Application Note
V-237

Automatic Detection of the Thermal Degradation of a Polymer

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Introduction

Similar to any other material, the properties of polymeric materials are closely linked to their chemical nature. What makes polymers so different from low-molecular-weight substances is the huge influence of their molecular weight (M_W) and their molecular weight distribution (MWD) on their macroscopic behaviour. Without changing its chemical nature, we can e.g. "select" the rigidity or elasticity of a polymeric material just by varying the parameters of the polymerization process.

Thus, to make a polymer with the desired properties we have to be able to quickly determine the right moment to stop the polymerization process in order to always get the same M_W and MWD. Also, these two parameters can be used to decide whether materials delivered meet the specifications or not.

One widely accepted method makes use of the fact that the crossover frequency determined with a frequency sweep (see Figure 1) depends on the M_W of a polymer, whereas the crossover modulus is related to its MWD.

From the crossover modulus the polydispersity-index (PI) can easily be calculated:

PI = 100.000/Crossover Modulus [Pa]

Fig. 2: The HAAKE MARS equipped with the CTC

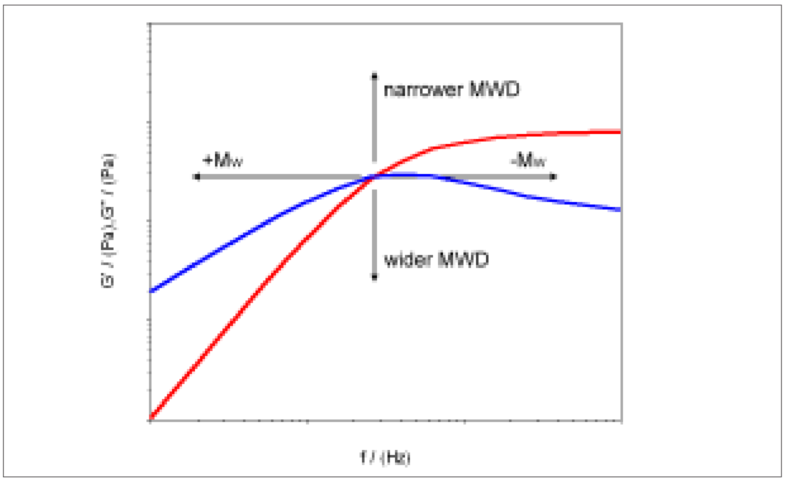

Fig. 1: Schematic crossover dependency on M_W and MWD

The Thermo Scientific HAAKE MARS is a high-end rheometer, which has a number of important advantages for polymer analysis. Amongst them is the sensitive normal force sensor, which allows the measurement of forces down to 0.01 N. In combination with the precise lift control this is a great tool to ensure the reproducible loading and axial relaxation of samples. Another unique feature of the HAAKE MARS is the Controlled-Environment-Chamber (CTC). Its powerful combination of convection and radiation heating guarantees the quick adjustment of temperature and low temperature gradients in the sample.

Measurements

For these measurements very narrowly distributed polybutadienes have been selected. Samples with a diameter of 25 mm were cut from a sheet of approximately 2 mm thickness. While the CTC was preheating to 190 °C in its parking position, the sample was put into the 25 mm parallel plate geometry of the HAAKE MARS and the gap was closed with a defined axial force to have the same starting conditions for different samples. With these preparations it

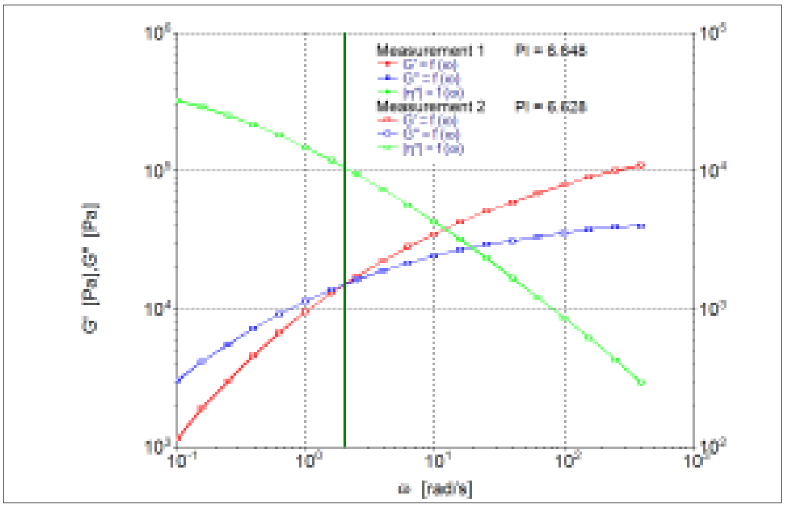

Fig. 3: The crossover of the storage modulus (red) and the loss modulus (blue) during a frequency sweep is related to M_W and MWD. From the cross-over modulus, here 15000 Pa, the so-called polydispersity-index can be calculated, here 6.6. Due to the good reproducibility, the 2 measurements are barely distinguishable.

was possible to run frequency sweeps in a very reproducible way as can be seen in Figure 3.

