Rheo–small-angle neutron scattering at the National Institute of Standards and Technology Center for Neutron Research

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We describe the design and operation of a modified commercial rheometer to simultaneously perform rheological measurements and structural studies by small angle neutron scattering (SANS). The apparatus uses a Couette geometry shear cell allowing two of the three scattering planes to be observed by performing experiments in either the radial or tangential geometries. The device enables small angle neutron scattering patterns to be obtained simultaneously with a wide variety of rheological measurements such as stress/strain flow curves, oscillatory deformations, and creep, recovery and relaxation tests, from −20 °C to 150 °C, for samples with viscosities varying by several orders of magnitude. We give a brief report of recent experiments performed on a dispersion of acicular nanoparticles and biopolymer network under stress demonstrating the utility of such measurements. This device has been developed at the National Institute of Standards and Technology's Center for Neutron Research (NCNR) and made available to the complex fluids community as part of the standard sample environment equipment. © *2011 American Institute of Physics*. [doi:10.1063/1.3609863]

INTRODUCTION

Complex fluids under the influence of a flow field exhibit an array of interesting behaviors from simple orientation of anisotropic particles within the fluid to a variety of phase transitions and transformations.[1–4] Even particle rearrangement and orientation can lead to large changes in rheological behavior. Beyond the fundamental scientific interest of these fascinating phenomena, understanding fluids under flow is also of great technological importance as most of these ubiquitous materials experience significant shear flow at some point in their processing and both particulate orientation and phase transitions can have profound effects on the final properties of the material. Several shearing devices have been developed over the years to investigate flow effect using small angle scattering techniques (X-ray, neutron, light) as these methods are non-destructive probes of structural changes on length scale ranging from the nanometer to the micrometer. The most commonly used of these devices is the Couette cell which consists of two concentric cylinders, one fixed and the other rotating, with the fluid being sheared in the gap between the two. Most Couette cells for scattering keep the inner cylinder (the bob) stationary while spinning the outer cylinder (the cup) at different speeds to achieve the desired shear rate in order to retard the development of Taylor instabilities.[5,6] Such a shear device has been widely used in scattering facilities world-wide as it provides a relatively simple flow field where the shear, for Newtonian fluids, is constant across the gap and readily allows structural information in two perpendicular planes (i.e. the shear gradient/vorticity and velocity/vorticity planes, also commonly referred to a the 2-3 and 1-3 planes) to be obtained by simple translation of the entire cell relative to the beam path. Scattered intensities in these two geometries are commonly recorded in order to reconstruct the 3 dimensional solution structure. However, in many cases, the behavior of the sample depends on its detailed history (shear history, aging, etc) which is often very difficult to ascertain. Thus it becomes imperative to measure the macroscopic rheological response simultaneously to measuring the microstructure in order to unambiguously describe the sample's response to shear and eventually tease out the structure-property relationships. While the science of Rheology is well established and excellent commercial rheometers have been available for many years, most major scattering facilities (X-ray and neutron)[7] have provided "home-made" or custom built devices which provide a reliably controlled shear rate but mostly neglect such issues as sample history, time dependence, and wall effects. In this paper, we describe the design and operation of a modified commercial rheometer that allows the collection of small angle neutron scattering (SANS) data while making its rheological measurements. The next generations of this rheometer has now become commercially available and is being procured by a number of SANS facilities, including the National Center for Neutron Research (NCNR). Two different examples are presented to illustrate the utility of the system: 1) shear stress effect on a dispersion of acicular nanoparticles and 2) effect of stress deformation on fibrin bio network.

CELL DESCRIPTION

The apparatus is based on a constant stress, Paar Physica UDS 200 system.[8] A full 3D rendering of the modified rheometer is shown in Figure 1 including the protective aluminum housing built to facilitate lifting and transfer of the equipment from its normal bench location to its position

