An Air-Bearing Sealed Cell for Overpressure Rheology Measurements

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Rheology is the branch of science that deals with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratory for characterizing component materials and final products, monitoring process conditions, as well as predicting product performance and consumer acceptance.

Rheometry is a powerful and straightforward measuring technique that until recently has not seen widespread acceptance, particularly in industries handling materials that change their integrity over a period of time. Due to instrument limitations for measuring samples without loss of the continuous phase, many industries, including food, pharmaceutical, petroleum, and coatings, suffer from limited and/or unreliable rheological properties.

Manufacturers and processors that rely on the functional properties of gelling agents are well aware that processing conditions such as time, temperature, and amount of shear during heating can alter the final viscoelastic properties and strength of the resulting gelled network, as well as gelling ability. To date, acquiring fundamental information on the viscoelastic properties of gels and steady shear properties has been difficult due to the experimental requirement of low-viscosity solutions above their boiling point. Although rheological characterization of these systems at elevated temperatures is extremely important to researchers, until now there has not been a viable method available to produce data on reaction kinetics and rheological properties of solutions during gelatinization.

With the advancements in technology and the necessity to determine the precise rheological behavior of different materials, various measurement systems have been developed in recent years. For materials that are processed or operated under pressure or that contain volatile ingredients, pressure rheology is the only means with which to characterize them. This paper discusses a patented system called the Sealed Cell (**ATS RheoSystems/REOLOGICA Instruments,** Bordentown, NJ) (see *Figure 1*). To preserve sample integrity, the system should apply the pressure to the sample above the vapor pressure of highest volatile ingredient at operating temperature. The following explains the Sealed Cell system and gives experimental data.

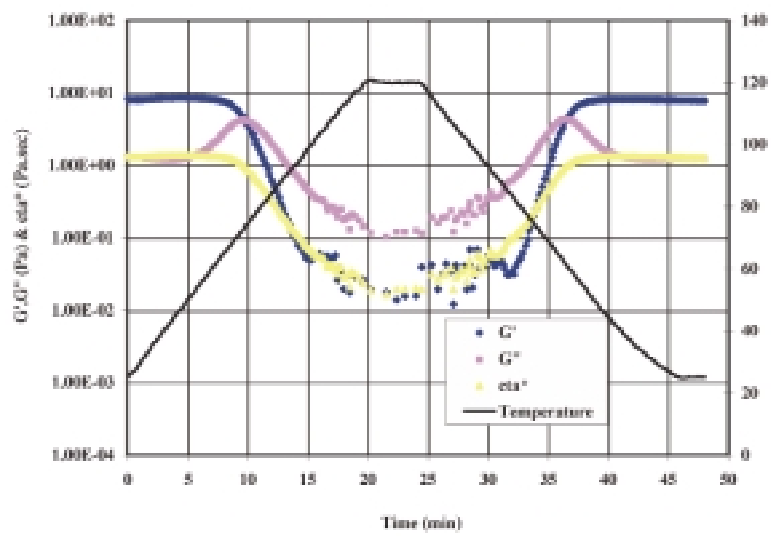

Figure 3 Results in the form of storage modulus (G'), loss modulus (G"), complex viscosity (η*), and temperature (°C) as a function of time for a dynamic experiment on a water-based gel using a 25-mm couette system.

Figure 1 *Sealed Cell.*

Figure 2 *STRESSTECH HR rheometer.*

Experimental

The Sealed Cell measuring system, used in conjunction with the STRESSTECH HR rheometer (**ATS RheoSystems**) (*Figure 2*), allows measurements under pressure with full dynamic oscillation and viscometric capability. The cell employs a noncontacting, air-bearing seal rather than standard "O" rings. This novel design allows the rheometer to deform the sample through direct mechanical contact rather than attempt to deform the sample through a magnetic coupling. The air-bearing seal is effectively frictionless, and permits measurements at extremely low torque values. In addition, the direct mechanical contact permits dynamic oscillatory testing throughout the frequency range of the instrument. Aqueous samples, along with solvent-based systems, can be measured above their boiling point.

