

Preparation and analysis of PET with additives in a micro compounder and rheometers

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Introduction

PET samples with several additives and plain resin have been 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 also gives 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 with co-rotating screws (Fig. 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 (Fig. 2) was monitored.

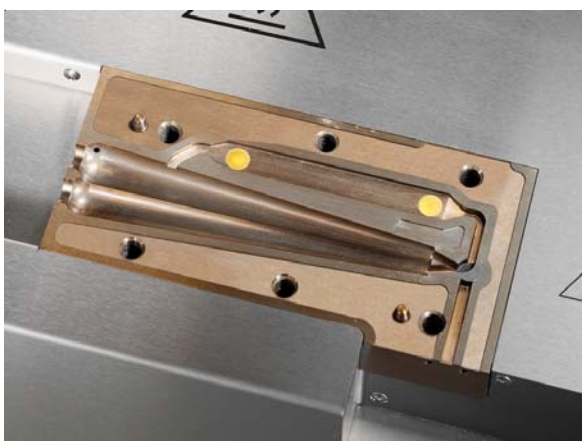


Fig. 2: HAAKE MiniLab backflow channel built as slit capillary with two pressure sensors.

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 (Fig. 3) for injection molding of test specimens (20 mm Ø and 1.5 mm thickness) for



Fig. 1: HAAKE MiniLab

further rheological tests. The temperature of the heated cylinder was 270 °C and the mold was heated to 80 °C. The samples have been injected with 500 bar for 5 sec and post pressure of 300 bar for 5 sec.

Rheological tests

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



Fig. 3: HAAKE MiniLab Pro and moulds

Results

For easier comparison all graphs have the same scaling.

