Notes on rheological measurements

Project Title: Polymer Informatics Tools for Sustainable 3D Printing (PITS3D)
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1 Executive Summary

This document summarises my notes on linear rheological measurements undertaken during my secondment at IESL-FORTH, Crete, Greece. This secondment was a part of my PITS3D project and it aimed to provide me with training in experimental rheological techniques. This experience was used for the detailed rheological characterization of commercially available poly(lactic acid) (PLA) and unentangled PLA samples synthesized in the host institution. The ultimate goal of PITS3D was to correlate these experimental findings with computational and theoretical approaches, thereby advancing polymer characterization within the host group and facilitating knowledge transfer in the field.

Consider this document a freely available set of instructions, created with the hope of aiding anyone who uses it.

2 Brief summary of the used materials

Commercially available PLA3D850 was used as the training material. PLA3D850 was in a form of pellets and therefore, the samples for rheology were prepared by a hot press. Some notes are also related to the unentangled PLA samples, which were in a form of powder and therefore, the samples were cold pressed in a mold and then carefully transferred to the plate.

3 Methods

3.1 Preparation of the samples by a cold/hot press

- the pieces, which the hot press consists of, are shown in Fig. 1
- set up the vacuum
- press: enough to apply up to 1 ton
- sample weight around 55 mg for a disc of diameter 8 mm and thickness of 1 mm
- sample weight around 250 mg for a plate of 25 mm and thickness of 0.6 mm
- in the case of the commercial sample, the pellets were firstly squeezed in the mold by a cold press and then the press was heated to 190°C. This temperature was kept for 5 minutes and then the sample was slowly cooled to the room temeperature.

Figure 1: Top: Pieces used for the press: bottom part of the outer chamber, bottom part of the inner chamber, inner chamber, cylinder with the hole of diameter 8mm, stick with the diameter 8 mm, rubber bands, upper load, upper lid of the outer chamber. Bottom Left: Assembled parts. Bottom Right: Hot press. The lever on the right is used to apply pressure.

3.2 Description of the rheometer

- ARES, air atmosphere
- Orchestrator program to set up the parameters
- upper part sensor (transducer)
- lower part oscillating (motor)
- sensor showing the normal and torque forces
- thermocouple to control the temperature
- plate 8 mm for the commercial samples, for the unentangled samples 25 mm plate because of the low torque

3.3 Starting the experiment

- switch on the transducer 2 to attach the plates: Utilities→Service→Transducer

- place the thermocouple: if the temperature does not change from -220 to the room temperature, we go to Utilities→Service→Instrument Configuration and change the Temperature Loop Control to Sample
- align the plates: the bottom part should be at 0 angle
- set the normal force to 0 (NORM CLR) when the plates are not touching each other
- set the gap to 0: initiate the contact between the plates and when the normal force positive, press GAP CLR

Setting the temperature:

- set the temperature to the reference one: icon with the thermometer, environmental controller ON, motor ON
- the chamber is closed, the plates are not touching, wait 15-30 minutes for the plates to reach the desired temperature
- set the normal force to 0
- set the gap to 0, because it has changed due to the thermal expansion: if the coefficient of the thermal expansion is unknown, write down the gap before setting it 0 and calculate the coefficient (gap(T_1)-gap(T_0))/($T_1 - T_0$), having in mind that gap(T_0)=0 and T_0 is the room temperature

Loading the sample:

- cool down the plates to the room temperature
- center the sample on the plate and lower the plates to touch the sample. If the sample is unentangled and in a form of a pressed powder, it might be convenient to first melt the sample (i.e., to increase the temperature above the melting temperature) and then lower the top plate to touch it.
- warm up the sample: as the sample is going to expand, increase the gap continuously until the shape of the edges is concave (see Fig. 2)
- wait 15 minutes to melt
- check the shape and change it to donut shape (i.e., rounded edges, see Fig. 2)

3.4 Removing possible bubbles in the sample

- Press Control-Edit/Start Instrument Test
- set Geometry-Parallel Plate Geometry, Edit geometry: put the dimensions of your sample (diameter 8 mm and the current gap)
- Step rate test-Edit (put settings below)

!! if the measurement doesn't start immediately, check Options in Start Instrument Test, there may be a delay set on from the previous measurement

