Application Note
LR-59

Evaluating the plasticization process of different soft-PVC samples

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- Soft PVC
- Mixer Test
- Plasticizer
- Evaluation routines
- Thermo Scientific HAAKE PolySoft

Abstract

A Thermo Scientific HAAKE PolyLab OS torque rheometer, equipped with a Thermo Scientific HAAKE Rheomix OS was used to test four different soft PVC samples. The type and amount of plasticizer was varied. The corresponding torque curves helped to differentiate the formulas. The Thermo Scientific PolySoft Mixer data evaluation is explained in detail in this application note, and valuable hints are given for substituting PVC blend ingredients, e.g. plasticizers, stabilizers.

Introduction

PVC blends are complex mixtures of PVC particles, fillers, lubricants, stabilizers and plasticizers. They are used to provide unique properties to a wide range of end products. However, manufacturers are often forced to modify these complex recipes due to technological advances, cost pressures or regulatory requirements. For example, two EU directives came into force, 2002/95/EG (RoHS) restricting hazardous lead stabilizers in the waste. CaZn systems now are well investigated, also in Mixers tests [1]. Another example is the precautionary EU regulation on phthalate plasticizers in children's toys [2],[3] which was widely discussed in the press.
Plasticizers are used in the PVC industry to soften the product. Approximately 100 different plasticizers are in use, which represents an estimated 7 billion EUR market. The type and amount of plasticizer have a major influence on the melt and processing behaviour when investigating alternate blends. In addition to tests on the final product, smal-scale tests in a mixer are advisable before starting production. The mixer test is used for quality control during production.
The Thermo Scientific HAAKE Rheomix system offers a quick method to characterize the influence of plasticizers on the plasticization and flow process of PVC dry blends. Using Thermo Scientific HAAKE Polysoft OS Software for mixer tests, the evaluation and comparison of different samples is quite quick and easy. Different routines are available, and it is also possible to create customized evaluation methods. Maxima, minima, points of inflection, thresholds and slopes can easily be calculated from all measurement data curves.

Materials and Methods

Test equipment:
Thermo Scientific HAAKE RheoDrive 16 with torque sensor

Thermo Scientific HAAKE Rheomix 600 OS, electrically heated laboratory batch mixer

Pneumatic Ram for Thermo Scientific HAAKE Rheomix 600

Roller rotors for Thermo Scientific HAAKE Rheomix

Thermo Scientific Polysoft OS software for mixer tests and data evaluation

Test conditions:
Mixer temperature: 150 °C
Rotor speed: 30 rpm
Sample weight: 59 g
5 bar pressure pneumatic ram
Start point Torque > 0.5 Nm

Materials:
Four different Soft PVC recipes were measured, compared and evaluated.

Sample 1 and sample 2:
Both samples contained the same amount of filler (30 phr), sample 2 contained more plasticizer than sample 1.

sample	Amount of plasticizer
1	43 phr DOP
2	75 phr DOP

Fig. 1: Thermo Scientific HAAKE PolyLab OS Torque Rheometer

Sample 3 and sample 4:
For sample 3 only DOP was used as a plasticizer. Sample 4 contained a different plasticizer.

sample	Amount of plasticizer
3	51 phr DOP
4	20 phr DOP, 30 phr polymer plasticizer

All samples were measured using the same project and were the measurement conditions stored as standard values for the whole project. Defining a Standard measurement is easy because the user is guided through all the necessary steps.

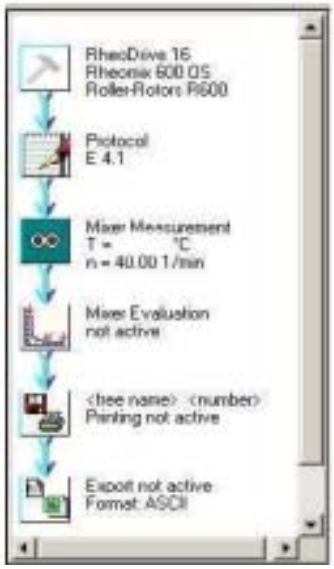


Fig. 2: job for a mixer measurement

The Job Control guides the user through the measurement process.

