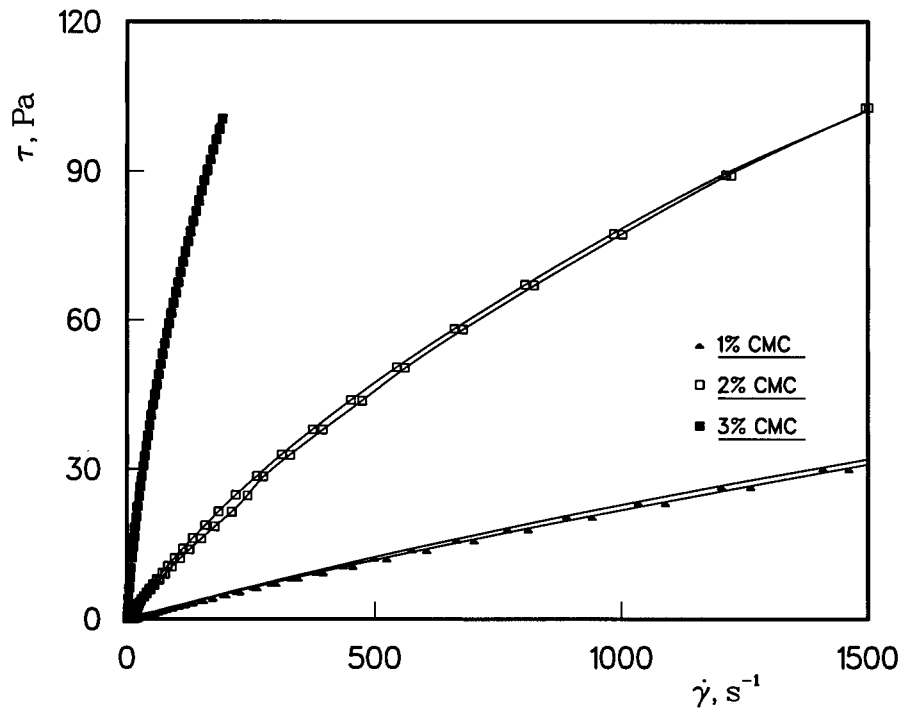


Figure 6 Yield stress and thixotropic response of 1–3% CMC solutions.

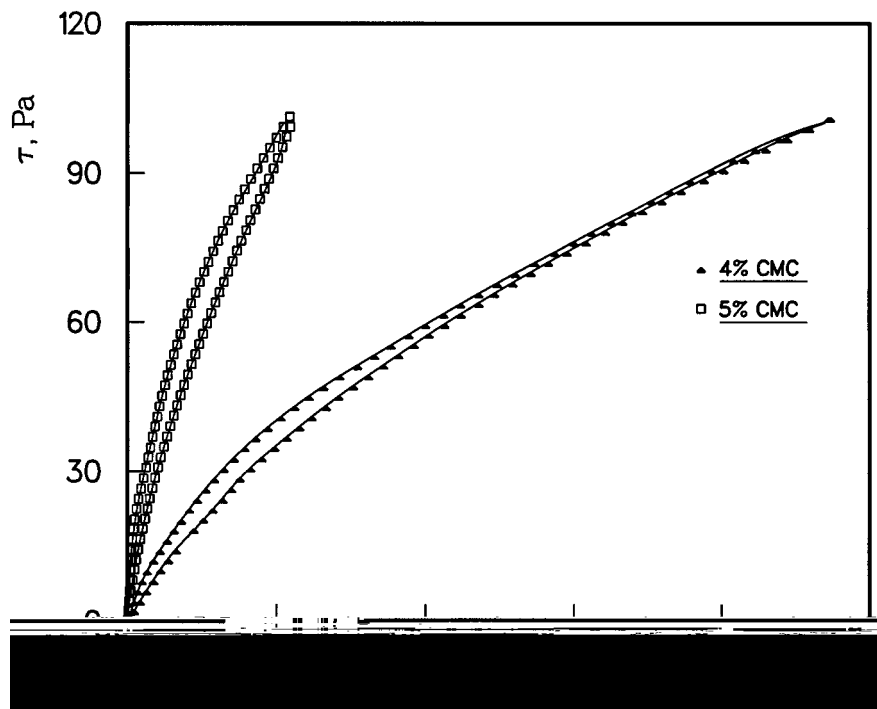


Figure 7 Yield stress and thixotropic response of 4–5% CMC solutions.

