Application Note
LR-52

Degradation tests – A new test procedure to examine polymers and antioxidants with the HAAKE MiniLab

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Rheology Application Notes

Key words:

- MiniLab
- Small Sample Mass
- Degradation
- Antioxidants

Introduction

Degradation of polymers, i.e. main chain scission, seriously impacts the processability and optical and mechanical properties of the end product. Commercial plastics contain additives and antioxidants to minimize the effects of degradation caused during processing. Even with the use of these substances, transport phenomena, including migration of additives, gas and vapour permeability, oxygen absorption and distribution of the additives, influence the kinetics of thermo-oxidative degradation, degradation (fig. 1) and stabilization.
Quality control tests of polymer thermal stability usually are conducted without a melt mixing process despite the effects of degradation. This is especially true when the polymer is expensive and even small amounts of the material cannot be wasted.

Method of Measurement

The HAAKE MiniLab microcompounder (Fig. 2) is a unique instrument because it combines key features of batch mixers, twin screw extruders and rheometers. To analyze small batches - typically 5 to 50 grams - different test setups are possible. Either continuous or batch processes with defined mixing times can be selected. Co- or counter rotating screws create pressure and melt and mix the polymer pellets or powders. The pressure is essential to extrude the polymer through a die or the rheological measuring device, a built in slit capillary.
For the purpose of the following studies of thermal stability, a batch mixing mode with simultaneous viscosity measurement was selected. Viscosity is calculated via two pressure transducers, a signal which is much more accurate than a correlation via torque or back force of the extruder screws [2].

Experimental Results

As viscosity is directly related to molecular weight, main chain scission should be observable if viscosity decreases. This is shown in Fig. 3, a typical test result with PE. The total time of the experiment takes100-300 mins. The speed is set in the mid range - 30 to 100 rpm. Materials are fed with a pneumatic feeder. To ensure proper filling, it is advisable to feed pellets in two stages and run at slower speeds (20 to 50 rpm). Fig. 1 shows the predominant role of oxygen in the kinetics of degradation. To enable these tests, an inert gas flush (in this case, dried nitrogen) can be switched on or off. At the end of the test, the material can be extruded as a rod and pelletized for further analysis, e.g. via GPC.

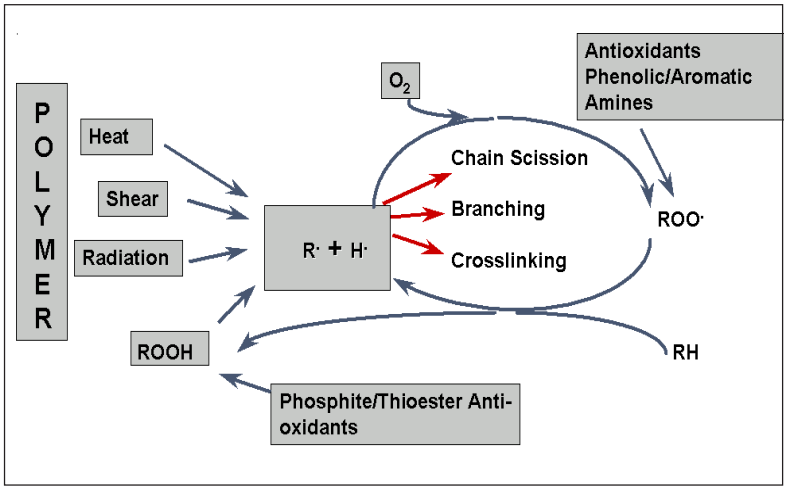

Figure 1: Principles of degradation and stabilization [1].

Figure 2: HAAKE MiniLab Microcompounder with pneumatic ram for batch feeding and force feeder for continuous extrusion

