TA Instruments

Thermal Analysis & Rheology

YIELD STRESS MEASUREMENTS USING CONTROLLED STRESS RHEOMETRY

BY

JOHN R. SEMANCIK

SUMMARY

The stress (force) required to initiate flow (yield) in fluid or semisolid products is an important parameter for predicting the product's processing and/or end-use performance. Quantifying yield stress, however, must be done carefully because the value obtained depends on the analytical technique used. Hence, the measured stress where yielding occurs is usually referred to as the "apparent yield stress". Controlled stress rheology provides a more sensitive measure of this apparent yield stress than controlled rate rheology.

INTRODUCTION

A number of rheological properties play an important role in determining how a material behaves as it moves from a static to a dynamic environment and vice versa. For example, the force or stress required to initiate flow of fluid and semi-solid products plays a significant role in the storage, transfer, packaging, and end-use performance of those materials. Likewise, the force or stress level at which appreciable flow stops once initiated may also be of interest (i.e., ideally discharge of a product from a loading nozzle or pouring spout should terminate without excessive dripping). The stress level required to initiate flow is usually referred to as "yield stress" and is related to the level of internal structure in the material which must be destroyed (overcome) before flow can occur. Conversely, the stoppage of flow once the stress is removed is related to the rebuilding of structure. This paper deals with the former phenomena (yield stress). Structure rebuilding and issues such as thixotropy are discussed elsewhere. (1)

The destruction and rebuilding of structure are kinetic processes with characteristic relaxation times. Hence, the time frame of the test used to determine yield stress may influence the value obtained. In addition, the sensitivity or smallest incremental amount of stress which can be added to observe a change in behavior also has an effect. As a result, the yield stress determined by a given analytical technique is usually referred to as the "apparent yield stress". Although this "apparent yield stress" may not represent the theoretically correct value, it is still extremely useful in comparing and predicting material behavior.

Rotational rheometry is an analytical technique which can be used to determine apparent yield stress. The two common approaches used in rotational rheometers are shown in Figure 1. In the controlled rate approach, the material being studied is placed between two plates. One of the plates is rotated at a fixed speed and the torsional force produced at the other plate is measured. Hence, speed (strain rate) is the independent variable and torque (stress) is the dependent variable. In the controlled stress approach, the situation is reversed. A torque (stress) is applied to one plate and the displacement or rotational speed (strain rate) of that same plate is measured.

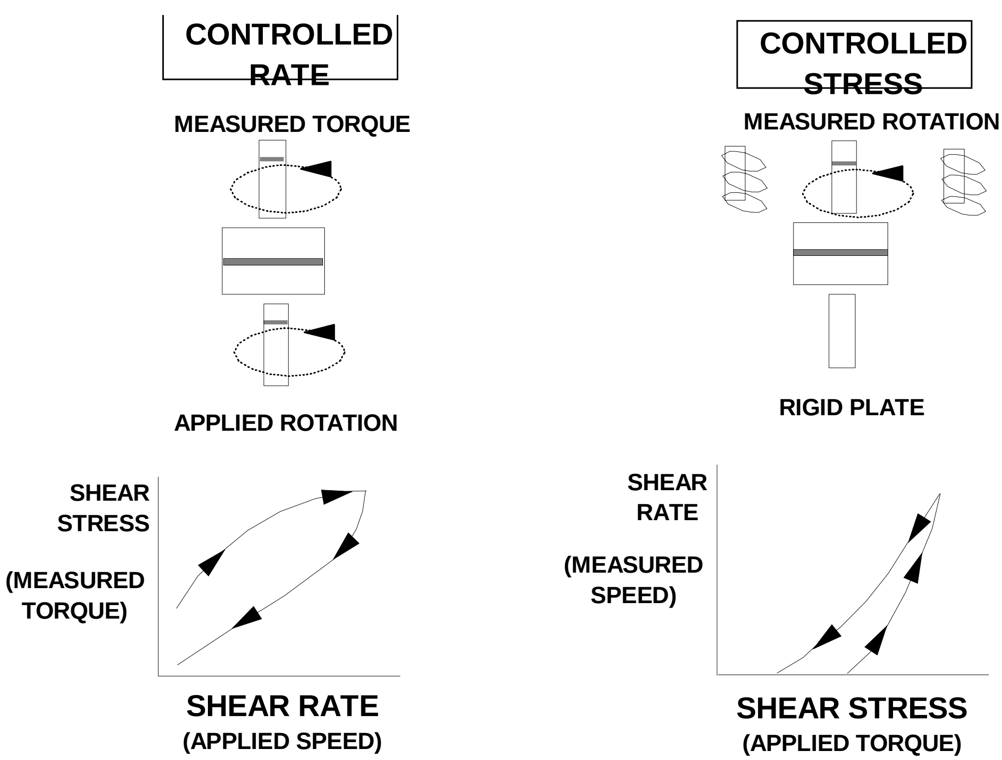

Figure 1

This latter approach (controlled stress) is the better approach for determining apparent yield stress because the variable of primary interest can be more carefully controlled. That is, in the controlled stress approach it is possible to gradually increase the stress applied to the material and detect the point at which movement (yield) first occurs. Conversely, in the controlled rate approach, movement (yielding) actually has to be occurring before measurement can even occur. Hence, apparent yield stress can only be measured by back extrapolation from a finite level of motion to the point of "zero motion" or yielding. The remainder of this discussion considers only controlled stress measurements.
The controlled stress approach provides three alternative experimental methods for determining apparent yield stress:

(1) Stress can be ramped slowly from zero to some higher value. The stress level at which motion first occurs is the apparent yield stress. As indicated previously, this value may be affected by the stress ramp rate (rate of stress increase).

(2) After initially shearing the material at a stress above the yield stress, the stress can be decreased in a slow ramp and the point where motion stops is the apparent yield point. Again as indicated previously, this value may be affected by the decreasing ramp rate and the time-dependent ability of the material to rebuild structure.

(3) A creep experiment can be used where stress is applied to the material and strain (displacement) is monitored with time to establish an "equilibrium" yield stress. Typical creep curves are shown in Figure 2. A purely elastic material (solid line) shows an instantaneous response to the stress and then no further response until complete recovery instantaneously occurs when the stress is removed. A purely viscous material (broken line) shows a constant rate of increasing strain until the stress is removed, at which time the material remains at its current level of deformation. Most real world materials are viscoelastic in nature and exhibit creep behavior between these two extremes (Figure 3). The resultant profile has three regions - a initial elastic region, a transition region, and a viscous region. From the slope of the viscous region, a viscosity (stress/strain rate) can be determined. By running a series of creep experiments at different stress levels and plotting viscosity versus stress, the apparent yield stress is represented by the point of abrupt change in viscosity.

Since creep is a low frequency (long-time) measurement, the apparent yield stress determined by this method agrees better with theory than the first two controlled stress approaches.