**Table II** 5% CMC Solution

Test (s)	Thixotropic Area (kPa s <sup>-1</sup> )
1 × 200	8.21
1 × 100	11.7
1 × 60	12.0
1 × 60	11.8

a terminal value. The stresses and the shear rates of flow were recorded. The resulting up curve was obtained in the process of gradually increasing the shear rate. After reaching the assigned maximum rate, a gradual decrease gives the down curve, which should be identical to the up curve for time-independent rheological behavior. The down curve of thixotropic solutions is different from the up curve. The curves form a hysteresis process that encloses an area A. Thixotropy of a solution is quantified by the solution ability to regain its gel structure when the liquid is allowed to rest for a longer period of time, after attaining the sol phase. The hysteresis area A of a sample that reached its sol structure is its thixotropy. It has the dimensions of energy over volume, i.e., the energy required to break down the thixotropic structure of the solution.

A linearly ramped shear rate cycle with a certain period of upward and downward shear change is often used to carry out the thixotropic test. The total breakdown of the thixotropic structure may not be completely attained in a single cycle. To completely destroy the thixotropic structure, a number of up and down cycles may be required before the up and down curves coincide. In a different approach, the sample is kept under the upper limit shear rate for a certain period of time. If the structure has been completely destroyed during this period, ramping down the applied rate establishes the full hysteresis area.

Tests were carried out for the 5% CMC solution using the two described techniques of studying the thixotropic behavior of CMC solutions. In the first technique, cycles of 200, 100, and 60 s for each of the up and down curves were carried out. The shear rate was ramped up from 0.15 to 749 s<sup>-1</sup> for the specified period and then immediately ramped down from 749 to 0.15 s<sup>-1</sup> in equal time. The total hysteresis area is summed up from the areas of all cycles. In the second technique, 60 second periods were used for the single cycle of upward ramped shear rate from 0.15 to 749 s<sup>-1</sup>,

constant 749 s<sup>-1</sup> rate, and downward ramped rate from 749 to 0.15 s<sup>-1</sup>.

Tests with more than one cycle for all experimental times showed a negative hysteresis area in the second or third cycles. A negative sign for the thixotropic area indicates that the down curve is positioned above the up curve. First, it was established that one cycle was sufficient to achieve the total hysteresis area. In addition, a rather high negative area of -3.52 kPa s<sup>-1</sup> was recorded in the second cycle of the experimental time 200 s per curve. This indicated that the sample was drying up during the test, and, consequently, the viscosity was increasing over the down curve. The thixotropic areas obtained in these tests are listed in Table II.

The test according to the second technique was essential to make sure that the gel structure of the 5% CMC solution has been completely destroyed. It included one cycle consisting of an up curve (0.15 to 749 s<sup>-1</sup>) for 60 s, a time curve at 749 s<sup>-1</sup> for 60 s, and a down curve (749 to 0.15 s<sup>-1</sup>) for 60 s. This process provided a thixotropic area of 12.8 kPa s<sup>-1</sup>, which was slightly higher than the 11.8 kPa s<sup>-1</sup>. Similar tests for the 4% solution were carried out using the second 3 × 60 s technique. The results of these experiments are reported in Table III.

Tests for 1–3% CMC solutions were conducted using a one-cycle, up and down curves, technique and the second technique, which included a time curve. All tests confirmed our earlier results of the transient study that these solutions (1–3%) are time-independent.

Our conclusion is that the thixotropic behavior of CMC solutions builds up with increasing concentrations. For solutions with concentration less than 4%, the thixotropic behavior is unnoticeable (Fig. 6). Solutions with 4 and 5% (Fig. 7) concentrations definitely exhibit thixotropic behavior, as described in Table III.

**Table III** Hysteresis Area (kPa s<sup>-1</sup>)

CMC Solution	4%	5%
Up curve	217.8	412.2
Time curve	0.0	0.0
Down curve	209.8	399.5
Total	8.0	12.7



### Creep Recovery Test

In order to reveal the viscoelastic characteristics of a solution, a sample should be tested for its response to a constant stress over time. Liquids that exhibit viscoelastic behavior have long chain molecules, which, at rest, loop and entangle with each other at a minimum energy state. Under deformation, these molecules stretch, increasing the bond vector angles and raising their energy state. If the cause of deformation is removed, molecules try to return to their original energy state. In pure elastic behavior, the deformation response to a constant shear stress  $\tau_0$  is linearly linked to its value and is maintained as long as the stress is applied. The deformation will disappear completely and simultaneously when the stress is removed. Viscoelastic response to an applied constant stress varies with the time of application. Initially, the network of molecules undergoes deformation within the mechanical limits of the network. Continuous deformations lead to dismantling of the network, and the liquid starts to flow. When the applied stress is removed, the total strain separates into a permanently maintained viscous part and a recovery elastic part. Viscoelastic behavior under lower values of stress usually has a linear response. In the range of nonlin-

ear responses, at higher stress values, elasticity and viscosity data are usually dependent on test conditions and the sensor system parameters.

