Thixotropy Measured Using a Weight-Actuated Viscometer

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Abstract □ A method of quantitatively measuring structure breakdown and buildup of thixotropic substances using a weight-actuated viscometer was proposed. This approach eliminated the problems involved in obtaining the classical loop of hysteresis and furnished, instead, data on the actual rates of breakdown and buildup of the systems. Bentonite magmas of different concentrations were prepared, and the change in the apparent viscosity was measured as a function of time. The effects of concentration and shelflife on the static yield values of the systems were evaluated.

Keyphrases □ Thixotropy measurements—using a weight-actuated viscometric method, bentonite magmas measured, concentration and shelflife effects □ Viscometry—weight-actuated viscometric method proposed for thixotropic measurements, bentonite magmas measured □ Viscosity—weight-actuated viscometer, used for thixotropic measurements of bentonite magmas

The Stormer viscometer has been used extensively in rheological research on pharmaceutical systems (1–7). Although certain investigators used the instrument to measure thixotropic systems by examining the typical area of the loop of hysteresis created by constructing an "up" curve and a "down" curve, the technique has considerable inherent difficulties. The problems arise because the Stormer is a weight-actuated viscometer where the independent variable is the shearing stress (expressed as g.) placed on the instrument. This stress imparts a given number of revolutions per minute to the rotor immersed in the sample fluid. The value for the rate of shear is usually obtained by measuring the time required for 100 revolutions of the rotor, which may range from 15 to 200 sec. depending on the material and the weight used. The disadvantage is that instead of obtaining an immediate value for the shearing rate, as is the case with many more elaborate commercial viscometers, it may take as long as 3 min. to obtain a reading. Not only is structure being lost during this time, but the rate of shear obtained is really an average value for the first 100 revolutions of the rotor. Frequently most of the structure may have been broken down by the end of 100 revolutions, and no information will have been gathered as to the rate of breakdown during this crucial period.

Another serious drawback lies in the manual rewinding of the thread and in the changing of weights. Although this can be done rapidly with practice, some structure rebuilding still occurs during the time elapsed. This becomes more critical in the case of materials that restructure quickly. It can be seen, therefore, that to obtain data properly for the classical loop of hysteresis representation, it is paramount to take stress-shear readings in immediate succession. In light of these considerations, it is not possible to use the Stormer viscometer.

In view of the established value of the Stormer viscometer as a rheological tool, the purpose of this investigation was to find a different approach to the measurement of thixotropic systems that would be compatible with the idiosyncrasies of a weight-actuated viscometer. The only reported attempt to use the Stormer viscometer in a different manner was to note the increase in time for 100 revolutions of the rotor at a constant shearing stress in the study of an antithixotropic magnesia magma (8). In this instance, of course, a buildup of structure rather than a breakdown occurred, and measurements were taken until the rate of shear decreased to an equilibrium value. The study, however, did not follow through with the calculation of any rates and it did not account for the fact that a large proportion of the buildup took place in the first 100 revolutions.

An attempt to demonstrate first-order dependence of the decrease in shearing stress with time of thixotropic emulsions exposed to a constant rate of shear was reported (9). The data obtained showed a linear relationship when the logarithm of the shearing stress was plotted against time. It was, therefore, postulated that a similar approach could be used for a weight-actuated viscometer, except that the weight or shearing stress would be constant and the increase in rate of shear would be measured as a function of time. This means that the apparent viscosity decreases as the constant stress is maintained, providing the evidence for structure breakdown. If the technique of reading data on the Stormer viscometer could be so modified as to record the time necessary for one or two revolutions of the rotor rather than for a minimum of 100, then a true rate of breakdown of structure as reflected by the decrease of the apparent viscosity with time could be shown.

The second part of the investigation, often neglected in thixotropic studies, would of necessity have to be the rate of buildup or healing of the structure. This aspect really presents no data-gathering problems since the minimum weight needed to produce movement of the rotor can be obtained for various sample shelflife periods and the rate of buildup or increase in static yield value with time can be graphically recorded.

EXPERIMENTAL

Preparation of Samples—Bentonite USP was the thixotropic material used because of its established characteristics and ease of preparation. The samples were prepared by spreading the bentonite over the surface of distilled water preserved with 0.2% benzoic acid and previously heated to 50°. After 24 hr. of hydration, the magmas were sheared for 5 min. in a blender (Waring) and stored in 100-ml. graduated beakers, sealed with aluminum foil. The concentration by weight of bentonite in the samples ranged from 5 to 10%.

