A Novel Rheological Microscope for Flow Studies of Thermotropic Polymers and Polymer Blends: Droplet Deformation

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ABSTRACT

We have recently begun investigating the rheological behavior of blends containing thermotropic liquid crystalline polymers (LCPs) and isotropic polymers. To aid us in our studies, we have designed a unique instrument for simultaneous visualization of morphology evolution and rheological measurements. Rectilinear shear is used, with a top glass bar being translated relative to a fixed bottom glass bar. The sample is heated by conduction from mica heaters embedded in the substrate materials supporting the bounding glass bars. Shear forces are obtained by measuring the (small) deflection of the bottom glass bar and heating assembly which is designed to be slightly compliant in the flow direction while rigid in direction normal to the sample.

INTRODUCTION

Studies of the rheological properties of liquid crystalline polymers and polymer blends have recently seen the use of a variety of rheo-optical instruments. Examples appearing in the literature most commonly consist of a rotational shearing geometry, such as the "parallel plate" shear cell[1,2,3] used in conjunction with tradition light microscopy, or small-angle light-scattering (SALS) optics. Other designs have utilized rectilinear shear at room temperature[4] or at elevated temperature[5] in which one glass bar is translated relative to another, shearing the sample for optical observation. A fairly thorough review of these types of rheo-optical instrumentation has recently appeared[6] and includes a collection of example applications of rheo-optical methods to polymer blends. With these shearing cells, researchers have focused mostly on the evolution of microstructure, such as disclination texture or phase-separated morphologies, under shear flow.

Our primary interest is in expanding the fundamental understanding of the rheological properties of blends containing thermotropic LCPs within the framework of Palierne's constitutive model for viscoelastic emulsions[7]. We, therefore, have a strong interest in simultaneously measuring rheological material functions and microstructure (at the droplet/fibril length-scale) at elevated temperature. None of the existing designs allow for this capability, however. In this paper we describe an instrument enabling such capability and, in addition, demonstrate its use in examining droplet deformation of two different thermotropic LCPs in an isotropic polymeric matrix.

INSTRUMENT DESIGN

The design of the rheological hot-stage, described as follows, was adopted to satisfy a number of stringent functional requirements. First, samples heated to temperatures in excess of 300 °C needed to be studied at thicknesses as small as 10 μm and with a high degree of alignment of the bounding surfaces. Also, due to the requirement of thin samples, small displacements of the moving plate needed to be possible to enable the measurement of linear viscoelastic properties. Finally, it was necessary that the method of stress measurement not

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compromise rigidity in the direction normal to the bounding surfaces. In addition to satisfying these requirements, we chose the general design approach of building a rheological "hot-stage" for mounting on an existing microscope – rather than building microscope-optics into an existing rheometer. We believe that this design does not compromise the quality of optics obtainable with commercially available microscopes (which are very reasonably priced) in comparison with their rheological counterparts. Finally, the sliding plate configuration in preference to a rotational configuration will enable us to examine mixed flows containing both shear and extension.

Linear Translator Framework.

The starting point for this design is an open-frame linear translation stage which features two rectangular plates, roughly 18 cm square, each with a centered rectangular cut-out. Attached to the bottom of the top plate are encapsulated bearing "trucks" which travel along rails mounted to the top of the fixed bottom plate. The top plate of the rheometer is driven by a fine pitch (1 mm) ball screw laterally offset from the center of the open frame and rotated by a microstepping motor being driven with stepping resolution of 50,000 steps per revolution. This leads to an ideal displacement resolution of ± 0.04 μm. The nut connecting the ball-screw to the translating open frame was designed to possess negligible backlash for optimum performance in oscillatory shear and in flow reversal. For oscillatory shear, the indexer (Compumotor 6200) is operated in "circular interpolation mode" such that the output to the single shearing axis is a displacement which is sinusoidal in time. The frequency and amplitude of the applied oscillation can be easily programmed from a control computer via RS-232 communication with the Compumotor indexer. With this motor/controller configuration, and for a sample thickness of 100 μm, the shear rate range of the instrument is $4 \cdot 10^{-4}$ s^{-1} to 640 s^{-1}.

Sample Containment and Gap Adjustment.

Heating assemblies, discussed in more detail below, which support glass bars (7.6 cm x 2.54 cm x 0.32 cm) are held in opposition through the cut-outs of both the top and bottom translator plates to contain a molten thin film for rheological and optical measurements. The arrangement of the heating assemblies is shown in Figure 1 using a side view of the linear translator. The top plate of the linear translator (a) is displaced relative to the bottom fixed plate (b) in the direction normal to the drawing along recirculating ball bearing trucks on hardened steel rails (e) by a ball-screw turned by a microstepping motor (d). The top heating assembly is vertically positioned relative to the bottom assembly using a kinematic mount consisting of three micrometers (c) (only two are drawn for this view), with spring-loaded screws (e) forcing the micrometers against their hardened steel housings. The bottom assembly is held vertically fixed using two support rods (g) mounted through four linear air-bearings (not seen in this view), one on either end or each rod. Light from either a tungsten lamp or Helium-Neon laser (i) is focused on the sample with a condenser (h) and divergent light is collected with an objective lens (k) and acquired for digitization with a high-resolution CCD camera (j).