PET with no additives

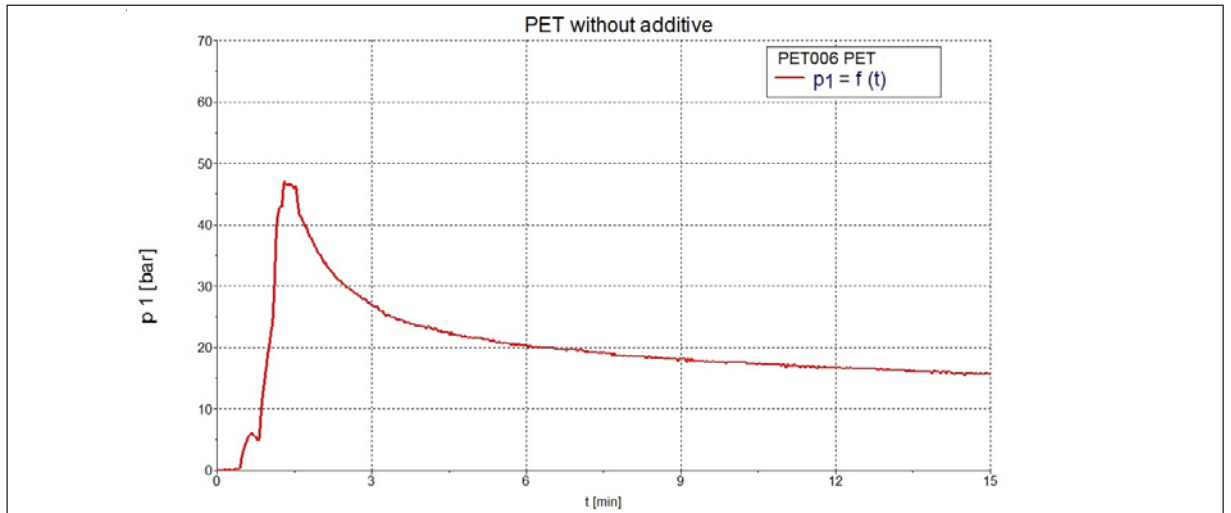


Fig. 4: Pressure dependence of PET with no additives

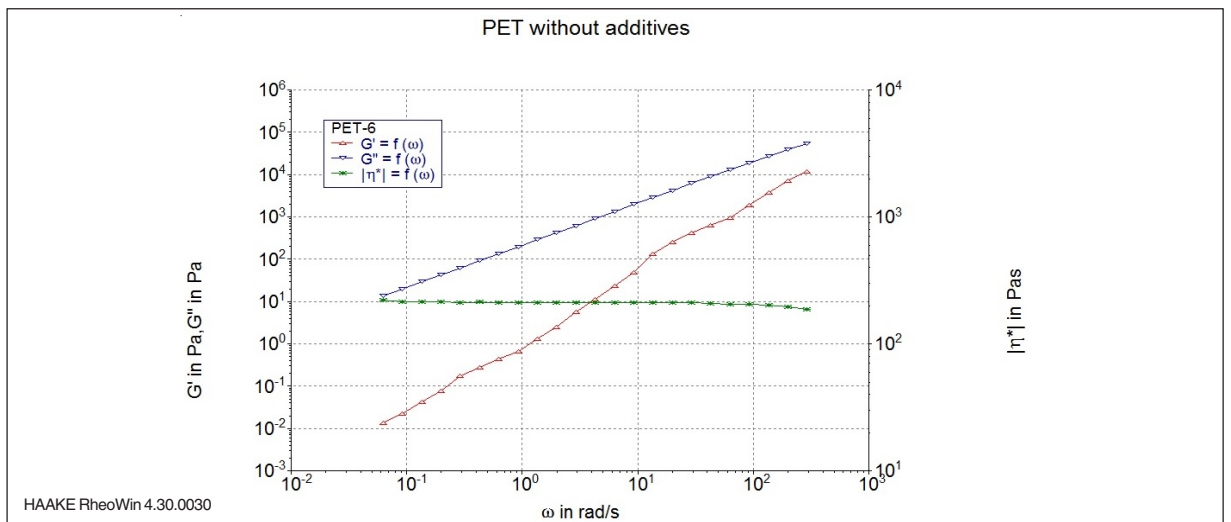


Fig. 5: Frequency sweep of PET with no additives

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 Fig. 2. At the beginning of the test, material is filled into the micro compounder. This results in a pressure peak. Once all material was filled in and the temperature equilibrated, the pressure profile over time can refer to a 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) 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 the chain length or branching which results in a higher viscosity. The samples for the rheological test have been prepared with material at the end 15 min recirculation in the HAAKE MiniLab in the final pressure value can be correlated with complex viscosity $|\eta^*|$ of a dynamic oscillatory test conducted with a rheometer. For the plain PET shown in Fig. 4 after the loading peak the pressure drop indicates a decomposition of the PET. After 15 min. pressure is almost constant with a value of approximately 18 bar.

In Fig. 5 the frequency sweep for the same sample shows that the loss modulus G'' is significant 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 smallest changes have major influences on G'' . The complex zero shear viscosity $|\eta^*|$ is 200 Pas.