Results and discussion

To emphasize the importance of the Sealed Cell system, dynamic experiments on a water-based gel using a 25-mm couette system were performed. The dynamic properties of the gel were determined over temperature ramp back and forth from 25 to 120 °C at 5 °C/min with a hold time of 5 min at the end temperatures. The study was performed at a frequency of 1.0 Hz at constant stress of 2.0 Pa for the entire scan. *Figure 3* shows the results in the form of storage modulus (G'), loss modulus (G"), complex viscosity (η*), and temperature (°C) as a function of time. The analysis shows that the material exhibits completely reversible behavior upon cooling. Since the gel is experiencing temperatures well above the boiling point of water, it becomes mandatory to use the Sealed Cell system, which can apply pressure above the vapor pressure of the sample at highest temperature, thereby maintaining the sample integrity thoughout the run.

The gel was also run under steady shear conditions with a temperature ramp back and forth from 20 to 120 °C at 2 °C/min at constant 100/sec (*Figure 4*). The sample shows gelation and/or cross-linking followed by a decrease in viscosity with a rise in temperature. The analysis indicates that, rheologically, the sample behavior is completely reversible. Again, this analysis emphasizes the importance of maintaining the sample's integrity above 100 °C via overpressure.

Finally, a shear rate sweep study was performed on the same sample at a constant temperature of 25 °C. The data are shown in *Figure 5*. The shear rate sweep was performed from 0.1 to 300/sec. The gel demonstrates highly shear thinning behavior. Shown for comparison purposes is a standard Newtonian 100-cps oil.

Starch rheology

One of the many applications of the Sealed Cell is in starch rheology. Often, starches undergo gelatinization at temperatures around 70 °C. This gelatinization temperature, however, is dependent

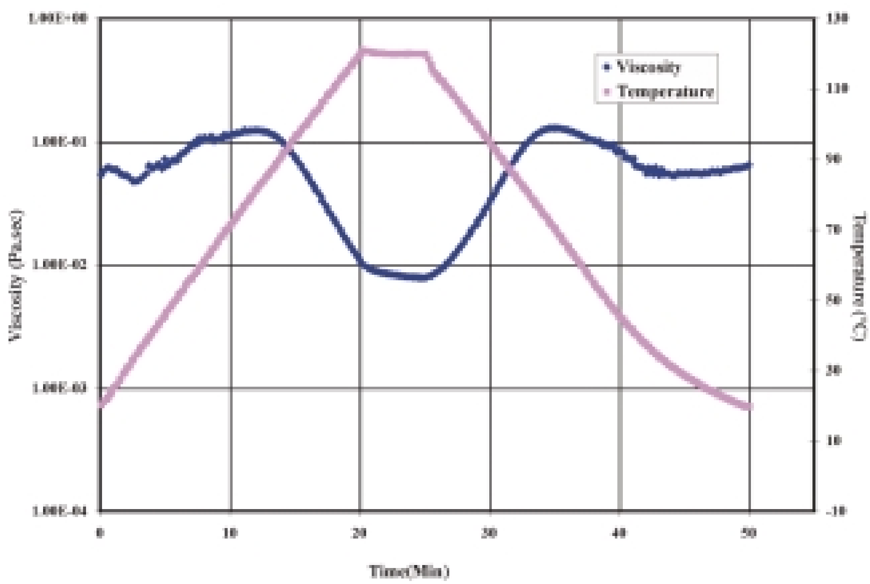

Figure 4 Gel from experiment in Figure 3 run under steady shear conditions with a temperature ramp back and forth from 20 to 120 °C at 2 °C/min at constant 100/sec.