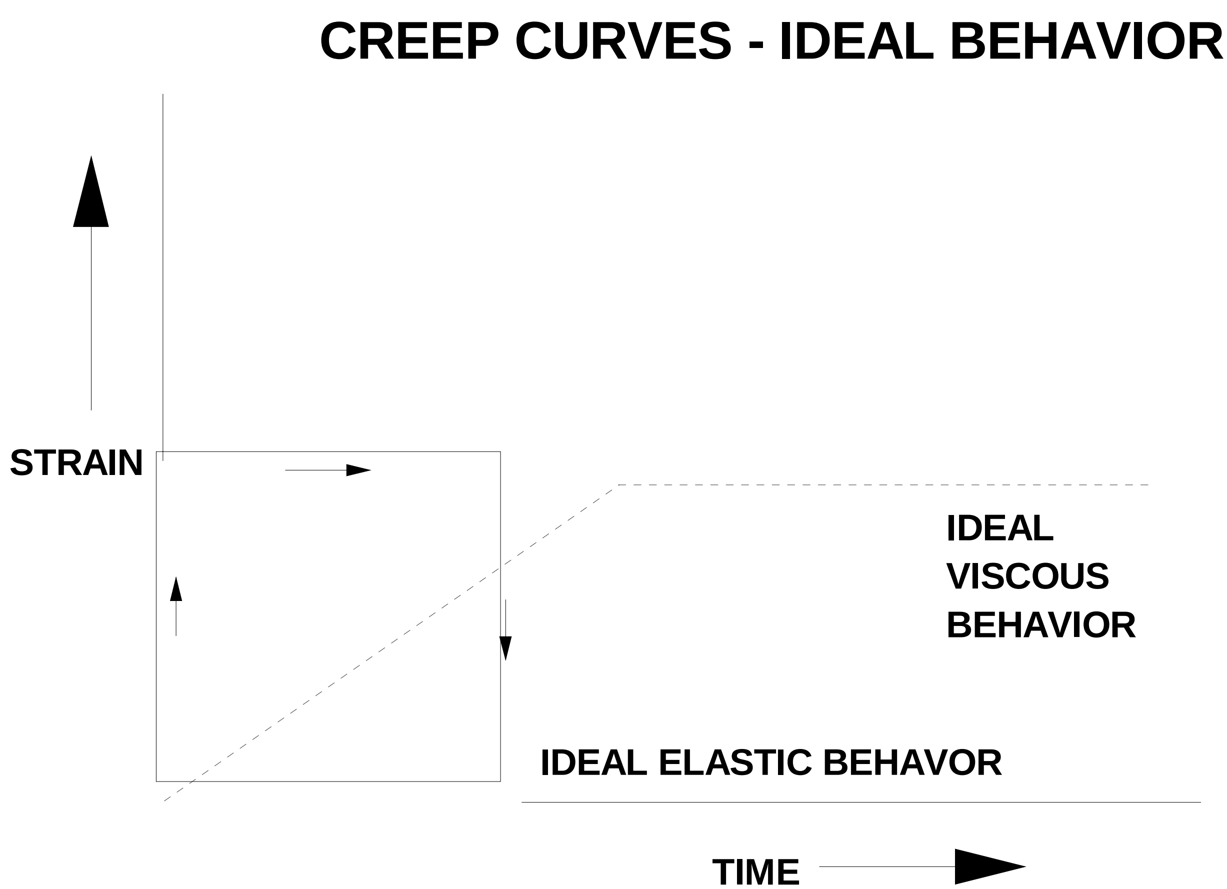

Figure 2

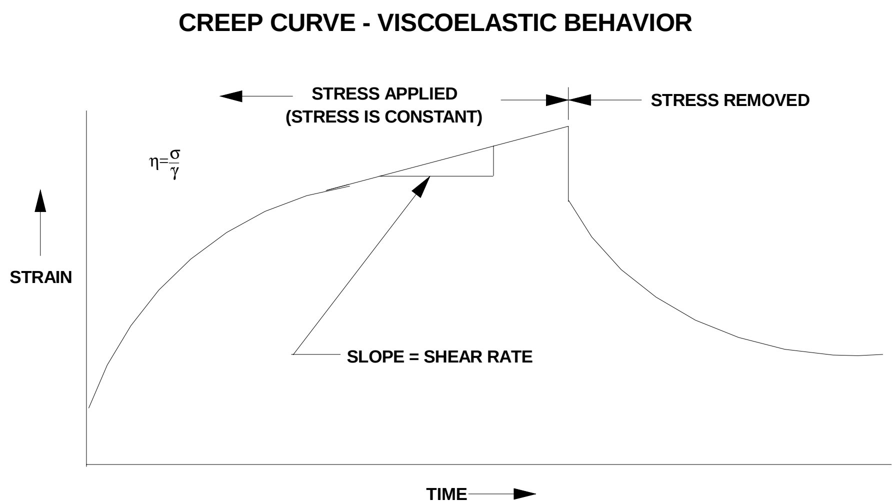

Figure 3

EXPERIMENTAL

A TA Instruments CSL² Controlled Stress Rheometer was used in this study to evaluate the yield stress behavior of a variety of typical food products. This unit has a drag cup motor drive system, an air bearing mounting for the measurement system, a sensitive optical encoder for measuring displacement and a rapid response Peltier heater (-15 to 100°C). These components, as well as other features (light weight measurement geometries with solvent trap capability, autogap set, and inertia & air bearing drag corrections) beneficial for evaluating softer solids and liquids (2, 3), make the instrument ideal for yield stress experiments.

RESULTS

Figure 4 illustrates the creep results for a commercially available cheese spread. In this case, a stress of 5 N/m^2 was applied for 5 minutes and then removed. The curve exhibits typical behavior for a viscoelastic material. The retardation portion of the curve can be evaluated with suitable software to give information about the specific theoretical model followed by this material. Of more importance here is the calculation and replot of the results to give the compliance versus time and viscosity versus shear stress plots shown in Figures 5 and 6 respectively. These figures are based on "Figure 4 - type" creep curves at several different levels of applied stress. Figure 5 shows that the material at low stresses has almost no compliance (yield) but at some level of stress yields dramatically. Figure 6 shows this phenomenon more clearly as a dramatic viscosity change once a sufficient amount of stress is applied. This "equilibrium yield stress" is 400-450 N/m^2(Pa).

