Application note | LR 74

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Rheometers

Preparation and analysis of PET with additives using a micro compounder and rheometer

Authors: Dirk Hauch and Bernd Jakob, Thermo Fisher Scientific, Karlsruhe, Germany

Introduction

The versatile and common plastic known as PET (polyethylene terephthalate) is often mixed with additives or resins to alter its strength, rigidity, or other physical properties. Attempts to recycle PET can be affected by these additives, leading to different requirements for processing.

In this test PET samples with several additives and plain resin were mixed for a specific time. During the mixing period the composition / decomposition was measured in the integrated slit capillary. When the mixture was ready it was transferred to a micro injection molding machine in order to prepare disc shaped test specimens. With these discs rheological tests of the polymer melt were performed afterwards on a rotational rheometer. The aim was to prove that a test in a micro compounder with only 7 g sample can be used for a fast screening of PET and additives and to give an indication for the chemical recycling of the polymer.

Methods

Sample preparation

The mixtures of PET with additives have prepared in the Thermo Scientific™ HAAKE™ MiniLab™ Micro Compounder with co-rotating screws (Figure 1) at 270 °C with a screw speed of 50 rpm. The sample was mixed by re-circulating for 15 minutes. During the mixing process the pressure drop in the slit capillary of the backflow channel (Figure 2) was monitored.

Injection molding of the test specimens

After the mixing step the polymer was directly extruded into the heated cylinder of the Thermo Scientific™ HAAKE™ MiniJet™ Pro System (Figure 3) for injection molding of test specimens (20 mm Ø and 1.5 mm thickness) for further rheological tests. The temperature of the heated cylinder was 270 °C and the mold was heated to 80 °C. The samples were injected using pressure of 500 bar for 5 sec and post pressure of 300 bar for 5 sec.

Figure 1: HAAKE MiniLab Micro Compounder.

Figure 2: HAAKE MiniLab Micro Compounder backflow channel built as slit capillary with two pressure sensors.

Figure 3: HAAKE MiniJet Pro System and molds.

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Rheological tests

The rheological tests were conducted with 20 mm parallel plates and a gap of 1.4 mm on a Thermo Scientific™ HAAKE™ MARS™ Rheometer with an electrical heated oven at 270 °C under nitrogen atmosphere. All samples first were tested in an amplitude sweep to determine linear viscoelastic range. For frequency sweeps from 0.1 to 46 Hz new test specimens were used. The deformation for all tests was with 0.5 % in a safe regime of the linear viscoelastic range of all samples.

Results

In the recirculation mode it is possible to monitor the pressure profile over time by the pressure difference of the two pressure sensors, built in backflow channel. (See Figure 2.) At the beginning of the test, material is filled into the micro compounder. This results in a pressure peak. Once all the material is filled in and the temperature equilibrated, the pressure profile over time can be used to assess the reaction of the polymer. A decrease of the pressure over time indicates a change of the material. For plain PET, for example, this can be a reaction of the polymer with water (moisture) where the polymer degrades. A decrease of the pressure is in accordance with a lower viscosity of the PET. When the pressure increases over time it is an indication of a condensation reaction of the PET increase in the chain length or branching, which results in a higher viscosity.

The samples for the rheological test were prepared with material that had been re-circulated for 15 min in the HAAKE MiniLab Micro Compounder. The final pressure value can be correlated with complex viscosity |η*| in a dynamic oscillatory test conducted with a rheometer. For the plain PET shown in Figure 4, it can be seen that after the loading peak, there is a pressure drop; this indicates a decomposition of the PET. After 15 min the pressure is almost constant, with a value of approximately 18 bar.

In Figure 5 the frequency sweep for the same sample shows that the loss modulus G" is significantly higher than the storage modulus G'. The slight bumpy curve of G" is due to the fact that the phase shift δ is almost 90° and even small changes have major influences on G". The complex zero shear viscosity |η*| is 200 Pas.