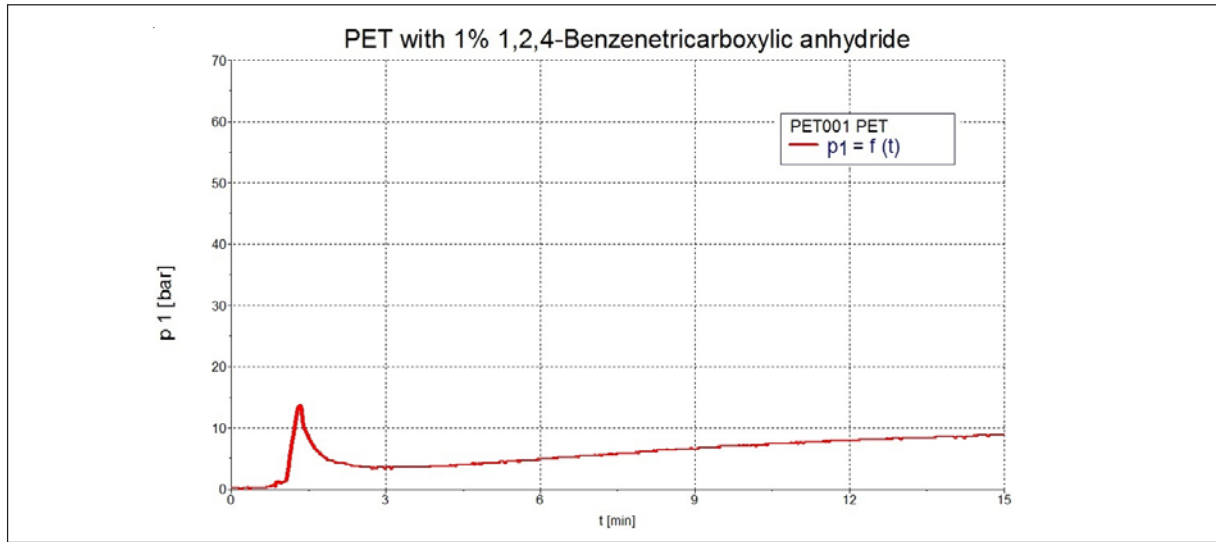


Fig. 6: Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride

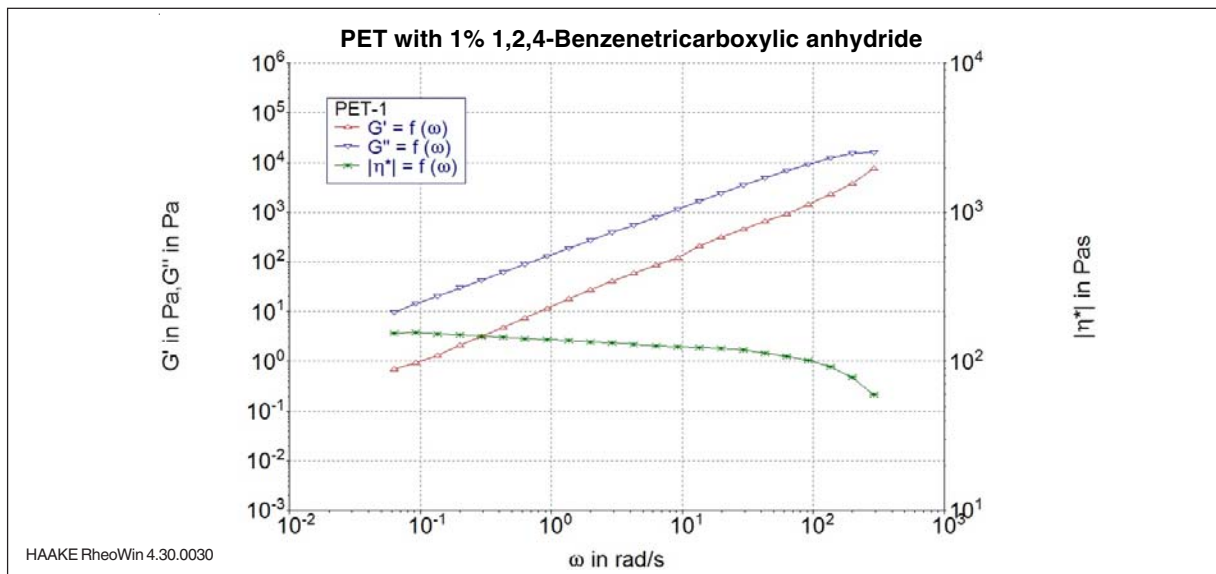


Fig. 7: Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride

The PET with 1% 1,2,4-Benzenetricarboxylic anhydride in Fig. 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 lower an indication of a lower viscosity.

A look at the frequency sweep in Fig. 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 $|\eta^*|$ is 150 Pas at low frequencies.

Compared to the plain PET the additive is responsible for the lower pressure and the lower $|\eta^*|$ on the one hand but on the other hand the additive induced a reaction of the PET.

PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene

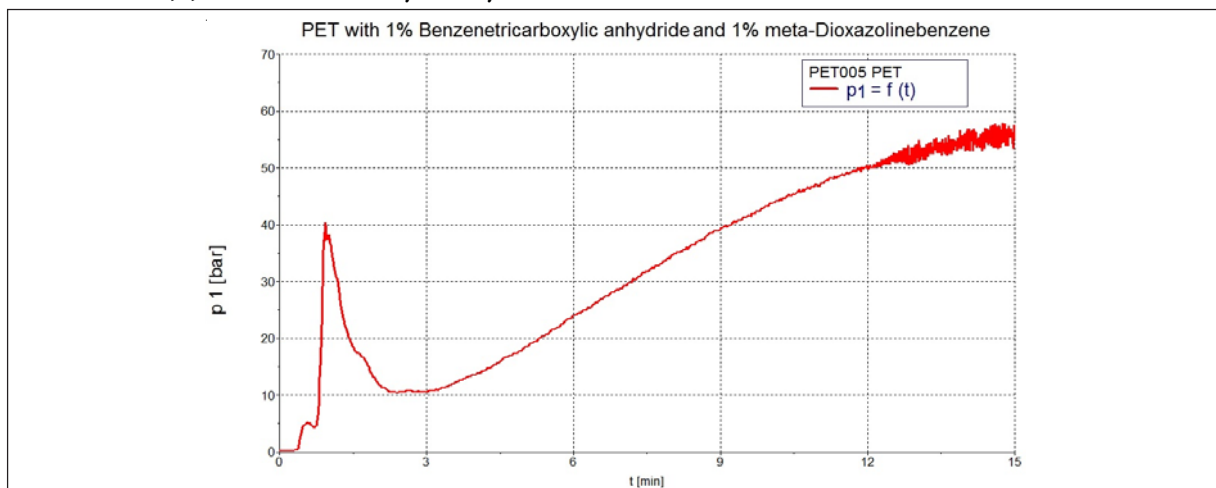


Fig. 8: Pressure dependence of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene

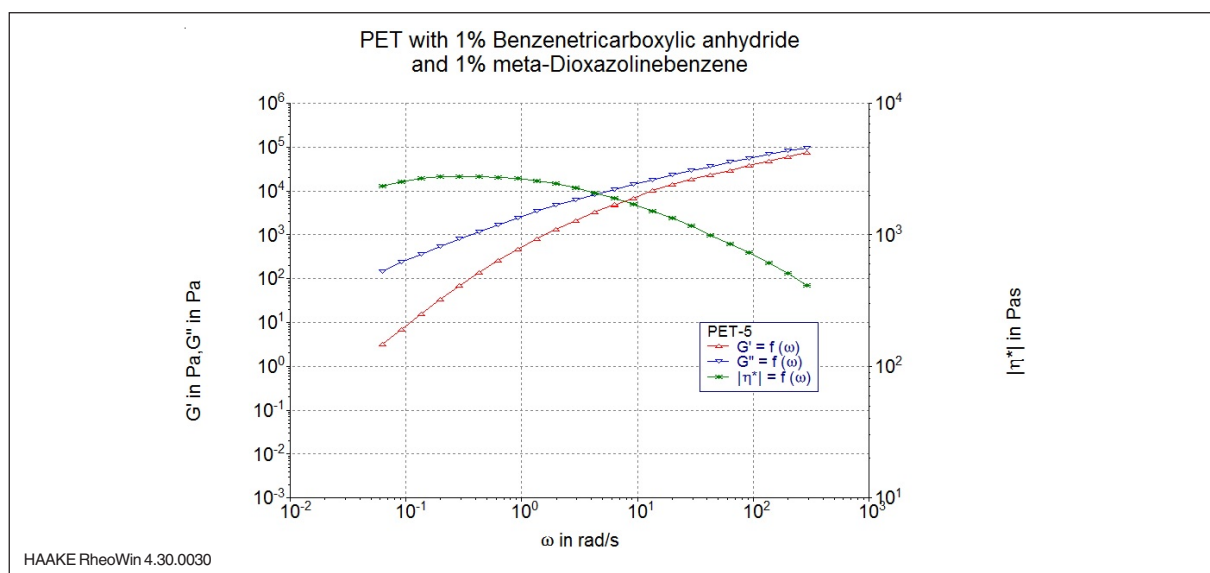


Fig. 8: Frequency sweep of PET with 1% 1,2,4-Benzenetricarboxylic anhydride and 1% meta-Dioxazolinebenzene

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

The frequency sweep in Fig. 9 shows the typical trend of G' and G'' for a visco elastic material.

The $|\eta^*|$ 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 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 de-composition of the PET followed by a reaction to build up a new structure. It's very likely that the molecular weight is significant higher. The increase of pressure and $|\eta^*|$ correlates 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 effect of different additives. Only a small amount of sample (7g) is required. Just a look at the pressure dependence gives a first indication of the functionality of the additives.

The time required for one test is moderate. If further rheological or other physical test have to be conducted the transfer of the polymer melt into the HAAKE MiniJet Pro is possible. Different test specimens can be prepared fast and reproducibly.

Further studies on the molecular weight and distribution either by extended rheological tests for example Time Temperature Superposition compared with GPC data could really proof the assumptions.

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