Rheological Measurements—A Stormer viscometer was used, and the shearing stress was applied by means of a weight hanger with various slotted weights. The instrumental constants, K_v, were

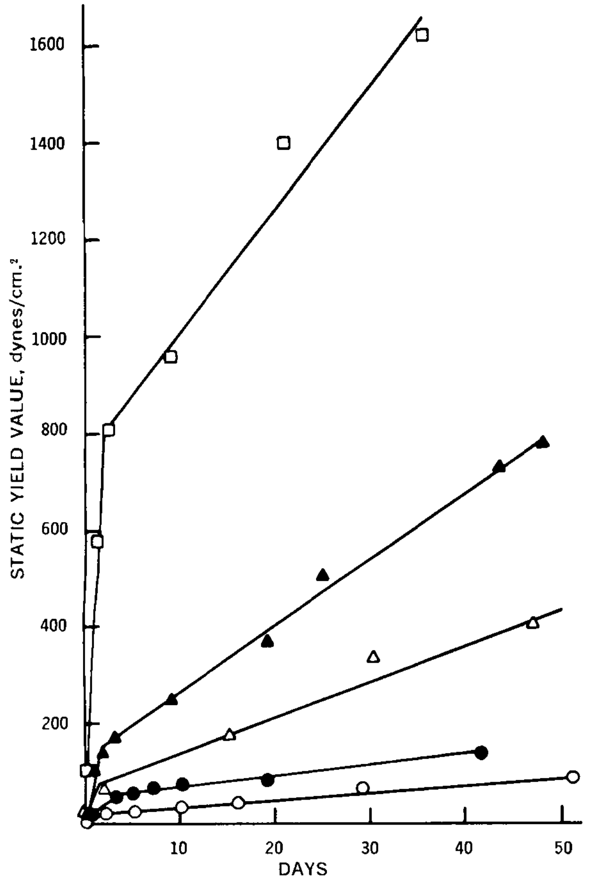

Figure 1—*Rate of restructuring of bentonite magmas. Key:* ○, *5%;* ●, *6%;* △, *7%;* ▲, *8%; and* □, *10%.*

determined from calibration data obtained using viscosity standard oils (Brookfield), and they were appropriately applied depending on the shearing stress to rate of shear ratio. The apparent viscosity was then calculated from the expression:

$$\eta = K_v \frac{\text{g.}}{\text{r.p.m.}} \qquad \text{(Eq. 1)}$$

where g. represents the shearing stress, r.p.m. represents the rate of shear, and η is the apparent viscosity in centipoises. All viscosity measurements were recorded at 35 ± 0.2°. The sample volume of magma used was 80 ml. The static yield value, f, was obtained from the expression:

$$f = K_f W_f \qquad \text{(Eq. 2)}$$

where K_f is a constant involving K_v and the dimensions of the instrument, and W_f is the extrapolated yield value intercept in shearing stress.

Several modifications were necessary which departed from the usual method of data collection with the Stormer viscometer. Instead of the cup furnished with the instrument, 100-ml. beakers already containing the samples were employed. This modification avoided structure disturbance of the samples caused by transferring from one container to another. To obtain satisfactory data, a specially designed star-shaped rotor[1] for thixotropic materials was constructed. The dimensions of the rotor were 3.8 × 3.2 cm. (1.47 × 1.25 in.). The slight variations in diameter among the various 100-ml. beakers did not affect the reproducibility of the measurements.

The dial provided with the instrument for recording the number of revolutions of the rotor is marked off in increments of one revolution. However, by using the dial, the minimum number of revolutions that could be read with any degree of accuracy was found to be 10. Since the time required for one, two, or five revolutions of the rotor was essential information in the initial breakdown period, these readings were actually made by etching two thin lines, one on the stationary part of the rotor housing and the other just below it on the movable rotor shaft. Thus, one complete revolution was recorded when the line on the shaft, as it rotated, returned to its initial position with reference to the stationary mark. This method greatly minimized the error involved in measuring a small number of revolutions. In timing 10 or more revolutions, the readings were made on the dial.

Table I—Rate Constants for the Restructuring of Bentonite Magmas

Percent w/w	K_1	K_2
5	7.38	1.50
6	14.4	1.93
7	29.5	7.57
8	63.0	13.7
10	269	25.2

Obviously, the readings have to be made rapidly and expertly. To accomplish this objective, a rig for three stopwatches which could be operated simultaneously was constructed. While one watch was registering the time for the revolution being run, the second watch was ready to start recording as soon as the first one stopped, and the third one was resetting. This setup gives a continuous reading of each revolution and enough time to record the setting on each watch. With a little practice, a technician can become proficient at taking readings in this manner.