The PET with 1 % 1,2,4-Benzenetricarboxylic anhydride in Figure 6 shows, after the loading peak, a pressure increase which correlates with condensation reaction of the PET. After 15 min the pressure is still increasing with a value of about 15 bar. Compared to the plain PET it's slightly less of an indication of a lower viscosity. A look at the frequency sweep in Figure 7 for the same sample shows that G' and G" are getting closer. This goes along with a lower δ of about 85° at low frequencies. The PET obtains more elasticity. The |η*| is 150 Pas at low frequencies. Compared to the plain PET the additive is responsible for the lower pressure and the lower |η*| on the one hand, but on the other hand the additive did induce a reaction of the PET.

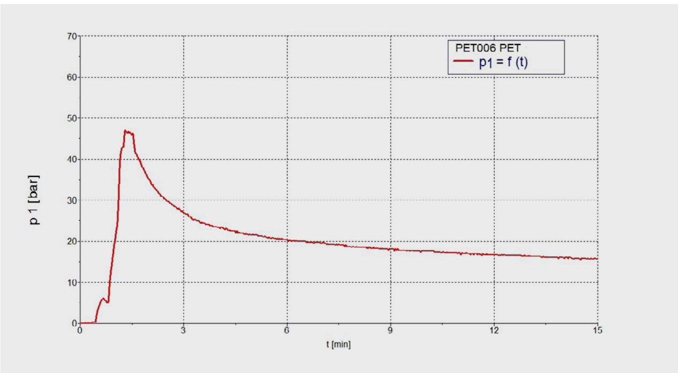

Figure 4:
Pressure dependence of PET with no additives.

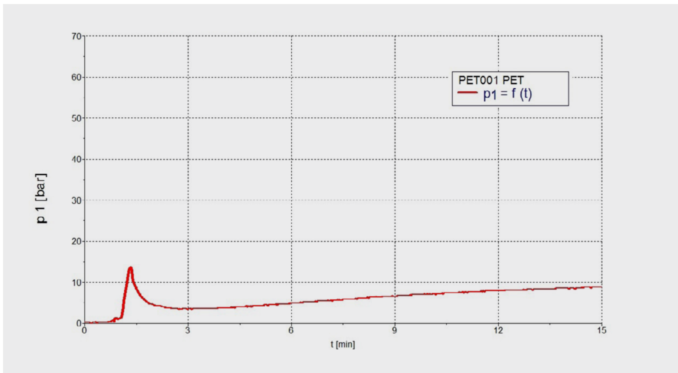

Figure 6:
Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride.

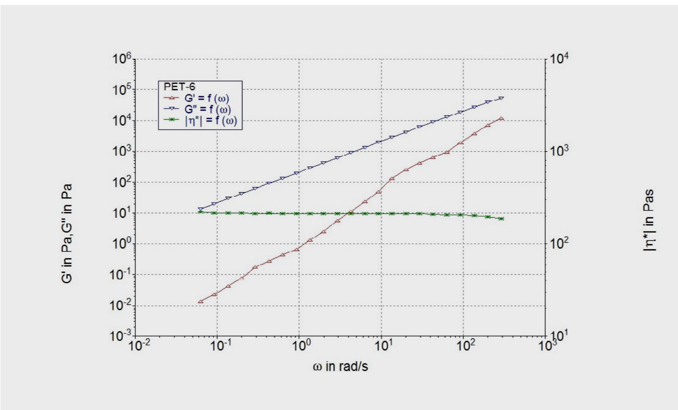

Figure 5:
Frequency sweep of PET with no additives.

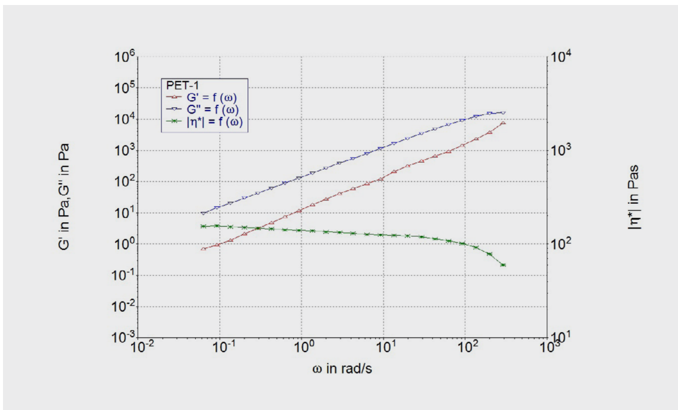

Figure 7:
Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride.