Rheological systems that exhibit creep show a time-dependent strain  $\gamma(t)$  under a constant stress  $\tau$ , where

$$\gamma(t) = \tau J(t) \quad (2)$$

where  $J$  is compliance,  $\text{Pa}^{-1}$ .

The compliance of a sample is a material constant. The higher the compliance, the easier the sample can be deformed by a given stress. In the linear viscoelastic range, the compliance is independent of the applied stress. Consequently, the proper creep and recovery test conditions within the limit of linear viscoelasticity can be defined. In addition, linear viscoelasticity is a nondestructive test of measuring the rheological behavior of a sample. The deforming energy is recovered when the applied stress is released. This indicates the network ability to elastically deform while keeping the network intact.

For creep and recovery tests, constant shear stresses of few Pascals were applied instantaneously for 300 s to the samples. Following this period of time, the applied stress was brought in-

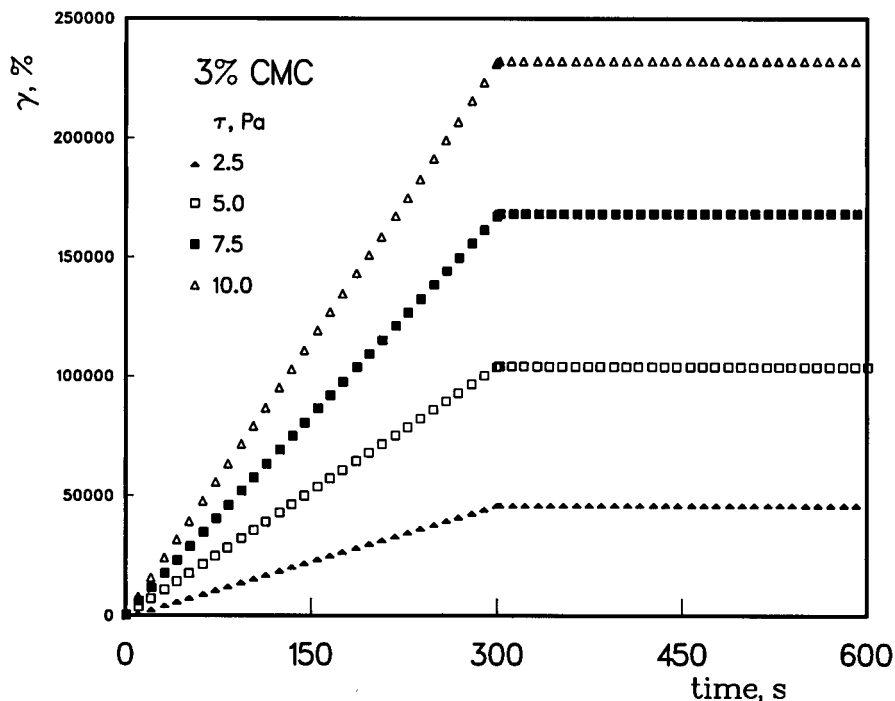
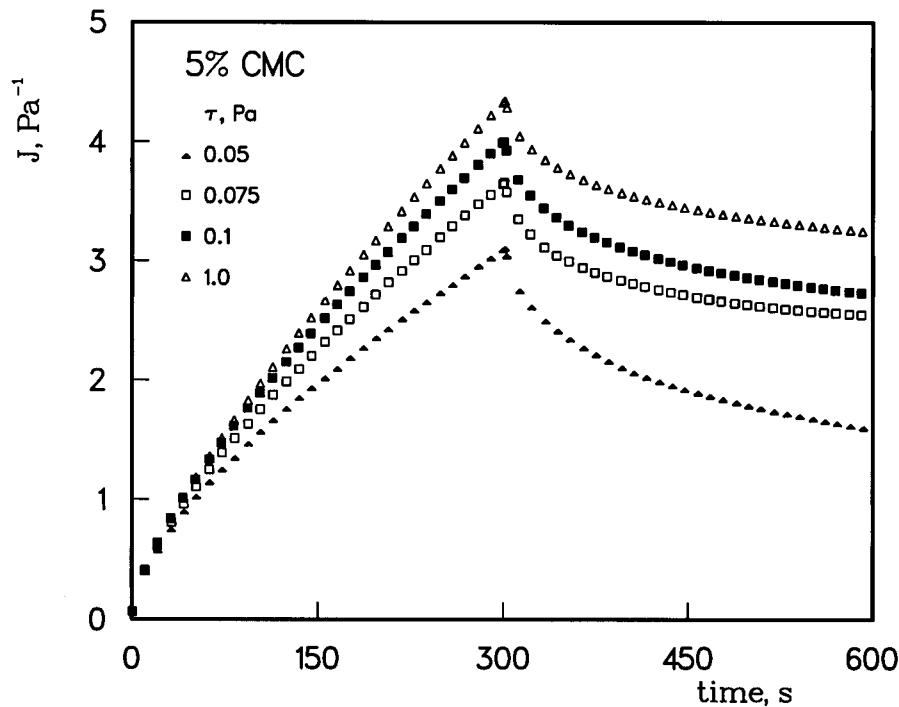