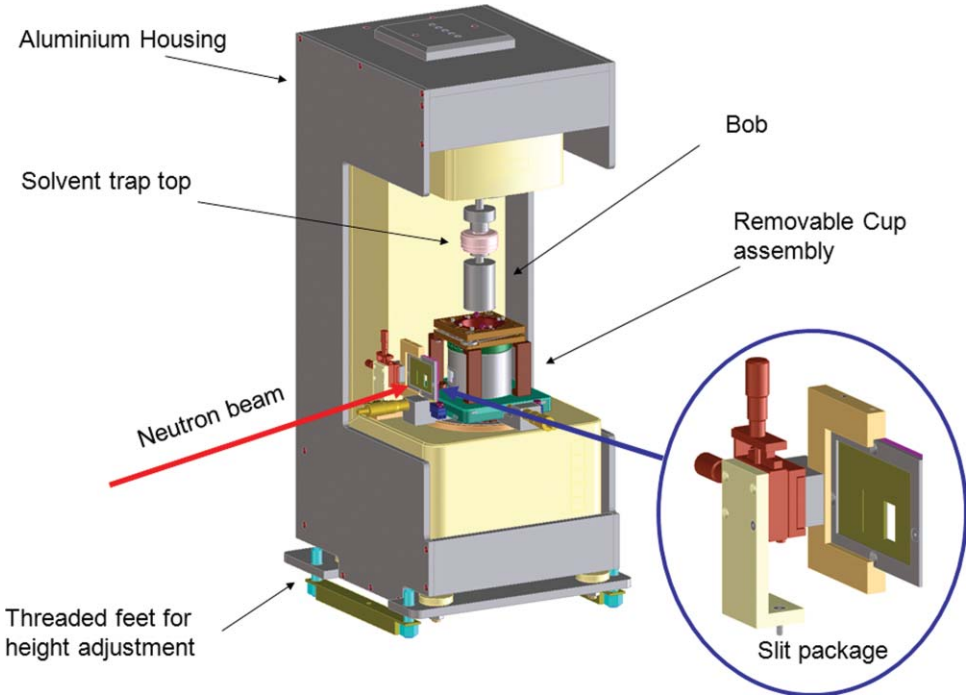

FIG. 1. (Color online) Full drawing of the constant stress rheometer in its protective aluminum housing with the slit package defining the beam size. The arrow represents the incoming beam path.

FIG. 2. (Color online) Rheometer installed on the NG3 SANS beam line at the NCNR. The arrow indicates the neutron path.

on either the NG7or NG3 SANS instruments at the National Institute of Standards and Technology's (NIST) National Center for Neutron Research (NCNR) while maintaining the operational integrity of the system. The required air gap for inserting the rheometer into the neutron beam is 50 cm. At NIST the Rheometer sits on a 558.8 mm (22 inch) diameter plate atop a Huber rotation stage (Figure 2). Once installed on the beam line, leveling is easily performed via four threaded feet that allow the aluminum housing to be raised or lowered by $\approx$ 50.8 mm (2 inches). The main characteristics of the rheometer are listed in Table I.

CELL AND TEMPERATURE CONTROL

In order to pass the beam through the sample being sheared while maintaining temperature control, a new

TABLE I. Principle operating parameters for the Rheo-SANS device.

Technical specifications	
Accuracy	1% of maximum value
Maximum torque	150 mNm
Torque resolution	0.01 μNm
Speed range	10^{-4} to 1000 min^{-1}
Shear rate range	$1.3*10^{-4}$ to $4.8*10^{3}$ s^{-1}
Shear stress range	0.67 to $3.5*10^{4}$ Pa
Viscosity range	$1.7*10^{-3}$ to $2.7*10^{8}$ Pa s
Temperature range	-20 to 150 °C
Volume	4, 8, 12 mL
Gap size	0.5, 1 mm