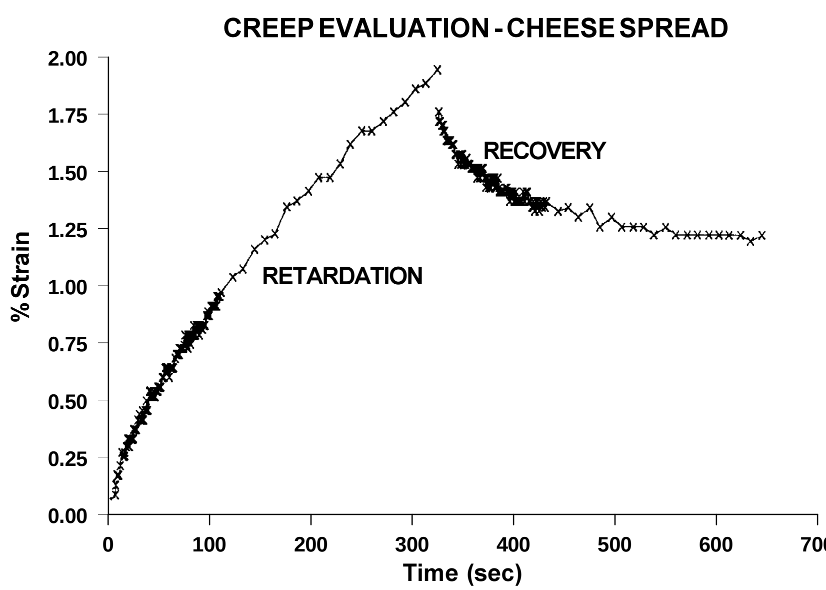

Figure 4

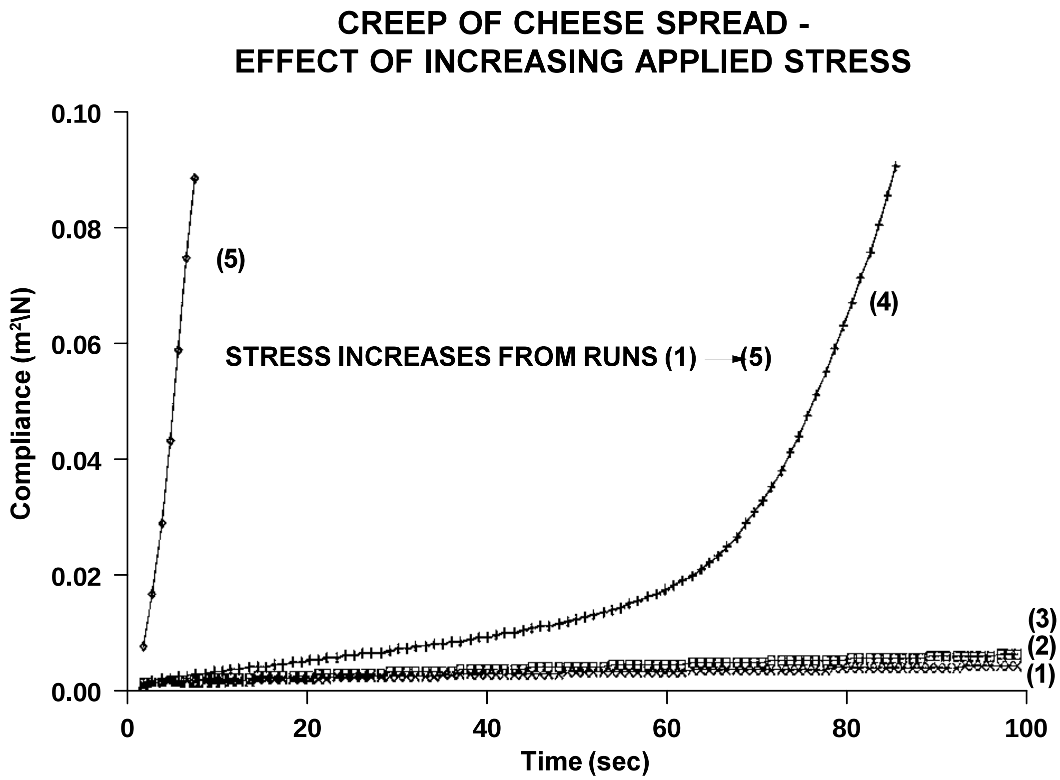

Figure 5

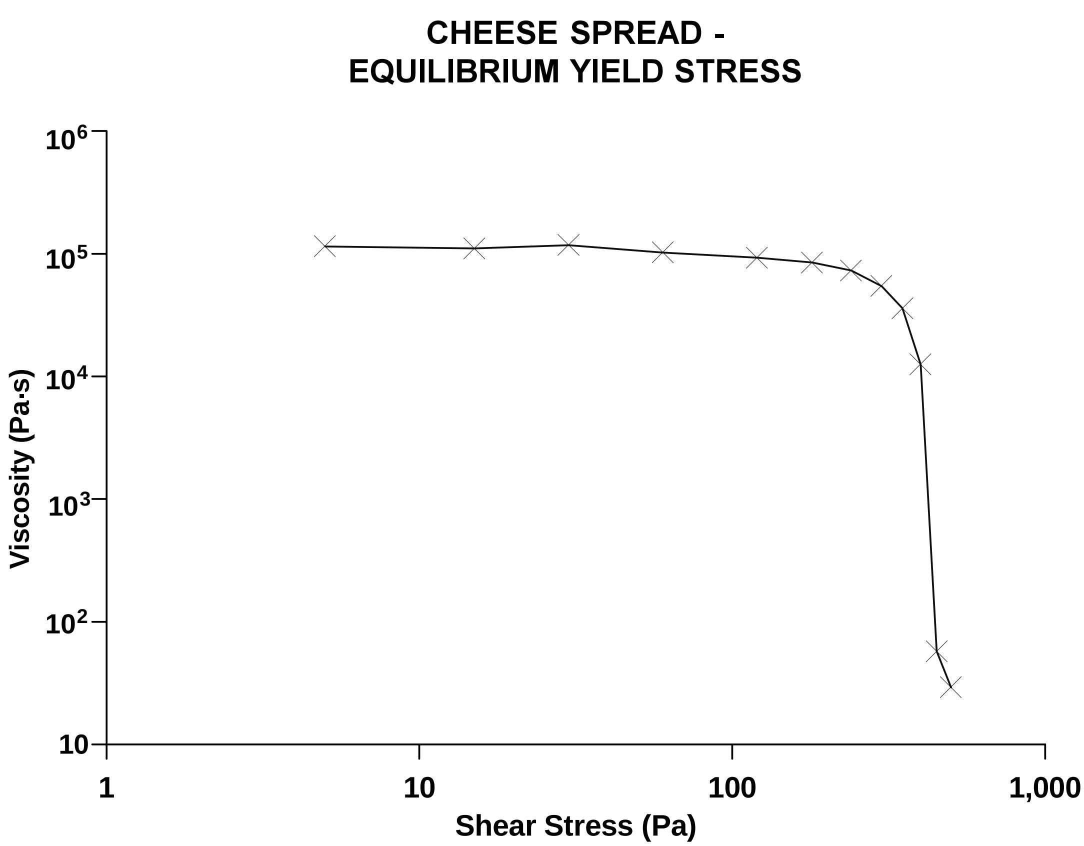

Figure 6

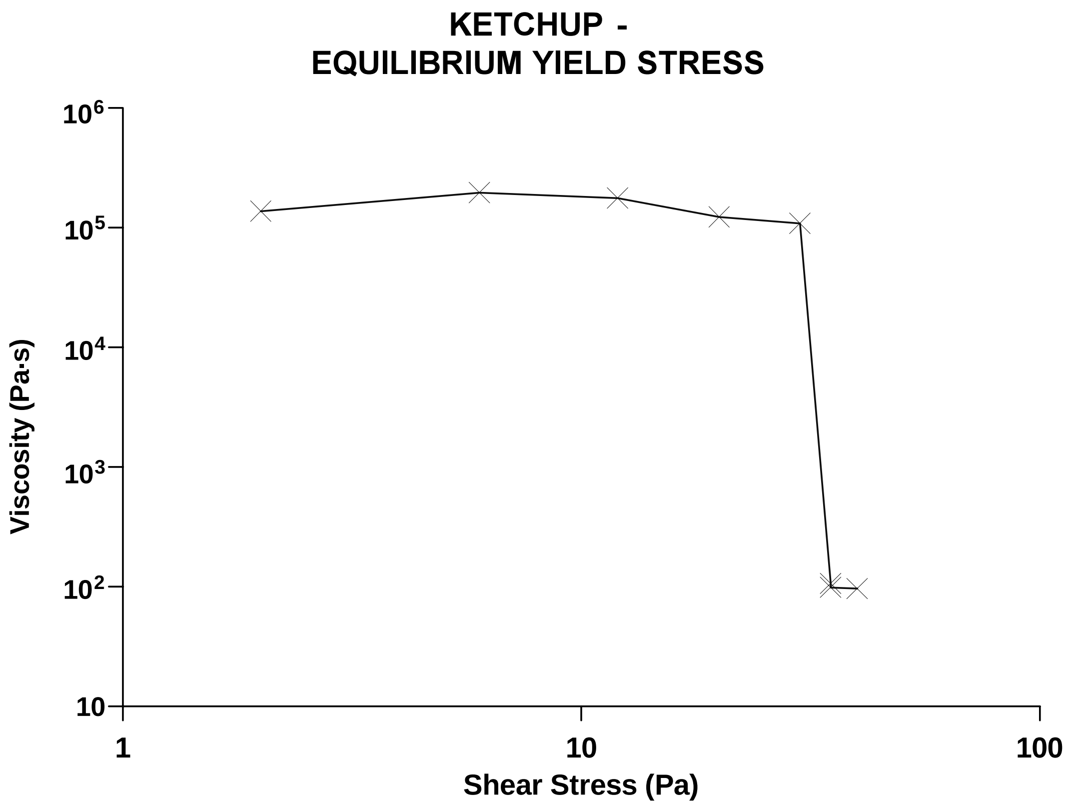

Figure 7

Figures 7-10 show the results of similar creep experiments for several other food products. (An overlay of all these individual curves is shown in Figure 11). Several additional comments relative to these curves are important:

- A specific measurement geometry with a serrated surface was used to evaluate ketchup to minimize slippage at the sample interface due to possible water migration.

- The viscosity drop for the salad dressing was not as sharp as for the other products. This suggests that the structure resisting flow may be weaker and that the structure breakdown/formation process may follow significantly different kinetics than the other products.