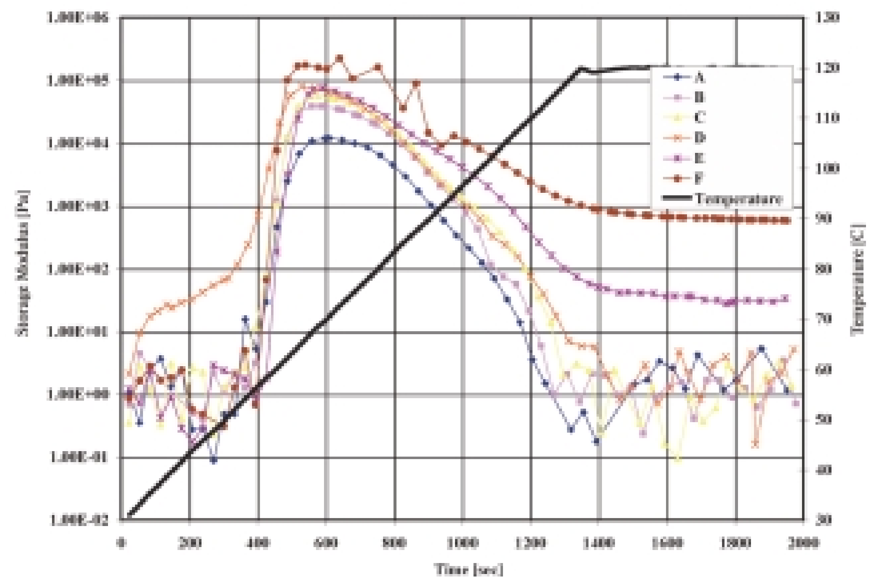

Figure 6 Storage modulus (Pa) and temperature (°C) plotted versus time (sec) for the six samples from the starch rheology experiment.

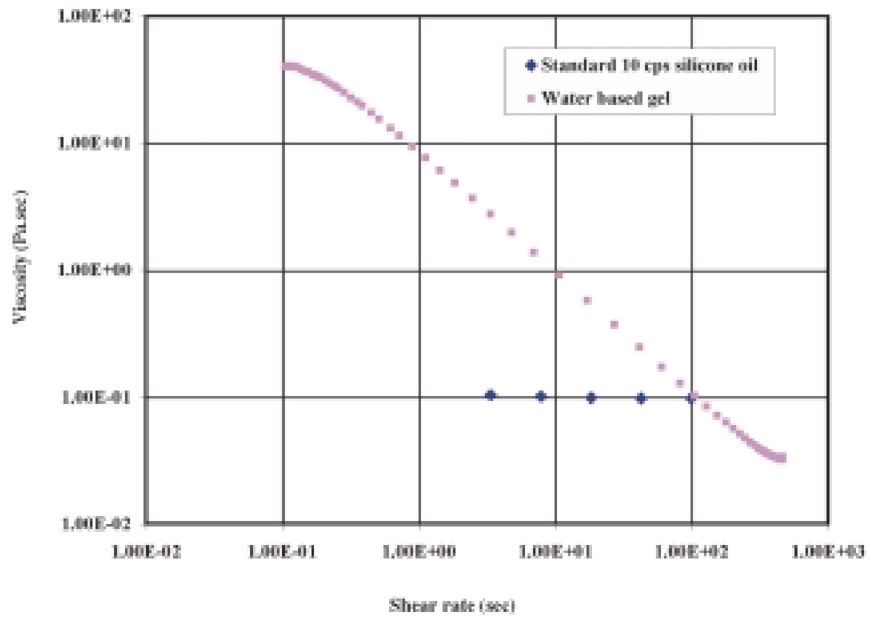

Figure 5 Shear rate sweep study performed on sample from experiment in Figure 3 at a constant temperature of 25 °C.

