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Electrically Heated Plates EHP and Active Temperature Control ATC

Aly Franck, Aadil Elmoumnia, TA Instruments

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SCOPE

For the characterization of polymers convection or radiant ovens are widely used, due to their ease of use and their wide temperature range from typically -150 °C to 600 °C. Although air convection or radiation ovens satisfy the needs of many testing requirements, they have limitations when the samples are very sensitive to degradation, the materials properties are strongly temperature dependent or high sensitivity torque measurements are required.

For those applications, electrically heated plates (EHP) have proven to be far superior. The EHP generate the heat directly in the plates. Because of the short time constants, temperature variations can be compensated for much better and faster. This results in better temperature stability, typically below 0.1 °C as well as much reduced radial temperature gradients. When upper and lower plates are heated directly and controlled independently, vertical temperature gradients can be virtually eliminated. With a preheated purge gas stream inert conditions with a very low rest concentration of oxygen are easily achievable in a tight (small volume) environmental enclosure. And finally, since there is hardly any convection of air or gas in the enclosure, the low end torque capabilities of the torque transducer or the torque motor are not affected – thus sensitive measurements such as recovery measurements are possible without any restriction from the environmental control system.

TECHNOLOGY

Electrically heated plates

The electrically heated plate system EHP for the AR series consist of a lower conduction and upper radiation heating/cooling assembly, which provide a uniform radial temperature profile throughout a sample. Parallel plates and/or cone plate geometries are possible. (Figure 1). The heat is gener-

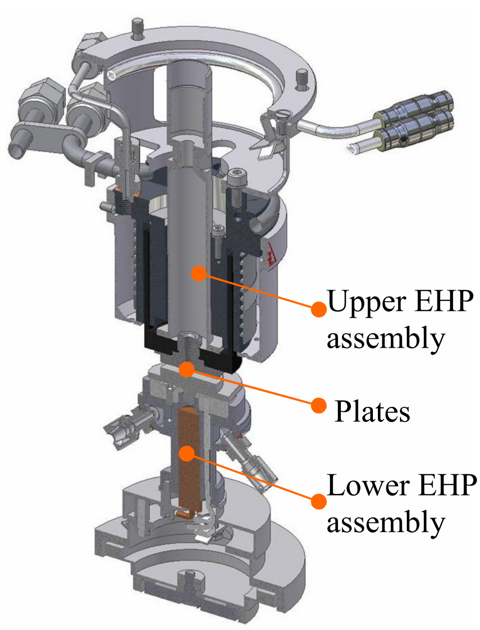


Figure 1: Schematics of the EHP for AR2000EX and AR-G2

ated by electrical heating and removed by a cooling medium, circulating through embedded channels in the heater block. The lower electrically heated plate assembly is mounted onto the smart swap base of the AR rheometer and the heater block is attached directly to the plate geometry. Since no mechanical contact to the rotating upper geometry (plate or cone) is allowed, a non contact radiation heating block is used to control the temperature in the upper plate. The heat spreader, attached to the upper plate geometry has been optimized for fast heat distribution with minimum radial temperature gradients in the plate. Due to the cylindrical design and vertical arrangement of the heat spreader, the heat transfer by radiation does not depend on the exact position of the heat spreader relative to the heater block – thus is virtually independent of the sample gap. A tight enclosure with optional window for sample visualization isolates the test area from the surrounding atmosphere. The pre-heated purge gas prevents oxygen from the atmosphere to enter the test section.

Finally, but nevertheless important, because no mechanical contact exists between the rotating test geometry and the test station, the low torque sensitivity of the torque motor is not affected.

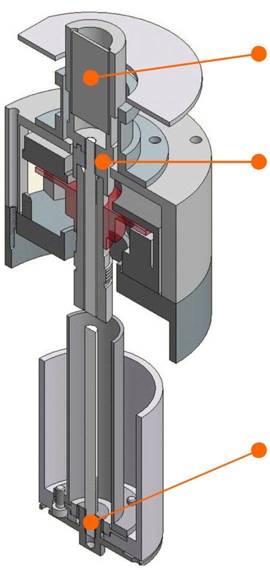


Figure 2: Upper test fixture for ETC with wireless temperature sensor (for ATC

Active Temperature control (only for AR-G2)

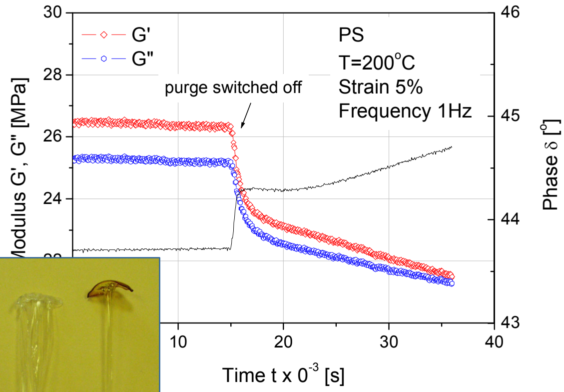
The ATC consists of a temperature probe[(1)] mounted directly in the upper rotating platen and provides, without any mechanical contact, a temperature read-out which is used to control the actual platen temperature. The PRT sensor is integrated in the tip of the draw rod and the temperature information transmitted via a micro printed circuit board mounted into knob of the draw rod at the top, to the system electronics (Figure 2). Both upper and lower heating assemblies have independent temperature controls. Since the temperature in the upper and lower plate are precisely known at any time, no complex calibration procedures are necessary for the upper heater and heating or cooling strategies can be optimized either to maximize the heating/cooling rates or to minimize the temperature gradients in the sample.