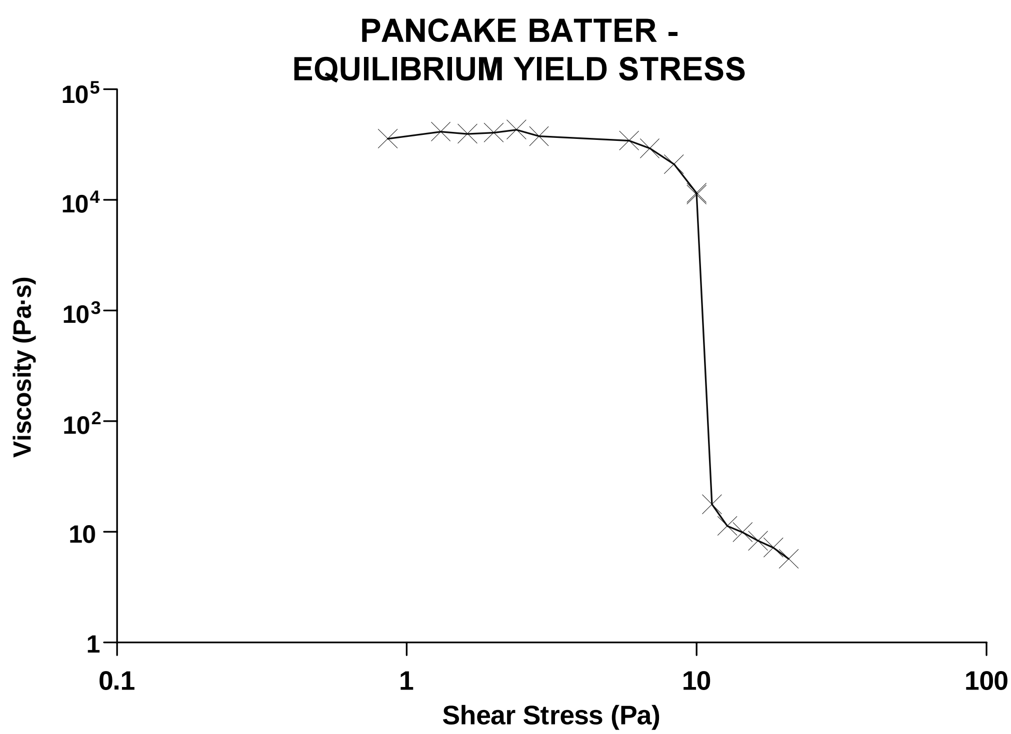

Figure 8

SALAD DRESSING -
EQUILIBRIUM YIELD STRESS

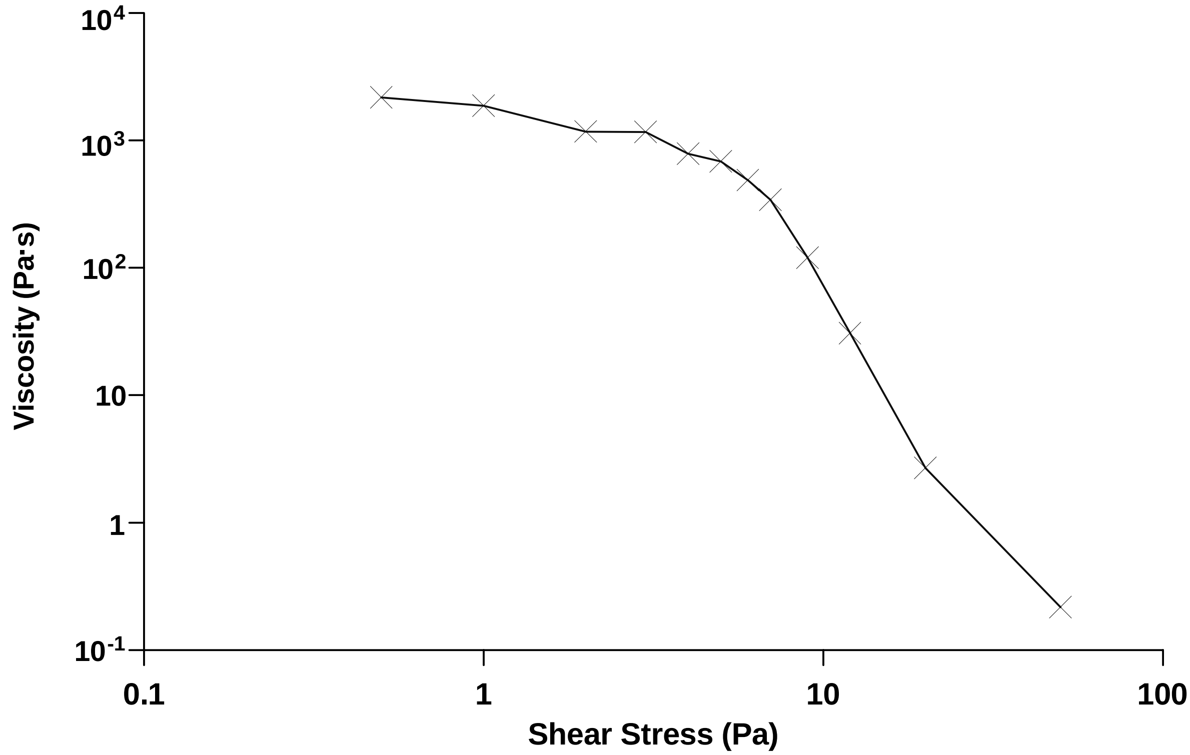

Figure 9

MAYONNAISE -
EQUILIBRIUM YIELD STRESS

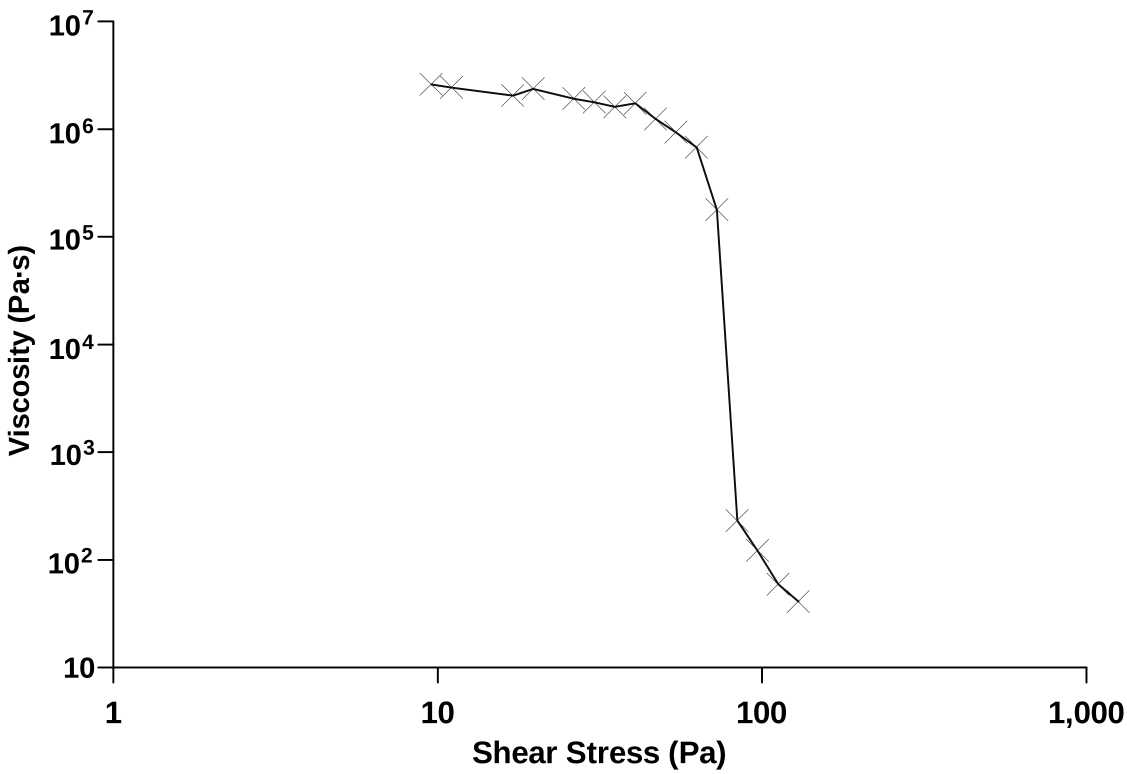

Figure 10

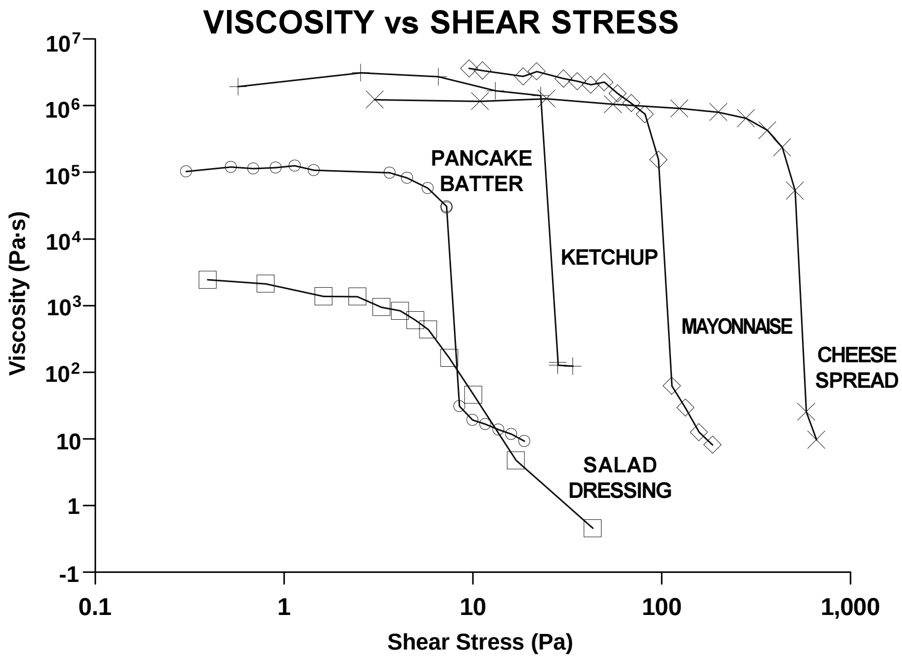

Figure 11

- A series of stress ramping tests was performed on the mayonnaise. Figure 12 shows the results from successive runs where the stress was increased from 0 → 200 Pa over a two minute period and then decreased from 200 → 0 Pa over a second two minute period. The material was allowed to equilibrate for four minutes between runs 1 and 2 and for fifteen minutes between runs 2 and 3. Differences in the apparent yield stress are seen between the successive runs undoubtedly due to the rate of structure rebuilding which occurs during the time allowed. The yield stress for run 3, however, is essentially the same as for