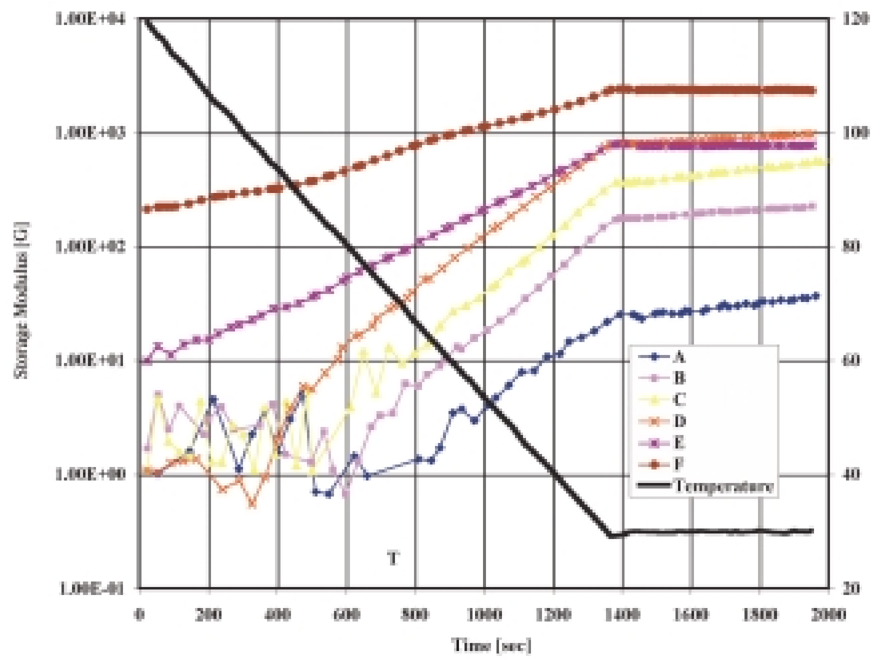

Figure 7 Linear viscoelastic properties of the gelatinized starch measured during a descending temperature ramp from 120 to 30 °C.

Table 1 Molecular weights of starches

Sample starch	Weight average molecular weight (g/mol)
A	264,000
B	638,000
C	1,779,000
D	4,441,000
E	9,998,000
F	>40,000,000
G	3,909,000

on the amount of water present in the sample. Using the Sealed Cell, the linear viscoelastic properties of a series of six (A–F) acid-thinned, modified starches were studied. The starches differed in their molecular weight (as measured by a size-exclusion chromatography-multiangle laser light scattering [SEC-MALLS] detector), according to *Table 1*. For each starch, a 50.0 wt% slurry in water was prepared and loaded into the Sealed Cell. The sample was then subjected to a temperature ramp from 30 to 120 °C at a ramp rate of 4 °C/min. The rheological properties were determined using the controlled-strain mode at a strain of 0.015 at a frequency of 1 Hz. The results are shown in *Figure 6*, where storage modulus (Pa) and temperature (°C) are plotted versus time (sec) for the six samples. The data demonstrate that the gelatinization temperature of the starch is not affected by the acid-thinning process.

The temperature was held at 120 °C for 10 min before a constant stress viscometry step was executed at 40 Pa of stress and a temperature of 150 °C. This constant shear stress step helped break up the swollen starch granules. The linear viscoelastic properties of the gelatinized starch were then measured during a descending temperature ramp from 120 to 30 °C (*Figure 7*). The modulus that develops in the cooling starch is highly dependent on the molecular weight of the starch.

The Sealed Cell rheometer can also be useful in studying reactions of starch that could not be studied under ambient pressures. One example of this is the cross-linking of starch using a cross-linking agent. *Figure 8* compares the cooking of mixtures of starch G and water with and without a cross-linking agent. The rheological results show that both starch samples undergo the gelatinization transition beginning, as evidenced by the drop in modulus. Once the cross-linker-containing sample reaches the appropriate temperature, however, the cross-linking reaction begins and the storage modulus increases rapidly. The sample without cross-linker, however, continues to show a decrease in the modulus as the temperature continues to climb. Understanding the temperature-dependence of this cross-linking reaction would not be possible without a Sealed Cell to contain the water in the sample.

Rheometer system setup

The STRESSTECH modular research rheometer has a wide range of measuring systems and accessories. Measuring systems are available as concentric cylinders, cone/plate, parallel plate, double concentric cylinders, sealed/pressure cells, and dynamic mechanical thermal analysis (DMTA) of rods, bars, fibers, and films. Special measuring systems for low volume, high shear rates, and high sensitivity are also available. The measuring geometries can be made in stainless steel, titanium, polycarbonate, or any user-defined material. The instrument is supplied standard with a patented Differential Pressure Quantitative Normal Force Sensor for reproducible sample loading history, thermal expansion measurements, and quantitative normal stress measurements. The diffusion air bearing has low inertia with high axial and radial mechanical stiffness.

Temperature control cells are available using circulating fluid, Joule Thomson effect, and cryogenic covering the range –180 to 550 °C. All measuring geometries are supported, i.e., cone/plate/parallel plate, concentric cylinder, and solids in torsion and