Figure 8 Strain of viscous response of 3% CMC.



**Figure 9** Viscoelastic response of 5% CMC in terms of compliance.

stantaneously to zero. The response deformations were recorded over a total period of 10 min in all cases. The RheoStress RS100 has an almost frictionless air-bearing for its rotor shaft. This feature was extremely important to creep recovery tests. The stress in the recovery phase of this test must be set to zero for full recovery to reach a final permanent strain level.

Compliance data  $J(t)$  for a 3% CMC solution at different values of applied shear stress 2 to 15 Pa were obtained. The linear viscoelastic range of this solution was limited to 10 Pa. The response to 15 Pa of stress was nonlinear. The resulting compliance for all shown stresses continued to be constant to the end of the test. The final strain (Fig. 8) was maintained when the stresses were removed. This is a purely viscous behavior. Similar results were obtained for 1 and 2% CMC solutions.

Figure 9 shows the creep and recovery test for 5% CMC solution for different values of applied stresses in the linear range 0.05 to 0.1 Pa, in addition to the value of 1 Pa in the nonlinear viscoelastic range. A time-dependent response is shown for the creep and recovery phases. In both phases, the response is nonlinear. The 5% CMC solution shows an elastic recovery in addition to

its viscous response. The response of the compliance  $J$  (Fig. 9) and strain  $\gamma$  to the instantaneous removal of stress can be reduced to three steps. Initially, both undergo a step reduction as a pure elastic response. This is followed by an exponential decrease related to a viscoelastic response. Finally, the  $J$  and  $\gamma$  values approach a constant limit, corresponding to the nonrecovered deformation of the viscous flow.

Figure 10 shows the creep and recovery results for the 4% CMC solution. In the creep phase within the first 300 s of the tests, there is a linear increase of compliance  $J$  and strain  $\gamma$  for all the applied constant stresses from 0.25 to 1 Pa. However, in the recovery phase, the response shows a viscoelastic behavior, which is less intense than the one shown by the 5% CMC solution.

### The Dynamic Test

Substances with thixotropic behavior have a weak structure that may be temporarily destroyed under a constant or dynamic shear. Viscosity drops with time and the substance structure changes from gel to sol. When left at rest, these substances can recover their original gel structure. The re-