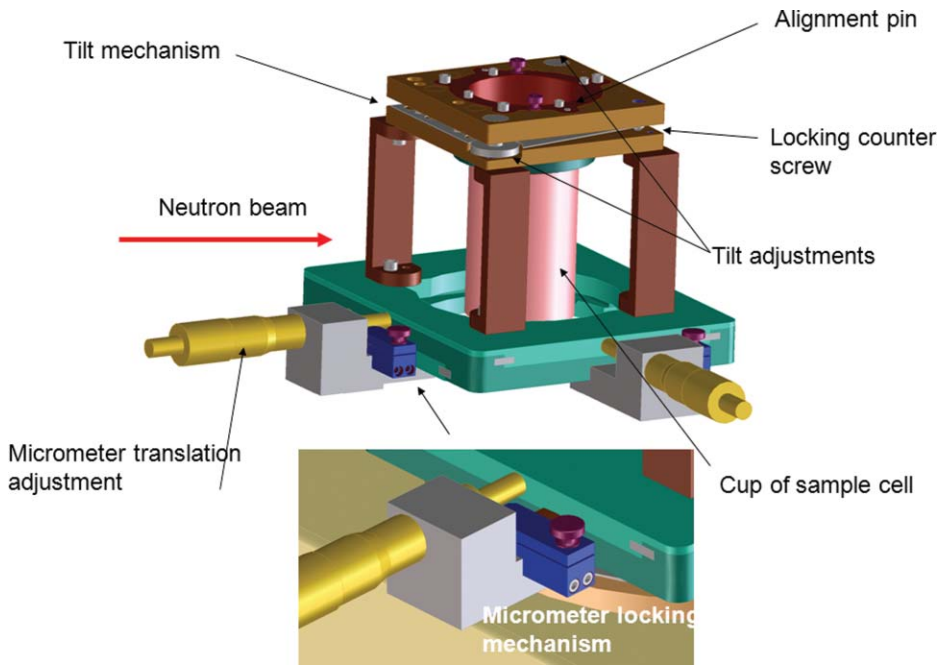

FIG. 3. (Color online) Cup assembly package allowing for fast and precise alignment. Cup can be removed for cleaning and replaced without loss of alignment. The various parts of interest are annotated directly on the figure.

Couette assembly and thermostating mechanism, relatively transparent to neutrons, was devised with the help of the manufacturer, Paar Physica (now Anton Paar). The sample temperature is controlled by heating liquid nitrogen vapor to a set temperature and blowing the gas between the cup and a quartz shield used to insulate the gas from the environment. The temperature can be varied from $-20\,^{\circ}$C to $150\,^{\circ}$C with a precision of $\pm\,0.2\,^{\circ}$C by use of a Eurotherm TC10 controller. The temperature is controlled off a sensor that is affixed to the underside of the cup. For low temperatures, nitrogen gas can be made to flow past the outer surface of the quartz shield to avoid water condensation from forming on the face of the shield. As with all temperature control systems controlling off a temperature probe somewhat removed from the actual sample, there will be a small offset between the set point temperature and the actual sample temperature when the temperature differential with the environment is large. We have provided a rough calibration curve, which is often sufficient. However, in order to properly account for viscous heating effects and other variables, the most accurate temperature control requires that a calibration be done immediately prior to the experiment using an oil of the same viscosity as the sample at the temperatures being probed in the experiment.

CUP ALIGNMENT MECHANISM

In order to achieve precise and accurate alignment of the shear cell, the upper part of the convection temperature control has been further modified to be able to mount the specially designed SANS Couette cell cup holder (Figure 3). The cup is held by a collar which fits into a tilt stage which itself is mounted on a x-y micrometer translation stage. The collar, and hence the cup, is precisely positioned by use of locating pins in the tilt stage. Using this fixture, concentricity alignment can easily be obtained using a dial indicator mounted on the rotation axis of the rheometer head (attached to the tool shaft) and tuning the micrometer screws iteratively until adjustment is performed with an accuracy of 0.01 mm. To preserve the alignment through the entire experiment, brass lockers have been mounted on the x-y translation stage to prevent the micrometer screw from turning accidentally (see Figure 3). A simple counter screw is used to eliminate any motion of the tilt stage. This set up proved to be very robust and the cup with sample can be repeatedly removed for cleaning and sample changes with no apparent loss of alignment.

CELL SIZES AND MATERIALS

The bob (which is a hollow cylinder for neutron transparency) and cup of the Couette cell are of a Mooney-Ewart type geometry in order to minimize sample volume. A standard solvent trap is also mounted on the shaft of the bob in order to reduce solvent evaporation during long runs. Many different Couette cell diameter dimensions have been used. A 70 mm height and 48 mm diameter bob is used with a 94 mm height and either 49 mm or 50 mm inner diameter cup in order to provide a shear gap of 0.5 mm or 1 mm respectively. The corresponding sample volumes are 8 mL and 12 mL. A second set of cells have 30 mm height and 27 mm, 28 mm and 29 mm diameter bob with a 30 mm inner diameter cup is also available requiring a sample volume of 3 mL, 5 mL, and 7 mL. In order to meet the robustness requirements for a broad range of materials, these cells are made of Titanium which experiences relatively short lived activation in the beam and is relatively transparent to neutrons with limited low q scattering of its own (i.e. relatively low background). For samples