The pressure dependence of PET with 1% 1,2,4-Benzene-tricarboxylic anhydride and 1% meta-Dioxazolinebenzene (Figure 8) shows a pressure decrease, and later on an increase after the loading peak. The end pressure with 55 bar is significantly higher compared to the plain PET and the compound with 1% 1,2,4-Benzenetricarboxylic anhydride as an additive. The pressure fluctuation at the end of the test is due to a rubbery morphology.

The frequency sweep in Figure 9 shows the typical trend of G' and G" for a viscoelastic material.

The |η*| with almost 2800 Pas is more than 10 times higher compared to the plain PET and the compound with PET and 1% 1,2,4-Benzenetricarboxylic anhydride as an additive. A look at the change of δ from 88° at low to 52° at high frequencies indicates a higher elastic behavior coming close to the crossover.

The combination of both additives shows first a decomposition of the PET followed by a reaction to build up a new structure. It is very likely that the molecular weight is significantly higher. The increase of pressure and |η*| correlate well in comparison to the tests of plain PET and the compound with 1% 1,2,4-Benzenetricarboxylic anhydride.

Conclusion

The HAAKE MiniLab Micro Compounder is a useful instrument to screen the effects of different additives. Only a small amount of sample (7 g) is required. A quick look at the pressure dependence data gives a first indication of the functionality of the additives.

The time required for one test is moderate. If further rheological or other physical tests need to be conducted, transfer of the polymer melt into the HAAKE MiniJet Pro System is possible. Different test specimens can be prepared quickly and are reproducible.

The results of these physical measurements could be combined with the knowledge of which specific qualities are caused by a given additive or mix of additives; in turn, this could provide guidance regarding the likely chemicals necessary to recycle PET samples. Additional studies on the molecular weight and distribution, either by extended rheological tests or, for example, Time Temperature Superposition compared with GPC data, could provide further evidence to validate these assumptions.

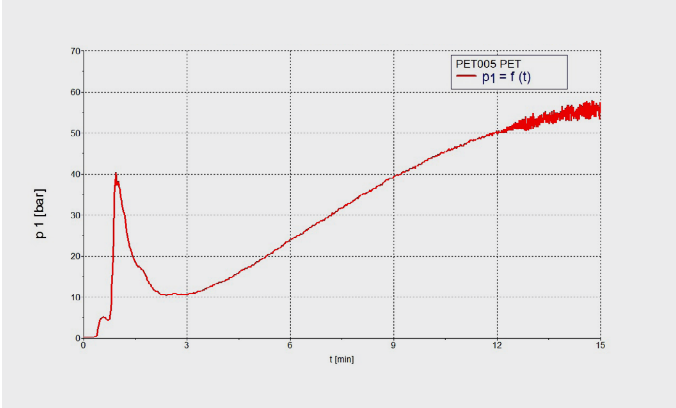

Figure 8:
Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene.

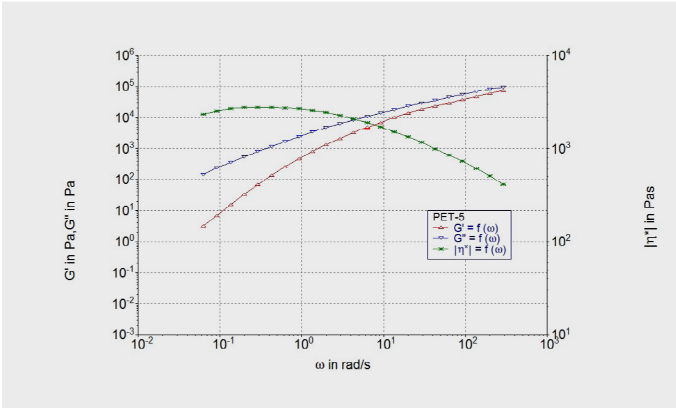

Figure 9:
Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene.

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