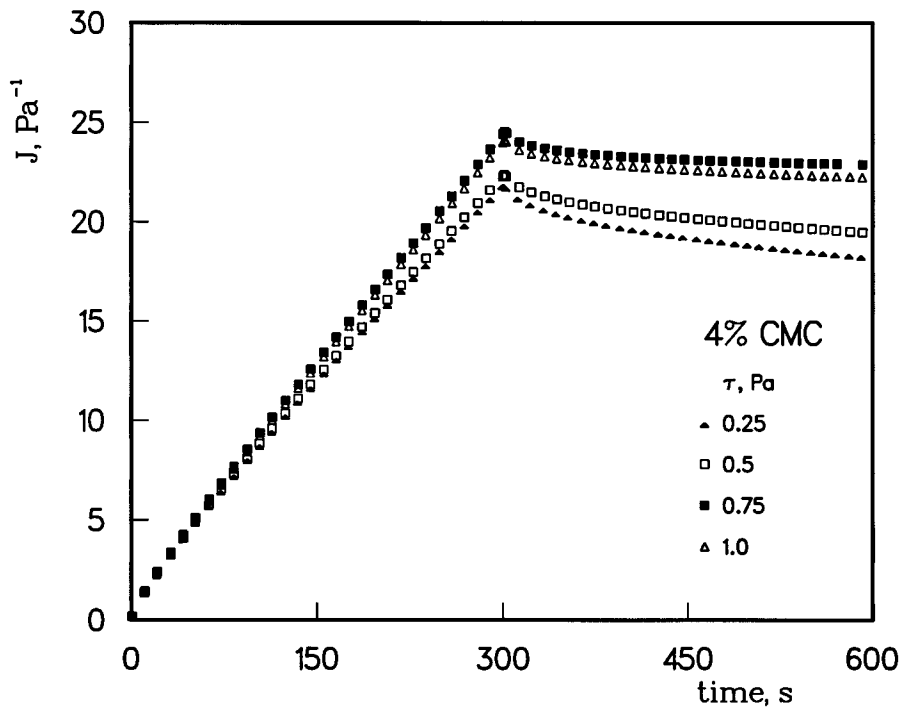


Figure 10 Viscoelastic response of 4% CMC.

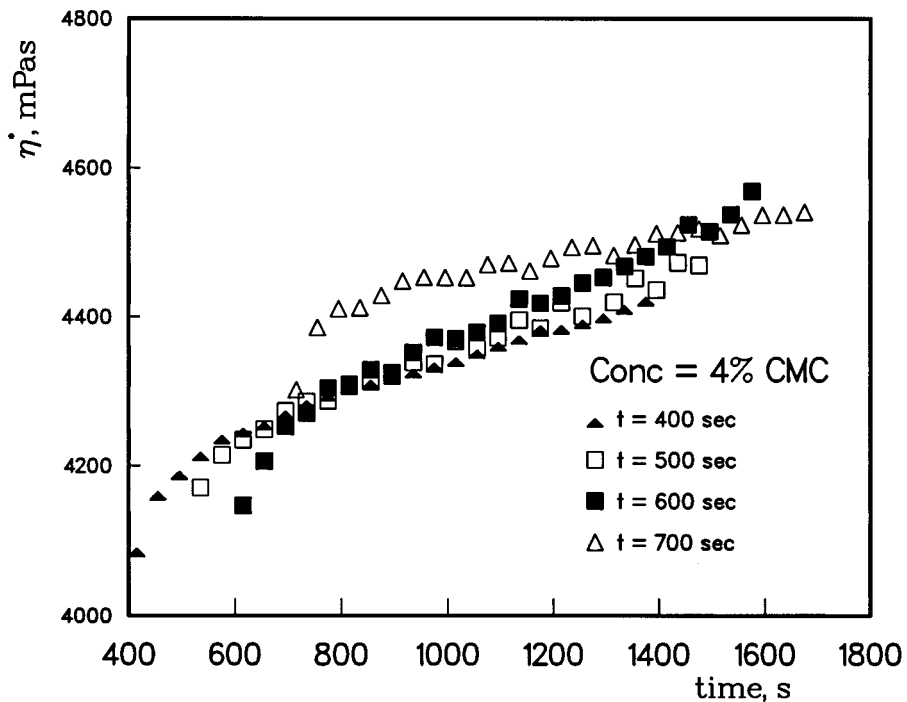


Figure 11 Recovery of complex viscosity for 4% solution.