EXPERIMENTAL

In order to prove the performance of the EHP and ATC, tests have been performed with a commercial and an anionically polymerized polystyrene. The PS samples were molded into 2mm sheets and 25mm discs were punched out. The samples were kept under vacuum and removed from the vacuum oven prior to testing only. All tests were run using the EHP and ATC option using the AR-G2 rheometer

Polymer thermal stability tests with and without inert gas purge

Two different test series were performed with the commercial polystyrene to show the effectiveness of the inert gas purge. In a first step, an oscillatory time sweep test was performed at 200 °C at a frequency of 10 rad/s for a period of 10 hours. Nitrogen purge gas was used. As can be seen from Figure 3, no change for G’ and G” were detected for 250 minutes. At that point the inert gas purge was turned off; immediately



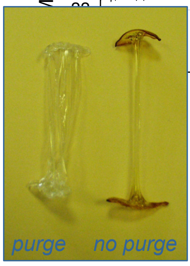


Figure 3: Sample stability at 200oC with and without purge gas

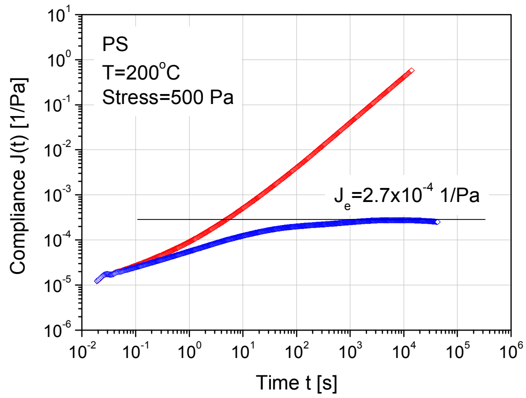


Figure 5: Creep Recovery test of the PSref at 200°C. Test time 16 hours

the sample started to degrade. After 600 minutes, the moduli G' and G" have dropped by 30% while the phase δ is increasing, approaching 45°. This means that the cross over frequency is shifting to higher frequency also, a proof that the MW is decreasing.

In a second experiment, a creep recovery test was performed on the commercial PS. Prior to the creep test, a frequency sweep test was performed to establish reference data of the material before subjecting it to an extended stay at 200 °C. Next a constant stress was applied to the sample for 300 minutes followed by a recoil test at zero stress (Figure 5). A steady state was reached after 400 minutes and this value remained constant for 16 hours. The test was stopped and a second frequency test was performed to detect eventual changes of the materials due to the extended stay at 200 °C. The overlay of the frequency sweep data before and after the creep recovery test shows that the data superpose completely (Figure 4). The variations of the cross-over frequency and cross over modulus were of the order of only a few percent.

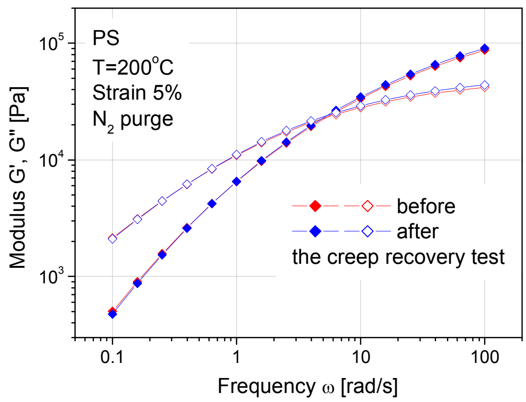


Figure 4:Frequency sweep before and after a16 hour creep recovery test

Low torque sensitivity for accurate recoil measurements

Recoil experiments of polymer melts are extremely sensitive to the residual torque of the rheometer. During the recoil experiment, the sample is free to recover to an equilibrium deformation, without any external stress acting on the sample. In a rheometer, this ideal situation cannot be obtained and in CMT rheometers, the lowest torque "residual torque" is defined by the air i.e. magnetic levitation bearing. In case an oven or furnace is used to control the temperature, the convection of the air or inert gas in the oven disturbs the freely rotating test fixture and increase the residual torque acting on the sample. When using EHP, the heat is generated in the test fixtures and distributed evenly to the sample via the heat spreader, in the upper and lower plate. The purge gas stream is very small and does not disturb the rotating upper plate.