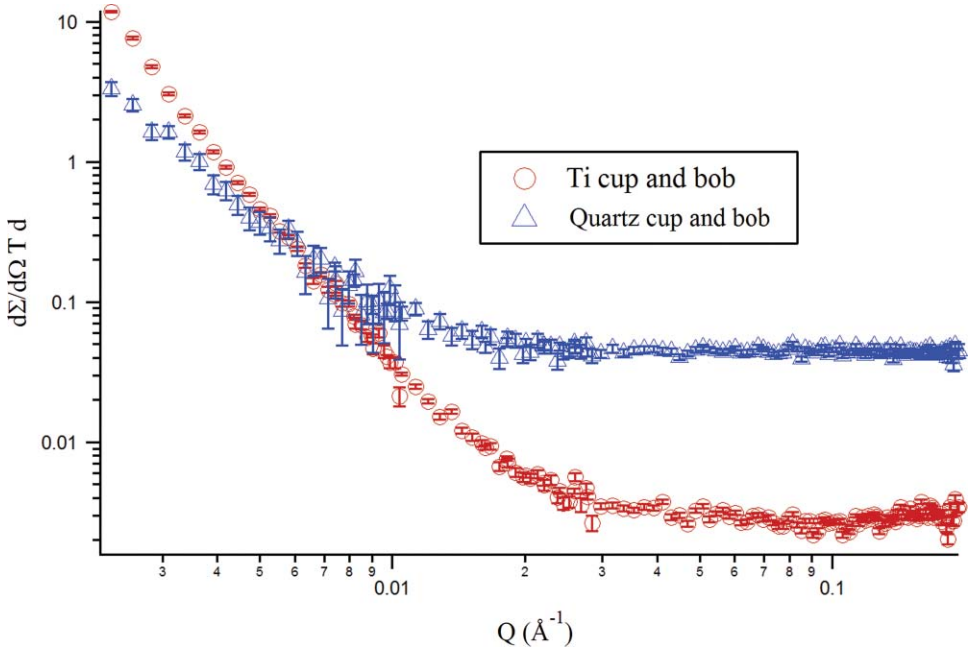

FIG. 4. (Color online) 1D scattering intensity curve from Ti and Quartz cup and bob (error bars on the points are for a one sigma uncertainty).

with very weak low angle scattering intensity which are non abrasive and do not produce dangerous normal stresses, a 70 mm height bob and 94 mm height cup made in quartz can be used with a gap size of 1 mm or 0.5 mm. Figure 4 shows the scattering cross section of the different Couette cells (quartz vs titanium) adjusted for thickness and transmission. Indeed, for sample holders the figure of interest is the background it contributes to the experiment not its absolute cross-section. Figure 5 shows the 2D pattern for the lowest scattering wave vectors Q. At high wave vectors ($Q > 0.02$ Å^{-1}), both scattering curves are flat and featureless and are effectively identical for scattering purposes though the titanium background is lower in this region. This is mostly due to the smaller thickness required for the titanium cell producing a total titanium pathlength of 0.5 mm $\times$ 4 = 2 mm vs 8 mm of quartz. The titanium scattering, however, increases faster at lower Q than does the quartz so that by $Q = 0.002$ Å^{-1}, the titanium background is about a factor of four higher and will clearly become a problem for weak scatterers at the very lowest Qs. Furthermore the titanium low Q scattering becomes slightly anisotropic compared to the scattering pattern from the quartz cell. For samples with weak contrast and low scattering cross section, the quartz cell is the appropriate choice. While the reduction protocol corrects for empty cell scattering, the time required to achieve acceptable statistics grows exponentially as the scattered intensity of interests approaches that of the empty Ti cell. In practice, however, a Ti bob with a quartz cup is almost always used. The quartz cup is far cheaper and easier to make than a quartz bob and provides the optical transparency necessary for visual inspection of the sample.