Preshear: Step Rate Test

- Test type: Strain-controlled
- Measurement Type: Transient

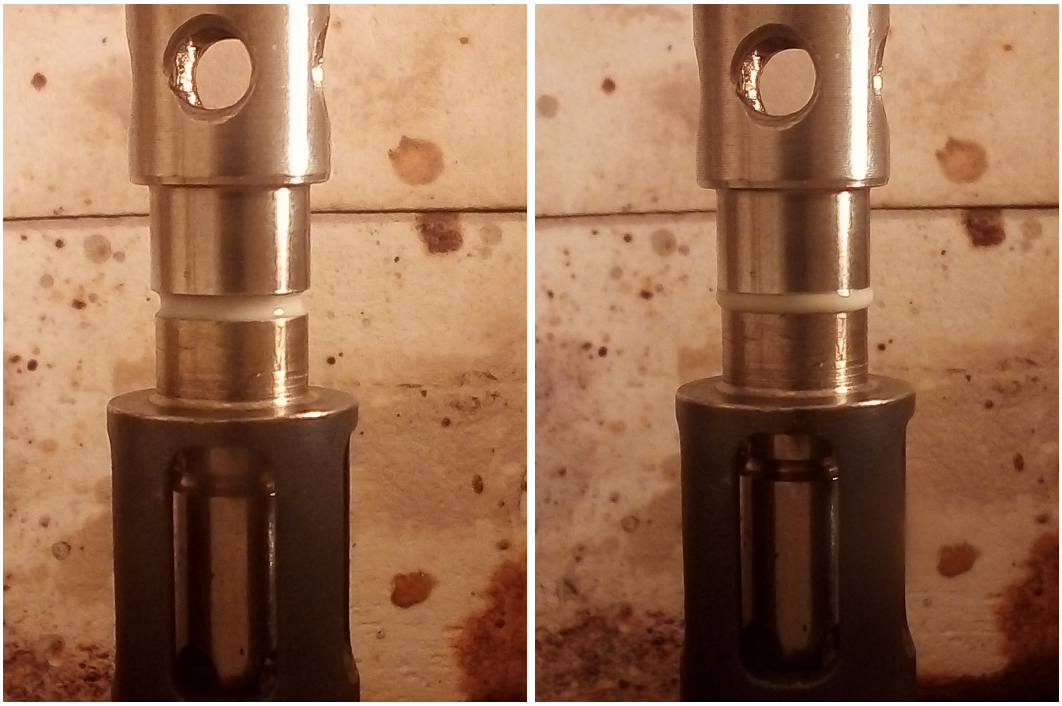

Figure 2: Left: Concave shape. Right: Donut shape

- Motor ON
- sampling mode log
- points per zone 350
- shear rate 0.5 s^{-1} (or 0.1 $^{-1}$ is the sample is sensitive, then longer time)
- time 60 s or until necessary
- clockwise

Setting motor after preshear

- the motor is misplaced: in order to put it in 0 position, the motor in temperature must be switched off, then the motor is moved manually to the position 0
- then the Control→Motor→Mode Dynamic
- Go to Temperature and set Motor on

Dynamic Time Sweep Test

- fixed frequency: 100 rad/s
- fixed strain 0.5 %
- run for at least 30 minutes
- increase strain if the bubbles do not move
- the shape of the sample can be concave

3.5 Linear Rheology Measurements

Generic procedure

- Dynamic Strain Sweep
- Dynamic Frequency Sweep
- Temperature Ramp Test (if desired)

Dynamic Strain Sweep

- switch to transducer 1 (Utilities-Service-Transducer)
- test to find the maximum strain at which the response of the material is linear at the given temperature: it needs to be repeated every time when we change the temperature
- Measurement type: Dynamic
- frequency: 100 rad/s
- settings: γ_{min}=0.5, γ_{max}=100
- stop when the moduli start to decay abruptly
- write down the value of the strain before the decay

Dynamic Frequency Sweep
Checking the slip: it is necessary to find the gap at which the results are reproducible: reduce the value of the gap and perform the linear rheology measurements (see settings below) until the data are consistent and overlap, i.e., the data remain consistent with respect to the last measurement:

- start dynamic frequency sweep, with the settings below, the variable will be the gap in Geometry Settings
- set the gap that is shown on the screen
- measure the spectra
- decrease the gap, so that the second decimal number changes, careful to not squeeze the sample too much: keep the settings of the DFS the same, change the Geometry Settings
- measure the spectra again and overlay them to see if they overlap: double click on the spectra, Overlay-select the data set
- repeat until the data overlap, i.e., they are consistent

When the data are consistent keep this gap fixed in Geometry Settings during the whole measurement, so even if the temperature is changing. Decrease the gap only manually, using the value calculated from the thermal expansion coefficient. For example, if the thermal expansion is 2.5 μm/°C and the change in the temperature between two measurements is 10°C, reduce the gap 25 μm.
Measurement settings for different temperatures:

- set Parallel Plate in Geometry Settings
- set Dynamic mode
- set the maximum strain obtained from DSS, measure from frequency 100 to 0.1 rad/sec.
- repeat the measurement for different temperatures:

- change the temperature in Temperature settings and wait for 10 min
- change the gap manually when the new temperature is set in rheometer to compensate for the thermal expansion of the plates
- do not change the Geometry Settings
- once the sample is equilibrated, repeat DSS and DFS with the new temperature settings

Temperature Ramp Test

- measure first DSS and DFS at the reference temperature and check if the data are consistent with the previous measurements. Note: some samples may degrade and therefore their G' and G" may be below the reference data.
- set the temperature at the beginning of the measurement and leave the sample to equilibrate
- settings: frequency (1-10 rad/s), initial and terminal temperature, ramp rate (1-10°C/min), strain (0.5%)
- important to change the gap manually during the whole measurement, usually after 10°C, as it changes due to the thermal expansion and it may cause a sample detachment at low temperatures
- in the crystallization region, it may be necessary to switch to the Transducer 2 to avoid overload
- for semicrystalline samples, the delay in setting the heating measurement right after the cooling measurement may cause a mismatch in the first values of G' and G" for heating and the last values for cooling, as the sample continued to crystallise during the time that the measurement was set