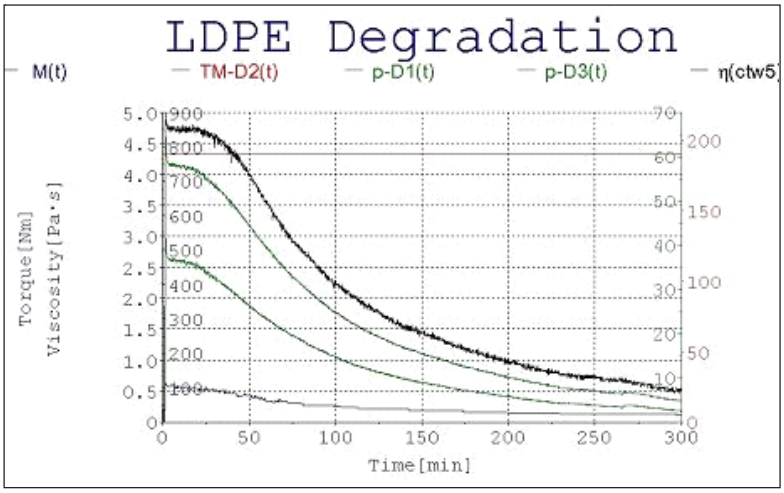

Fig.3: LDPE Degradation curve (screen shot of PolyLab Monitor software 4.16), 190°C 50rpm

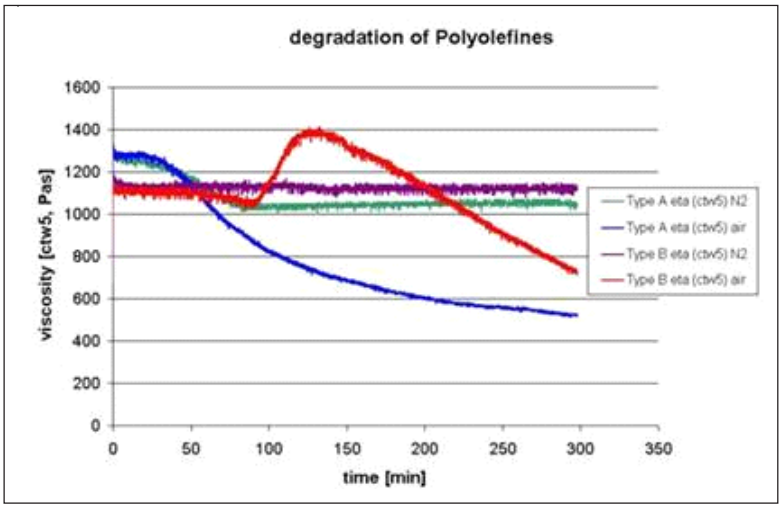

Fig.4: Degradation curves (Polypropylene)

Similar tests were done with two different grades of PP samples, one with inert gas purge (dried Nitrogen) and one without. The viscosity curves are shown in Fig.4. Curve „Type A eta ctw5 air" shows the same behaviour as the LDPE sample, but with inert gas the decrease of viscosity stops at 90 min and further degradation cannot be measured („Type A eta ctw5 N2"). Initial degradation might be related to an improper inert gas flush during the feeding process.

Type B shows a stable viscosity with inert gas flush. „Type B eta ctw5 air" shows a drastic raise of viscosity related to cross linking or grafting reactions. After 140 min, the growth of higher molecular weight molecules slows down and degradation is predominant.

Conclusion

Various polymer resins including EVA copolymers are tested in industrial environment for quality control and research. The effects of stabilizers and antioxidants can be tested via degradation curves to monitor the effect of degradation for a given residence time. Alternatively, the test samples can be compared to a standard sample. This technique is similar to PVC dry blend mixer tests with the HAAKE PolyDrive Mixer. Until now, standard equipment comprised internal mixers with sample amounts of 30 to 300 grams and precise torque measurements. Process conditions in extruders were investigated by multiple turns in extrusion and pelletizing. Degradation was monitored via the melt flow measurements.

Small amounts of sample and viscosity curves are tested in Capillary Rheometers (e.g. HAAKE RheoCap S20) running a thermal degradation test. The residence time can be set and the viscosity measured in defined time intervals but no mixing process is applicable.

Compared to these methods the HAAKE MiniLab offers the following advantages:

- Reduced sample mass (approx 5g is required)
- Defined and long residence time
- Extrusion and mixing process
- Online viscosity measurement
- Easier handling: Reduced time for cleaning and heating up the equipment.

A simple procedure for the degradation test is given. It can work in the research lab as well as in a more rough production environment for QC purpose. With a minimal amount of material, tests can be run in real processing conditions.

Referenses

[1] The Role of Phosphites in the Stabilization: Presentation, Dr H. Ashton, W. Enlow ,T Nelen GE Specialty Chemicals.

[2] LR43 MiniLab – Compounder and Reactor: G. Isaakides, Dr. A. Frendel, M. Jaehrling, Application note, Thermo Fisher Scientific (Karlsruhe), 2001

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