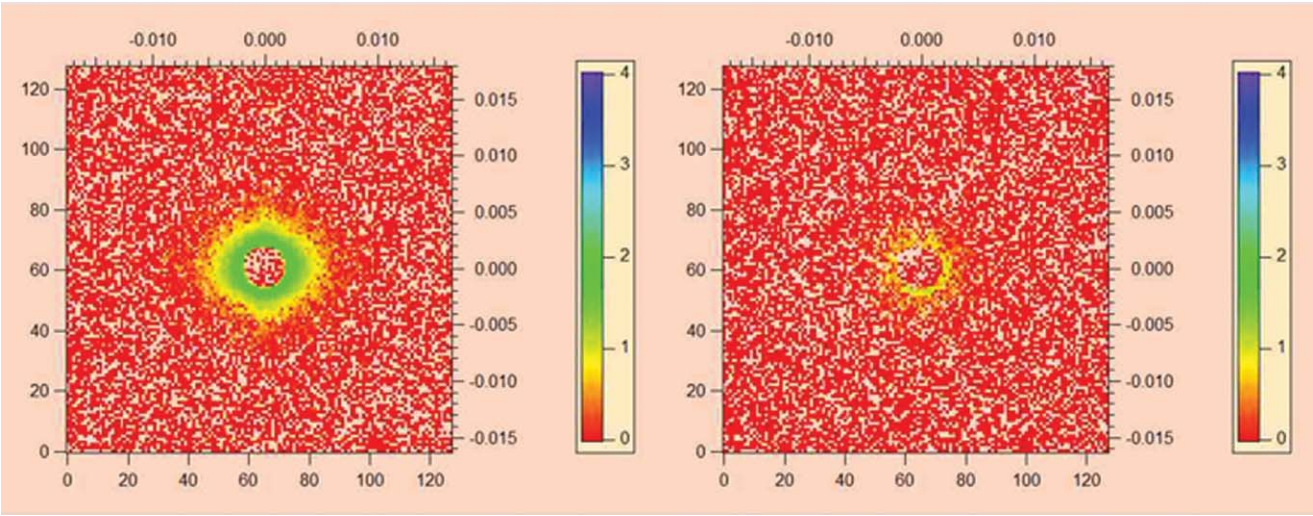

FIG. 5. (Color online) 2D scattering intensity from Ti (a) and Quartz (b) cup and bob showing a slightly anisotropic intensity distribution at really small angles for the Ti cup and bob.

SLIT PACKAGE AND SLIT ALIGNMENT

A pre-aligned aperture package attached to the rheometer allows scattering measurement in the 2 standard scattering configurations and is shown in Figure 1. As noted previously, in the radial configuration the neutron beam passes along the velocity gradient direction while in the tangential configuration, the beam passes along the flow direction through the side of the cell. The apertures defining the incident beam are machined in a single 1 mm thick Cadmium sheet. In the radial configuration the beam is defined by a 12 mm × 18 mm rectangular aperture for the high volume cell while a 6 mm × 18 mm rectangular aperture for the small volume cell. In the tangential, the rectangular apertures are 18 mm × 0.2 mm, 18 mm × 0.4 mm, or 18 mm × 0.8 mm depending on the gap size, and are separated from the radial aperture by the radius of the bob. Note that the design allows for either side of the cell to be used for the tangential geometry depending on the constraints at the sample position at the beam. In fact, the NG7 and NG3 SANS lines at NIST are near mirror images of each other and the slit package thus mounted differently depending on the line being used. To reduce background and gamma radiation, the cadmium sheet only defines the edges of the beam and is mounted behind a boron aluminum tapered plate. This aperture package is fixed to a micrometer stage that allows horizontal and vertical translation.

As described above, in tangential scattering mode the beam defining aperture is tall and narrow, but still as wide as possible in order to maximize the intensity on this severely restricted sample volume. This however leads to the need for extreme precision in vertical alignments as a slight mismatch in the vertical axis of the cell and the slit can easily lead to a part of the incident beam clipping either the cup or the bob (or both). A theodolite is used to align the vertical edge of the bob with the vertical edge of the slit. Once the vertical axes are matched, the slit is carefully aligned so that the beam impinges on the gap by a procedure described elsewhere[9] where the transmission is plotted as a function of slit position as the slit is translated across the gap. For scattering in the radial geometry, the raw data sets are then corrected for detector background, sensitivity and empty cell scattering and placed in an absolute scale using the direct beam measurement as done for conventional SANS data[10,11] while in the tangential geometry, a procedure as described in Ref. 9 is adopted. It should be noted that while physically the sample aperture in the tangential geometry is a slit as described above, from the point of view of the scattering experiment this is still effectively a pinhole camera and the data not "slit smeared" and thus suitable for azimuthally anisotropic data. That said, the corrections required for extracting maximum information from the tangential geometry are not yet completely routine.