The resulting curves were practically identical and the PI values calculated differed only about 0.3 %.
These measurements were performed under laboratory conditions, so the whole procedure before starting the measurements, i.e. sample loading, closing of the geometry, was the same in all cases. In working environments where this is not possible, it is especially important to know, whether the polymer regarded is stable e.g. against oxidation at elevated temperatures. Otherwise different results can simply be based on different times it took to start the measurements. This possible degradation of a polymeric sample can be detected using the HAAKE MARS. For that purpose a different polymer sample was prepared and loaded into the rheometer at 190 °C as described above. After equilibration, 15 identical frequency sweeps were done over a time span of 60 min. From earlier measurements we knew roughly, where the crossover could be observed. Therefore, to save time the job was programmed to collect only 6 data points between 10 rad/s and 100 rad/s, which lead to less then 1 min pure measuring time. Due to the capability of the Thermo Scientific HAAKE RheoWin to create and run complex testing procedures, the whole test runs completely without any input from the operator’s side once the sample has been loaded.

As shown in Figure 4, the G’ and G“ curves shift to lower values the longer the sample is exposed to the 190 °C inside the CTC. Subsequently the crossover shifts to lower moduli and higher frequencies (Figure 5), indicating a decrease of the average molecular weight of the polymeric material tested and a broadening of its molecular weight distribution. Expressed in terms of the polydispersity-index we see an increase from 3.9 to 4.2. For usual technical polymers with a broader distribution any kind of degradation would initially affect the higher molecular weights and lead to a narrower distribution. Since the polybutadienes used for this study had a very narrow distribution, degradation leads to an increase of smaller molecular weights and thus broadens the molecular weight distribution.

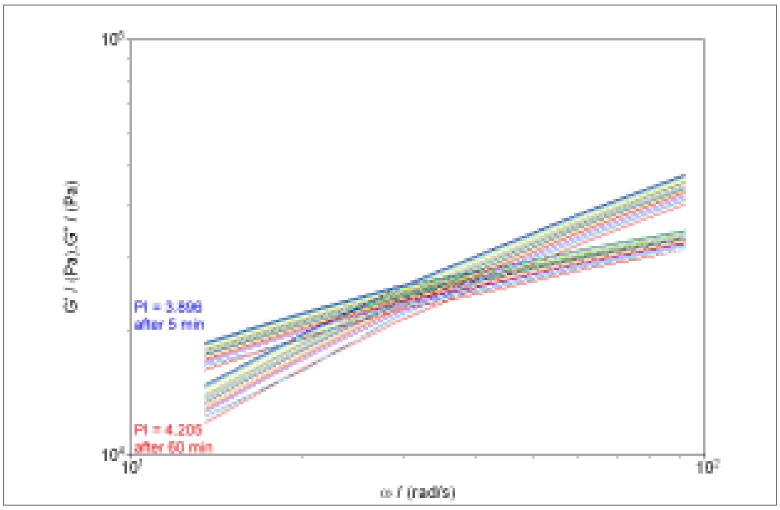

Fig. 4: Polymer sample kept for 60 min in the rheometer at 190 °C while running 15 frequency sweeps. From run to run the curves of both G’ and G“ shift to lower values (from blue to red).

The data evaluation from this test clearly shows that indeed a thermal degradation of the polymer has occurred.

Summary

Using the normal force controlled sample loading for polymer samples of an unknown thickness, the HAAKE MARS equipped with the CTC shows perfectly reproducible results from frequency sweep measurements.
Having seen this great reproducibility any decrease of the crossover modulus and increase of the crossover frequency can be solely attributed to a thermal degradation of the polymer sample tested. The possibility to preheat the CTC in its parking position and the selection of a suitable frequency range minimized the time needed for the measurement. The method described enables a very cost-effective polymer analysis and is also suitable whenever a quick answer is needed.
With the capabilities of the HAAKE RheoWin to run a fully automated test method, the HAAKE MARS equipped with the Controlled Test Chamber (CTC) is the perfect tool to determine if a polymer shows thermal degradation in a very time saving and cost saving way. In case the rheological properties of an oxygen-sensitive polymer have to be measured at higher temperatures over a longer time, the CTC can be flushed with nitrogen instead of air to exclude the damaging influence of the otherwise unavoidable oxygen.

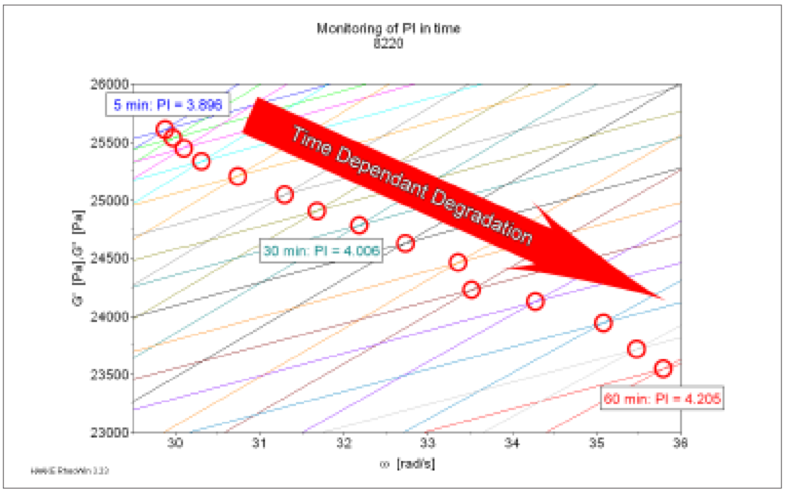

Fig. 5: During 60 min at 190 °C the crossover shifts to higher frequencies and lower moduli showing the decrease of M_w and the broadening of MWD.

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