Use of the kinematic mount is quite versatile in that the orientation of the top plate can be directly manipulated relative to the lower, stationary plate. Two obvious applications of this capability include the prescription of a wedge-type flow containing mixed shear and extension kinematics in which the moving plate is tipped by a small rotation about the vorticity axis (the axis perpendicular to both the flow and flow gradient directions). The other flow geometry easily obtained with the kinematic mount is a variable shear rate gradient obtained by rotating the top plate a small amount about the flow axis. This flow geometry may be useful in simulating mold-filling flows in which large shear rate gradients may exist. With this kinematic mount system for gap adjustment, sample thicknesses ranging from 10 μm to 2 mm ± 1 μm can be obtained.

Heating.

A schematic drawing of the side view of the heating assembly design is shown in Figure 2. In this drawing, the fully assembled unit is shown at the top, with the lower drawings showing each individual component separately. Two aluminum tabs (a) secure the beveled-edge glass bars (b) to the aluminum substrate (c) which is heated conductively by a thin mica heater (e). The heaters are forced against the aluminum substrate with even pressure from plate (f) made of Macor™, a machinable ceramic. Heating assembly components intersecting the optic axis of the microscope feature beveled center slots for optical access with a total included angle of 60° (for conoscopic observations) and a minimum slot width of 3.175 mm. To minimize heat conduction to the supporting hardware of the hot-stage, the heating assemblies are offset with thin walled steel tubes (d). A thermocouple is embedded in each of the two heating assemblies within the aluminum substrates (c), and the temperature of each is controlled independently using PID controllers (Eurotherm 808). With this heating system, sample temperatures spanning the range $25\ ^{o}C < T < 400\ ^{o}C \pm 0.5\ ^{o}C$ are easily accommodated.

Force measurement.

A tension-compression load-cell (Omega Engineering, LCF) is used for force measurement and subsequent determination of rheological material properties. In this design, the lower stationary glass/heating assembly is held vertically fixed by mounting the assembly to two hardened steel rods which are each mounted through two linear air bearings. It is essential to use the bearings to prevent compliance of the bottom surface in the direction normal to the shearing flow, since most of the experiments are performed on very thin samples and on loading the samples between the glass plates any compliance would lead to significant uncertainty (and perhaps time dependence) of the sample thickness. The load cell is mounted with one end attached to the fixed bottom linear translator plate (see figure 1, (b)) and with the other end attached to the steel rods (and thus to the bottom heating assembly) via an aluminum clamp. The force range measured in this way can range from 0.5 to 50 grams-force, for the most sensitive load cell, to 1 to 1000 grams-force for our most frequently used load cell.

Optics

A convenient feature of the design of the rheological microscope is that it is mounted onto an existing light microscope with no modification to the optics, except for necessary use of long-working-distance objective lenses.

SAMPLE EXPERIMENT

To demonstrate use of this new instrument, we have examined the deformation of LCP droplets in a poly(dimethylsiloxane) (PDMS) matrix. The LCPs are semiflexible homopolyesters synthesized from the condensation of 4,4'-dichloroformyl-α,ω-diphenoxyhexane and t-butyl hydroquinone. For one of the LCPs, tHOB6-*e*-B, the phenol chain terminations are end-capped with benzoyl chloride to prevent further polymerization in the heated melt state. The second LCP, tHOB6-*e*-POSS, is derived from the same parent polymer, but both carboxylic acid and phenol chain ends are end-capped with polyhedral oligomeric silsesquioxane (POSS) groups. Details of the synthesis and characterization of these polymers have been reported elsewhere[8] and are the subject of a forthcoming paper[9]. The PDMS has a weight-average molecular weight of 400,000, while the parent LCP from which both LCPs are derived has a weight-average molecular weight of 20,000. tHOB6-*e*-POSS and tHOB6-*e*-B differ in both the magnitude of viscosity (tHOB6-*e*-B's viscosity is 100 Poise, which is a factor of 10 smaller than that of tHOB6-*e*-POSS), and in interfacial tension with PDMS (tHOB6-*e*-POSS/PDMS features

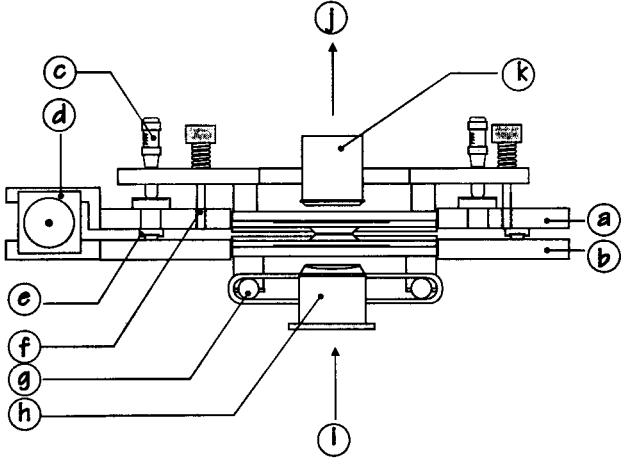

Figure 1: Side view of rheological microscope heating stage. Labeled components included: (a) top translator plate, (b) bottom translator plate, (c) gap adjusting micrometers, (d) stepper-motor/ball screw, (e) recirculating ball bearing trucks, (f) spring-loaded screw, (g) steel rods supporting bottom heating assembly, (h) microscope condenser, (i) light from tungsten lamp or laser, (j) light to CCD camera, and (k) microscope objective. See text for full description.