Experimental data and discussion

The modified rheometer can be used on any of the SANS beam lines as well as on the ultra SANS (or USANS) instrument at the NCNR, though a few modifications are necessary when switching from the NG7 SANS to the NG3 SANS to accommodate the "mirror image" nature of these instruments. The quality of the rheological data recorded with these modified SANS Couette cells are equal to that from the normal tool sets. Furthermore, any type of rheological tests can be performed automatically during SANS data collection as the rheometer control software is coupled to the SANS data acquisition system. Here we briefly present two different studies where the use of the rheometer was essential to elucidate the structure property relationship of the materials.

THE SHEAR THICKENING TRANSITION IN A SUSPENSION OF RODLIKE PARTICLES

The first example involves anisotropic precipitated calcium carbonate particles (PCC) dispersed into polyethylene glycol (PEG) solution that exhibit continuous or discontinuous shear thickening behavior depending on the particle concentration and aspect ratio.[12] Figure 6 shows the steady shear rheology of a PCC/PEG at different particle volume fractions. Depending on the packing, continuous or discontinuous shear thickening behavior is observed during the rheo-SANS experiments. The corresponding radial geometry scattering patterns are also shown in Figure 6. A quantitative analysis of the scattering intensity distribution reveals that for samples exhibiting continuous shear thickening, the degree of particle alignment decreases slightly at the onset of shear thickening. However, for sample exhibiting discontinuous shear thickening, the degree of alignment remains constant throughout the shear thickening regime clearly demonstrating that the origin of the mechanism of reversible shear thickening must be of an hydrocluster formation type rather than an order to disorder transition type (e.g., tumbling) as had been previously suggested. The structural evidences described in

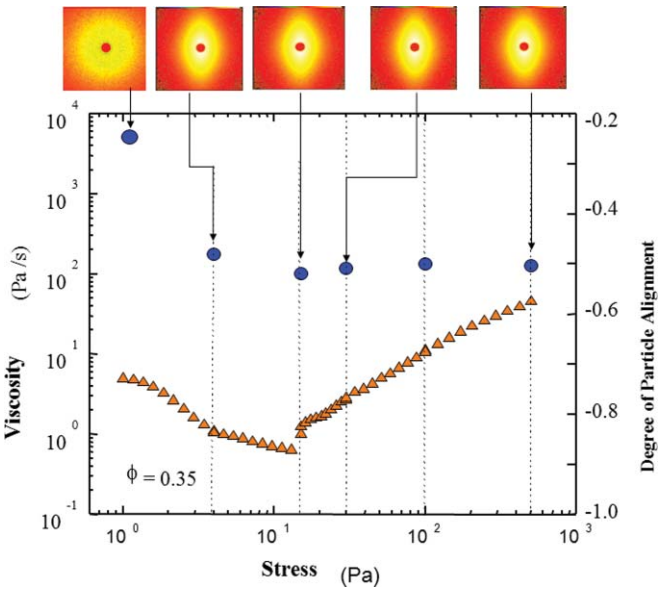

FIG. 6. (Color online) Anisotropic calcium carbonate particles dispersed into polyethylene glycol solution. The rheology data exhibit a discontinuous shear thickening transition while the scattering curves (2D images across the top) and the particle alignment factor calculated from them (right hand axis) show no change in particle orientation through the transition. Data were collected in the relevant radial geometry.

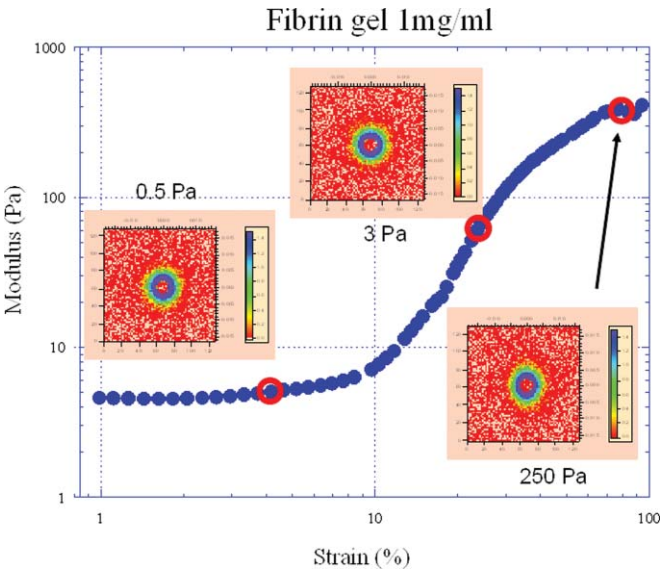

FIG. 7. (Color online) Gel modulus as a function of strain deformation for a fibrin clot formed with a fibrinogen concentration of 1 mg/mL and corresponding scattering patterns taken in the relevant radial geometry.

this experiment can only be obtained using a stress controlled rheometer as the usual strain controlled devices would not be able to capture the continuity or discontinuity of the transition.