Creep recovery experiments have been performed on a narrow distributed PS (PS145) with an M_w of 145000 g/mol and

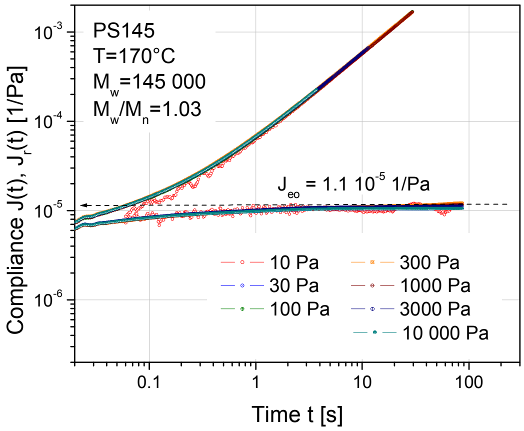


Figure 6: Creep Recovery of a narrow distributed PS145 over a stress range from 10 to 1000 Pa

an M_w/M_n of 1.03. For a narrow distributed polystyrene the total recovery is very small and at low stress (linear region), the creep due to instrument residual torque can easily dominate the recoverable deformation. This effect shows as a continuous decrease or increase (depends on the direction of the torque) of the recoverable strain. Equilibrium is not obtained in this case.

The results in figure 6 represent the creep compliance and the recoverable compliance for the PS145 in double logarithmic plot over a stress range from 10 to 1000 Pa. All the data superpose, which means the sample behaves linear viscoelastic. More important is, that down to 10 Pa, the recoverable compliance reaches a steady state value and no drift due to residual torque is detected. The value of the equilibrium compliance is 1.1×10^{-5} 1/Pa, a value which has been confirmed by oscillation data also.

Accurate temperature control in both the upper and lower plate

Without ATC, the temperature is measured in the heater block used to control the plate temperature and not in the upper plate itself. This requires a careful calibration with a reference PRT in the upper plate prior to the experiment. With ATC, this is not necessary, as the temperature is measured continuously directly in the upper plate during the experiment. Figure 7 shows G' for the commercial PS at 200°C, with and without Active Temperature Control ATC. A significant higher G' is found for the experiment without ATC. In order to match the G' data with those obtained from the experiment with ATC, the upper heater set temperature had to be increased by 4 °C. This means that the temperature in the heater block and the sample plate is off by 4 °C and has to be corrected by the calibration, performed prior to the experiment, when ATC is not available.

With the ability to measure the temperature in the upper as well as in the lower plate, the temperature can be changed in both plates at the same rate - thus avoiding temperature gradients in the sample during heating and cooling. The heating or cooling strategy can be optimized for maximum heating rate with minimum temperature gradients in the sample. In figure 8 this is demonstrated with a temperature step from 180 to 220 °C. Control with ATC and optimized control strategy provide a faster response than without ATC.

CONCLUSION

The EHP provides fast and localized temperature control from sub-ambient to 400 °C. A new patented non-contact temperature sensor allows active temperature control (ATC) of the upper plate temperature. The fast control response, due to the proximity of the heater and the control sen-

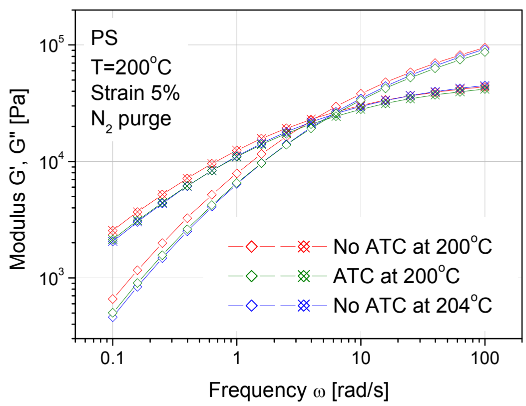


Figure 7: Frequency sweep performed with and without ATC. Without ATC, the a 4 °C temperature offset is needed to match the data obtained with ATC ON

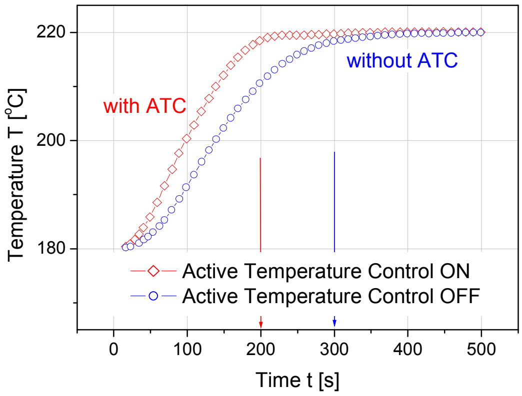


Figure 8: Temperature profile for a temperature step from 180 to 220°C with and ATC ON and OFF

sor reduces temperature fluctuations to less than 0.1 °C. The independent control of lower and upper plates eliminates vertical temperature gradients.

Since the test fixtures are heated directly by heat conduction and not gas convection or distant radiation, air/gas turbulences, decreasing the torque sensitivity of the instrument do not existent. EHP is therefore the heating system of choice for creep recovery measurements on polymer melts.

The EHP, due to the integrated inert gas purge, effectively eliminates diffusion of oxygen from the atmosphere into the sample and as such reduces degradation of temperature sensitive materials.

REFERENCES

1. US Patent 6,931,915