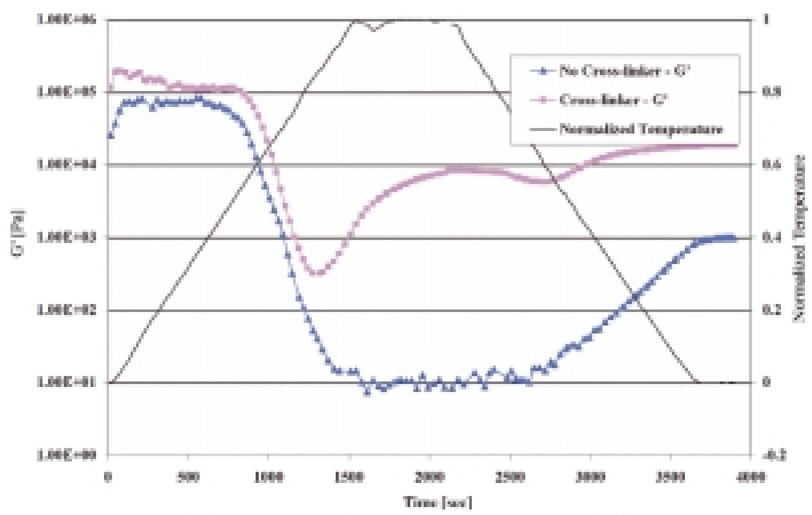

Figure 8 *Cooking of mixtures of starch G (see Table 1) and water with and without a cross-linking agent.*

tension. Several high-pressure cells with an upper range of 10,000 psig are offered.

Electronic unit

The instrument electronics are contained within the mechanical unit and the instrument is built around a dedicated, high-speed central processing unit (CPU). This consolidation enhances performance and versatility due to electrical connections on the motherboard bus, rather than through cables to a separate electronics cabinet. In addition, valuable bench space is kept to a minimum. The motor control is based on digital rather than analog drive technology. The unit comes with a built-in diagnostic system and quick diagnostic service port for service engineers. Also included is a port for remote control operation and fault diagnostics for service via the Internet.

Rheometer software package

RheoExplorer 5.0 software is based on the Windows operating platform and runs under Windows 2000/XP (**Microsoft Corp.,** Redmond, WA). The standard software package is a true multitasking interface with selectable user levels, thus offering many advantages to the scientist. It is designed to provide flexibility for configuring and using the rheology system. The computer is not dedicated to simply running the instrument, and is available for other use when making measurements. The computer can be used for printing previous results, writing a report, or performing measurements with another instrument.

Viscometry, oscillation, creep and recovery, constant rate, yield stress, fast oscillation, process control, and project (multiexperiment linking), time–temperature superposition, and spectrum transformation packages allow the sample to be analyzed via different rheological procedures. Powerful data analysis capabilities allow model fitting, graph and table customization, and cut/paste operation to all other Windows-based software.

The software permits automatic gap adjustments and thermal expansion compensation using the patented Differential Pressure Quantitative Normal Force Sensor. This system enhances measurement reproducibility since the sample loading history is reproduced identically each time.

Rheometers for any user level, application, and budget

DYNALYSER research rheometers (**ATS RheoSystems/REOLOGICA Instruments AB,** Lund, Sweden) are modular research-level rheometer systems designed specifically to address the challenging and diverse testing needs and requirements of the serious rheologist. The instrument's capability and performance are the direct result of a design and development effort focused exclusively on input and recommendations from rheometer users.

The DYNALYSER is designed for testing any rheologically significant material, i.e., thermoplastics, thermosets, elastomers, semisolids, and/or fluid systems. The instrument is highly accurate and versatile.

VISCOTECH, an entry-level research rheometer system (**ATS RheoSystems**), is fully upgradeable to a STRESSTECH unit as the user's needs and requirements dictate.

All **ATS RheoSystems** rheometers are produced according to ISO 9001 and are tested to operate according to the electromagnetic compatibility rules within the European Community. The instruments are tested to be labeled with the CE mark.

Conclusion

This article highlights the importance of the Sealed Cell system for materials subjected to operational conditions under which their integrity changes at atmospheric pressure. The applicability of **ATS RheoSystems/REOLOGICA Instruments** rheometers for a wide range of materials is demonstrated. A detailed interpretation of data and correlation of the rheological response with the physical/chemical properties is presented. The rheological characterization of materials at operational conditions provides precise information for engineers and scientists to improve and optimize their products and manufacturing processes. Today, most researchers and manufacturers rely on rheological measurements to develop customer-favored products with a competitive edge in the marketplace. A reliable research-level rheometer and a thorough understanding of rheological measurements are now a necessity for success in industry.

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