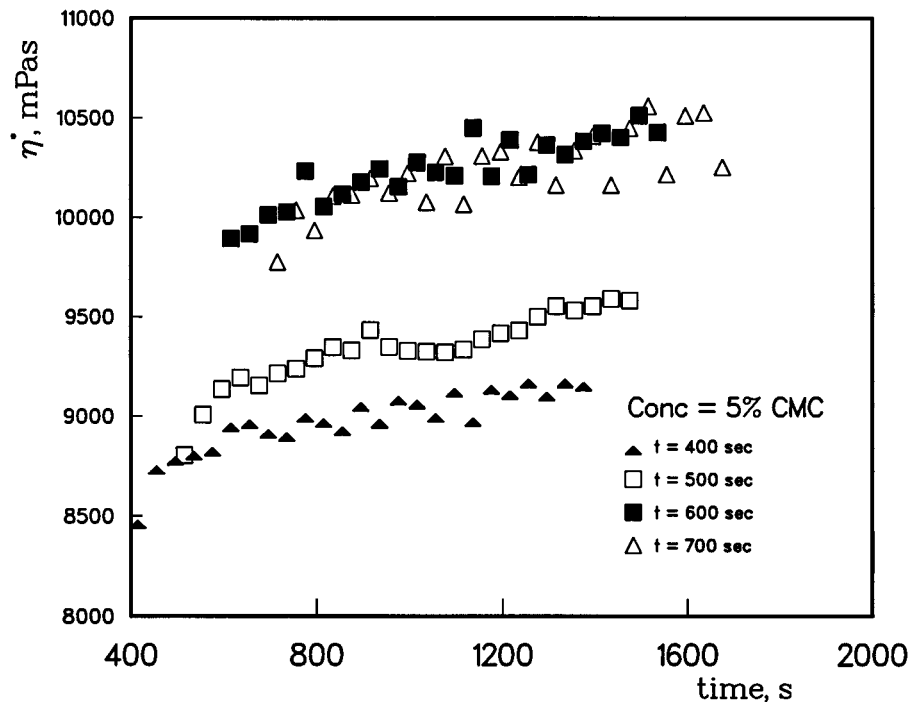


Figure 12 Recovery of complex viscosity for 5% solution.

building of this structure and the associated increase in viscosity is time-dependent. For many applications, the rate of structure regeneration is very important. This is particularly so in cases of liquid coating.

In a preliminary test, the value of shear rate required to completely destroy the structure of CMC solutions was determined. A constant shear rate of  $500 \text{ s}^{-1}$  was applied to the CMC solutions over different periods of shear time (10, 50, and 100 s). The amount of recovery was increasing with the initial duration of network destruction. We concluded in this test that the application of shear rate of  $500 \text{ s}^{-1}$  over 600–700 s is sufficient to completely destroy the structure of 4% CMC solution. We used the same experimental routine in measuring the recovery response of 4 and 5% CMC solutions, after a complete destruction of their structure. Figures 11 and 12 show these recovery responses. It takes both the 4 and 5% CMC solutions about 900 s to recover its viscosity. Dynamic tests for 1 to 3% CMC solutions confirmed that they don't exhibit thixotropic behavior.

## CONCLUSIONS

The rheological behavior of 1 to 5% carboxymethyl cellulose solutions were measured using a Rheo-

Stress RS100 rheometer at room temperature of  $23^\circ\text{C}$ . The rising concentration of CMC in the solutions transforms the behavior from Newtonian to shear thinning. The higher the concentration is in the solution, the lower the flow behavior index. The increase in CMC concentration is accompanied by stronger time-dependence of the rheological properties. This was particularly noticeable at lower shear rates ( $<10 \text{ s}^{-1}$ ). The time-dependence was not detected for CMC solutions lower than 4% weight concentration. Rheopexy behavior is attributed to the structure recovery of the CMC solution, which is dependent upon the CMC concentration and the shear rate applied. Our measurements did not depict yield stress for any of the tested solutions. The thixotropic hysteresis area significantly increased when the concentration increased from 4 to 5%. The creep recovery tests showed that CMC solutions with weight concentrations lower than 4% exhibit purely viscous behavior. Linear visco-elastic behavior was observed for the 4 and 5% CMC solutions. The higher concentration showed stronger viscoelasticity. The solutions were subjected to a dynamic test. The data were measured in terms of the complex viscosity  $\eta^*$  as a function of frequency. The recovery time of the 4 and 5% CMC solutions to their origi-

nal gel structures after preshearing to sol was determined to be about 900 s.

## REFERENCES

1. M. Windholz, S. Budavari, R. Blumetti, and E. Otterbein, *An Encyclopedia of Chemicals, Drugs, and Biologicals*, Merck, Rahway, NJ, 1983.
2. S. Irving and R. Lewis, *Hawley's Condensed Chemical Dictionary*, Van Nostrand Reinhold, New York, 1987.
3. S. McCoy, C. Zuritz, and S. Sastry, ASAE Paper No. 87-6536, ASAE International Winter Meeting, Chicago, Illinois, 1987.
4. K. Abdelrahim, H. Ramaswamy, G. Doyon, and C. Toupin, *Int. J. Food Sci. Technol.*, **29**, 243 (1994).
5. M. Planas, C. Garcia, J. Dominguez, and R. Maximino, *J. Pharmaceut. Sci.*, **80**, 75 (1991).
6. S. Young and C. Shoemaker, *J. Appl. Polym. Sci.*, **42**, 2405 (1991).
7. Y. Nakai, Y. Ryo, and M. Kawaguchi, *J. Chem. Soc. Faraday Trans.*, **89**, 2467 (1993).