the initial run indicating that the time allowed for equilibrium is sufficient to totally rebuild the material's original structure. Experiments such as this help predict end-use properties such as the material's "plate appearance" (4,5); that is, its visual richness or appeal once it's dispensed. Figure 13 summarizes these results numerically and compares them to the yield stress obtained from the creep experiment (Figure 10). The stress ramping test as expected gives a slightly higher yield stress, probably due to kinetic considerations. Also, the yield stress values obtained from the decreasing stress ramps are considerably lower than those obtained during the increasing stress ramps indicating again that unless sufficient time is allowed for structure rebuilding, the yield stress information obtained will be incorrect.

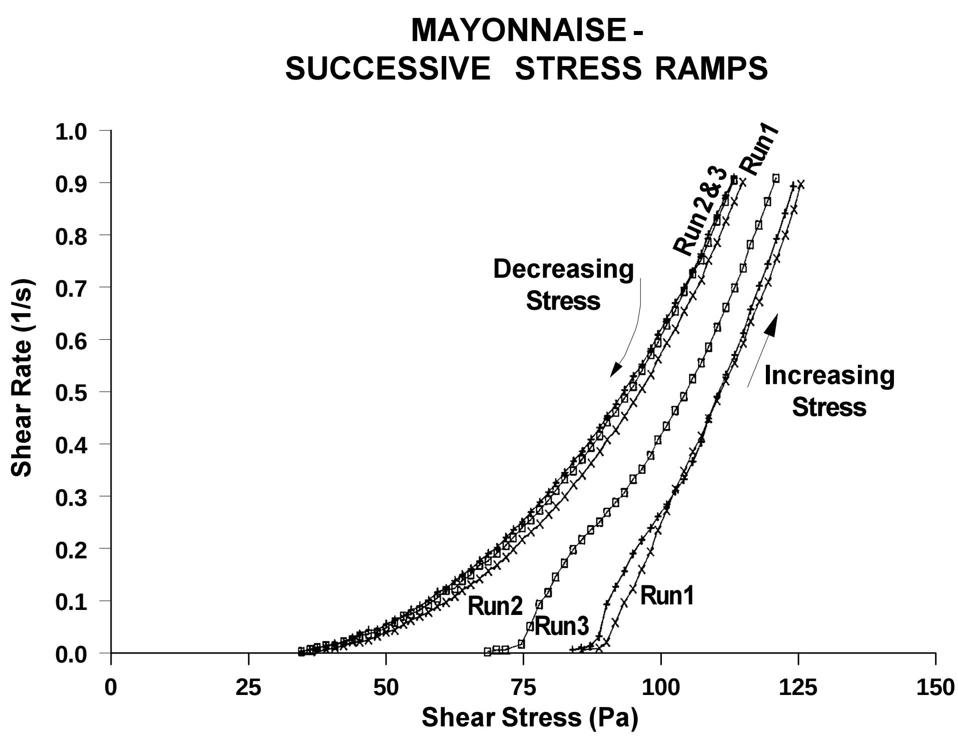

Figure 12

YIELD STRESS OF MAYONNAISE

EQUILIBRATION TIME (min)	YIELD STRESS INCREASING (Pa)	YIELD STRESS DECREASING (Pa)
CREEP	75-84	---
INITIAL RUN	87.4	34.3
4	68.9	31.9
15	85.7	31.9

Figure 13

REFERENCES

1. An Introduction to Rheology; H.A. Barnes, J.F. Hutton, K. Walters; Elsevier; Amsterdam; 1991.
2. TA Instruments CSL^2 Brochure, Reference No. RH-001.
3. "Controlled Stress Rheometer: How Does It Work", TA Instruments Publication RH-007.
4. "Evaluation of Foods with Reduced Fat Content", TA Instruments Publication RS-10.
5. "Tailoring Ketchup Flow Properties for Specific Containers", TA Instruments Publication RS-13.

For more information or to place an order, contact:

TA Instruments, Inc., 109 Lukens Drive, New Castle, DE 19720, Telephone: (302) 427-4000, Fax: (302) 427-4001
TA Instruments S.A.R.L., Paris, France, Telephone: 33-01-30489460, Fax: 33-01-30489451
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