STRAIN HARDENING IN A BIOLOGICAL HYDROGEL

The second example uses Rheo-SANS to investigate the strain hardening effect of a fibrin network under deformation. It is well known that biopolymer networks can possess mechanical properties remarkably different from those of synthetic materials.[13] Fibrin is a filamentous protein that is the major structural component of blood clots. When activated by the enzyme thrombin, fibrinogen proteins aggregate into linear structures and form fibrin filaments. At sufficiently large concentrations, fibrin filaments will generate a bifurcating network that shows a strong and reversible strain hardening mechanical response. Fibrin gels have attracted significant interest from researchers because of their important role in blood coagulation and related diseases like thrombosis and hemophilia. These materials are also interesting from a purely rheological and mechanical standpoint because the structural origin of strain hardening is poorly understood and various theoretical models are still being debated. Figure 7 shows the instantaneous shear modulus $G = d\tau/d\gamma$ where τ and γ are, respectively, the applied stress and measured strain of a fibrin gel of 1 mg/mL as a function of the strain deformation. In this experiment, the gel has been polymerized *in-situ* by the addition of thrombin and the gelation process has been tracked simultaneously with oscillatory rheology and SANS. After complete gelation, a stress ramp is applied to systematically deform the network over a wide range of strain values while structural information is also simultaneously collected by SANS in the relevant radial geometry. One can see that the gel modulus increases by 2 orders of magnitude when strained whereas purely elastic cross-linked gels, such as polyacrylamide, will typically present a constant modulus until the fracture point. This reversible strain hardening behavior is the essence of the structural integrity of biological tissues being flexible or stiff dependent on the deformation. However, to date there is no consensus description of the structural origin of strain hardening, mainly because of lack of available tools that can provide simultaneous microstructural and macroscopic information. As seen in Figure 7, the SANS pattern at low deformation is isotropic due to the random distribution of the fibers in the network. At moderate deformation, when the gel modulus increases by one order of magnitude, the fibers still present an isotropic distribution and the structure is identical to the one at rest. However at large deformation, when the modulus increases by 2 orders of magnitude, a clear anisotropy in the scattering intensity in the direction of the deformation is observed. In this regime the fibers are partially aligned in the direction of the strain. These preliminary results are the first evidence for a direct correlation between network deformation, fiber alignment and strain hardening. Our observations indicate that the primary mechanism responsible for strain hardening might be more complex than initially predicted by currently accepted theoretical models.[14] Thus, by simultaneously combining rheological and structural measurements, new insights are being brought to this fascinating problem of the structural origin of strain hardening in these biopolymer networks.

CONCLUSION

In this paper, we report on the modification of a commercial rheometer to simultaneously perform macroscopic rheological measurement and microstructural studies by SANS over a broad temperature range. Our Rheo-SANS set up uses a Couette geometry allowing small angle scattering from both the gradient/vorticity and velocity/vorticity planes (scattering in the radial and tangential configurations) in order to reconstruct the 3D structure of the sheared fluid. Furthermore, small volume cells (as small as 3 mL) provide the capability of performing Rheo-SANS measurements on unprecedentedly small sample volumes, allowing measurements on extremely precious samples, as well as increase the accessible stress. Aside from polymer melts and other samples with torque requirements above 150 mN · m, use of the rheometer restricts the accessible samples due to the normal forces on the bob when loading very thick samples (a problem not encountered with the old style strain controlled devices shear cells). The device is thus ideal for the study of most complex fluids and the ability to measure stress and structure simultaneously should open up new areas of research as demonstrated by the studies of shear thickening sample and strain hardening gels (where gelation was been performed *in situ*). This device is now a standard sample environment at the NCNR and available for general use.

It should also be noted, that based on this collaborative effort, Anton Paar's new rheometer, the MCR501, can be purchased with a neutron package which includes the convection temperature control and quartz and Titanium tools. Some

details such as solvent traps continue to be fine tuned, but the facility will still be responsible for the slit package and mounting on and off their beamline. This provides an option for acquiring a nearly turnkey system for doing Rheo-SANS.

ACKNOWLEDGMENTS

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