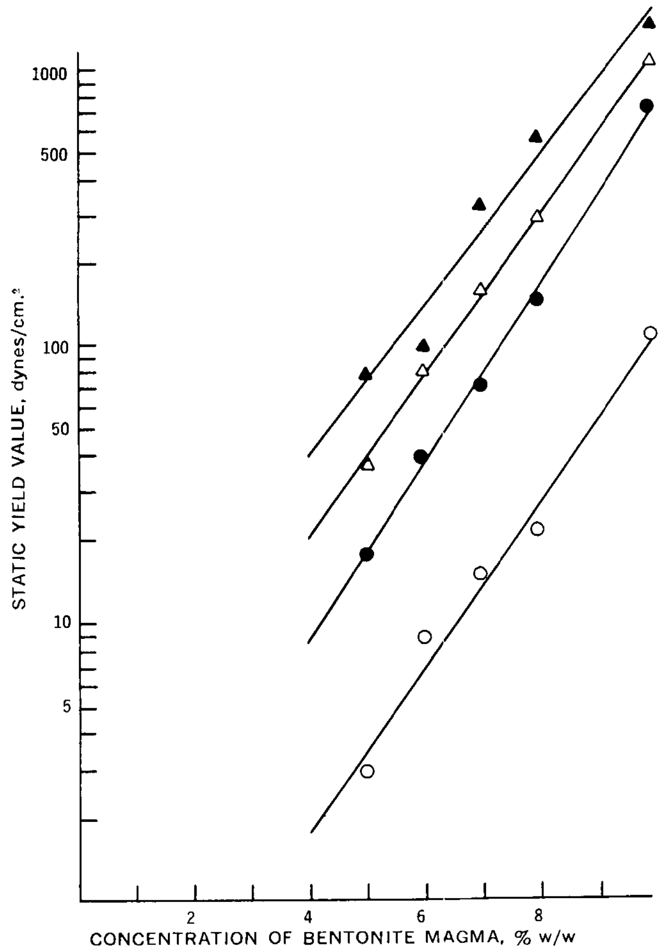

Figure 2—*Effect of concentration and shelflife on the yield value of bentonite magmas. Key:* ○, *no shelflife;* ●, *2-day shelflife;* △, *10-day shelflife; and* ▲, *30-day shelflife.*

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[1] Its design is similar to the star-shaped rotor series used with the Haake Rotovisco rotating viscometer (Haake Rotovisco FL Series Rotors, Polyscience Corp., Evanston, Ill.).

Table II—Rate Constants for the Breakdown of Bentonite Magmas

Shelflife, Days	K_1	K_2
	5% w/w	
2	0.0373	0.00901
5	0.0778	0.0149
10	0.1089	0.0308
16	0.3297	0.0951
29	0.2939	—
51	0.6209	—
	6% w/w	
5	0.0755	0.00401
7	0.1643	0.0161
19	0.1938	0.0434
42	0.5018	0.0345
	7% w/w	
2	0.2622	0.0664
9	0.3782	0.0521
15	0.5651	0.0760
24	0.2998	0.2281
47	0.5838	—
	8% w/w	
4[a]	0.3051	0.0741
2	0.3483	0.1992
25	0.4896	—
	10% w/w	
2[b]	0.0535	0.0882
10[b]	0.0223	0.0987
62[a]	0.1486	0.4035
21	0.0015	0.5180

[a] Shelflife in hours. [b] Shelflife in minutes.

RESULTS AND DISCUSSION

The approach used to describe the thixotropic systems studied permitted the calculation of rate constants for both phases of the investigation: breakdown and restructuring of the bentonite magma.

Restructuring of Bentonite Magmas—Figure 1 shows the rate of restructuring of the various concentrations of the bentonite magma. There appear to be two different rates of recovery for each. A rapid buildup occurs within the first 2 days and a slower rate is observed subsequently. Both rates, however, seem to follow a zero-order relationship. The two zero-order rate constants, K_1 and K_2, which constitute the slope of the line at each stage were calculated for each concentration (Table I). At the end of 45 days, restructuring was still occurring.

Certain inferences can be derived from the results shown in Fig. 2. The increase in yield value with increased concentration of bentonite over the range studied apparently followed a first-order relationship. This was observed regardless of the shelflife of the sample. Furthermore, the slopes of the lines in Fig. 2 for the four storage time intervals vary only from 0.279 to 0.319. This seems to indicate that the rate of increase in yield value with concentration does not vary significantly with the shelflife of the sample. These considerations seem to indicate that the mechanism of restructuring is the same irrespective of storage time.

Breakdown of Bentonite Magmas—In this phase of the study, the static yield value stress was applied to a sample of a given concentration and a given shelflife. The time required for one revolution of the bob was recorded. The same stress was continually maintained, and the time for subsequent revolutions of the bob was measured.

The apparent viscosities at increasing intervals of time under the given stress were calculated until the apparent viscosity of the sample became constant. This constant apparent viscosity (cps.$^{\infty}$) was subtracted from the apparent viscosity measured at different times, and the first-order plot was obtained showing the rate of decrease in apparent viscosity with time.

The rate of decrease in apparent viscosity with time, much like the restructuring of the bentonite magmas, occurred in two stages: an initial rapid rate of breakdown of structure followed by a second, less pronounced, linear decrease in viscosity until the cps.$^{\infty}$ was reached. The two first-order rate constants, K_1 and K_2, which constitute the slope of the line at each stage were calculated for each sample (Table II).

It can be seen that, in general, the higher the concentration of the sample the less difference existed between the two rate constants. Actually, in the case of the 10% samples, the second rate constant was higher than the first, possibly because of the greater resistance to a given stress shown initially in the higher concentration samples; this resistance seems to be overcome after a certain period. Some samples with very long shelflives evidenced only one rate of decrease in the apparent viscosity throughout the application of the static yield value stress.

Thus, it is possible to characterize fully a thixotropic system by means of a weight-actuated viscometer and to calculate rate constants for the rate of recovery and the rate of breakdown of bentonite magmas.

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