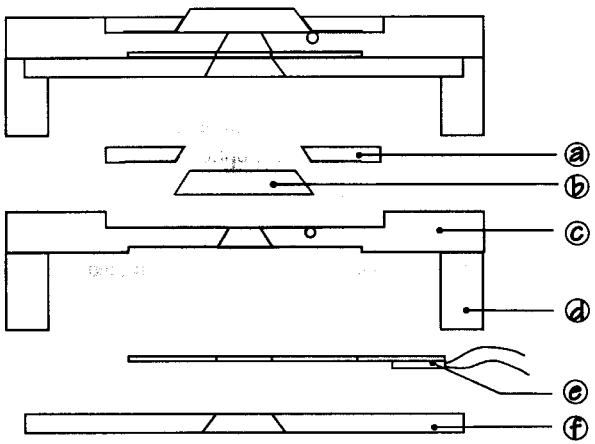

Figure 2: Schematic of heating assembly. Two aluminum tabs (a) secure the beveled edge glass bars (b) to the aluminum substrate (c) which is heated conductively by a thin mica heater (e). The heaters are forced against the aluminum substrate with even pressure from plate (f) made of Macor™, a machinable ceramic.

vanishingly small interfacial tension, while tHOB6-*e*-POSS/PDMS features an interfacial tension on the order of 20 dynes/cm.)[9]

Droplets of each LCP were dispersed in the PDMS matrix at 180 °C and oscillatory shear was applied with a frequency of 2.5 rad/sec and an amplitude of 80%. The results as observed in a light microscope with a 25x objective lens are shown in Figure 3. Figures 3(a-c) (left column) show the deformation of the tHOB6-*e*-B droplet at +80%, 0%, and -80% strain, respectively, when viewed with polarized light and no analyzer. For this polymer and these deformation conditions, the viscous stresses are large enough, relative to interfacial stresses, to deform the droplet, although with each oscillation the droplet returns to a roughly spherical shape at zero strain. Figures 3(d-f) (right column) show the contrasting behavior of the tHOB6-*e*-POSS droplet at +80%, 0%, and -80% strain, respectively, when viewed between crossed polarizers with the incident light polarized perpendicular to the flow direction. Under the same flow conditions, and after several oscillations, this LCP droplet does not return to a spherical shape at zero strain, but instead remains ellipsoidal for all values of strain during the oscillation. Upon cessation of oscillatory shear, the tHOB6-*e*-POSS droplet remained ellipsoidal for a time much longer than tHOB6-*e*-B (several hours) and this time scale difference could not be accounted for by viscosity differences alone. This observation is consistent with independent observations of lower interfacial tension of PDMS and tHOB6-*e*-POSS relative to PDMS and tHOB6-*e*-B.[9]

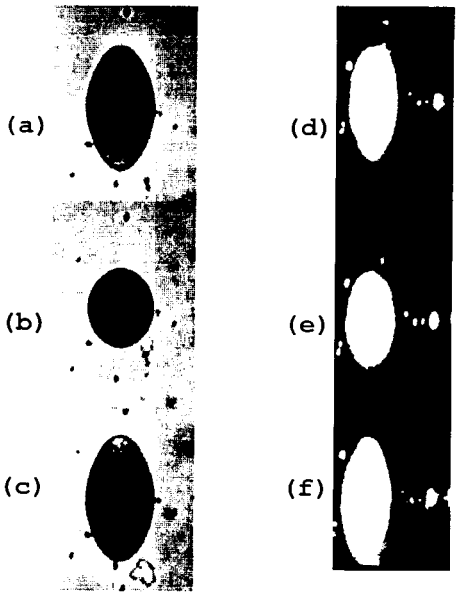

Figure 3: Oscillatory shear response to droplets of two thermotropic liquid crystalline polymers in PDMS. Sample thickness is 500 μm, temperature is 180 °C, oscillation amplitude is 80%, and the droplet diameter in (b) is 40 μm. LCP tHOB6-*e*-B, viewed with polarized light and no analyzer, appears on the left column for shear strain values of, top to bottom: (a) +80%, (b) 0%, and (c) -80%. LCP tHOB6-*e*-POSS, viewed between crossed polarizers, appears on the right column for shear strain values of, top to bottom: (d) +80%, (e) 0%, and (f) -80%.

CONCLUSIONS

A novel rheological microscope has been designed which enables observation of morphology and microstructure during shear flow of thermotropic melts and polymer blends at elevated temperatures. Experiments have been performed to examine the deformation of two end-capped liquid crystalline polymer droplets in an isotropic matrix. Preliminary results have revealed distinctive droplet deformation dynamics when the end-capping group is changed.

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