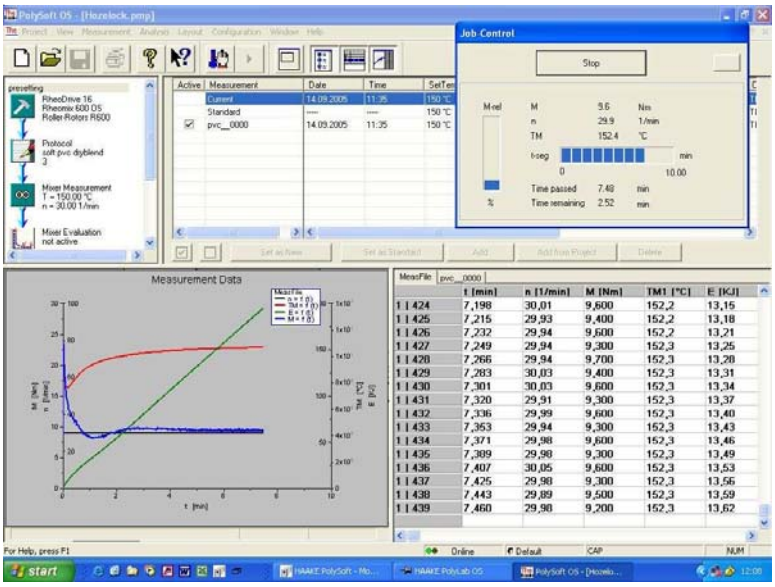


Fig. 3: measurement job control

Results and Discussion

Incorporation of a plasticizer can be divided into five distinct stages [3].

- Plasticizer is mixed with PVC resin.
- Plasticizer penetrates and swells the resin particles.
- Polar groups in the PVC resin are freed from each other.
- Plasticizer polar groups interact with the polar groups on the resin.
- The structure of the resin is re-established, with full retention of plasticizer.

Using HAAKE Polysoft Software OS for mixer tests, it is easy to compare measurement curves.
During a measurement, the user can even compare the measurement with another one.
For example, a standard can be loaded as overlay, and deviations from the standard curve can be seen even during testing.
The following measurement, curves show torque M(t), melt temperature TM(t) and energy E(t) as a function of test time. The energy calculation is based on the area beneath the torque curve over the test time.

Sample one shows a typical behaviour of PVC dry blends in a mixer. After the initial filling peak, the torque curve drops to a minimum value. Due to friction and material heating, the torque value rises again, and PVC fusion takes place. After some time an equilibrium between shear heating and constant mixer temperature is reached, which results in a stable torque curve.

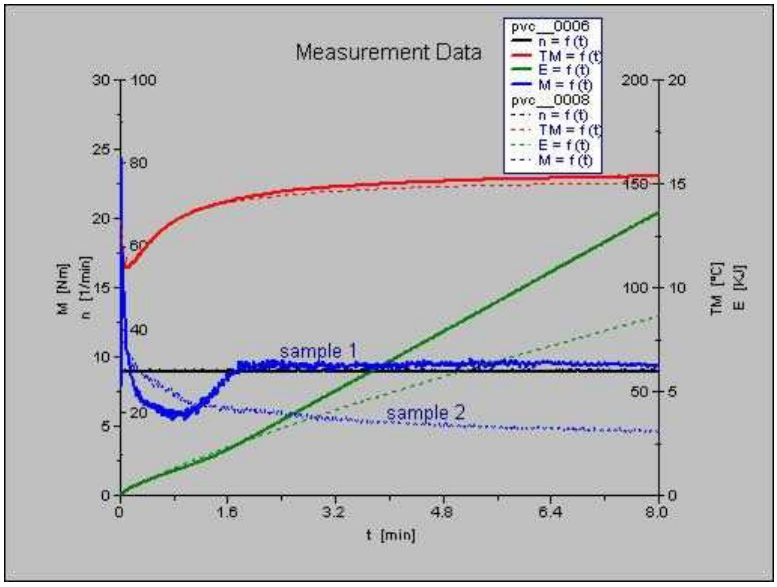


Fig. 4: comparison of sample 1 and 2

The resulting minimum value of the torque can be used as a relative value of the PVC melt viscosity.
The resulting torque curve of measuring sample two is determined by the high amount of plasticizer. Although both samples contain the same amount of filler, the viscosity of sample two is much lower than for sample one.

Sample four, which contains two different plasticizers in the dry blend mixture, gives a completely different torque curve in comparison to sample three. This mixture of plasticizers results in a higher melt viscosity. The polymeric plasticizer cannot replace the phthalate based plasticizer.
The samples can also be evaluated with routines by selecting the appropriate routine. Calculated points will be displayed on the measurement graph. Customized points can be added easily, and the user can create a specific evaluation routine.
By using the statistic view in a mixer project, the user can get an overview of different measurements. It is easy to evaluate the reproducibility of samples by calculating mean values and standard deviation of defined curve points.

Summary

The Thermo Scientific HAAKE Rheomix system is an easy to use, modern means of analyzing and differentiating between various types of Soft PVC samples.
Haake Polysoft OS Software is a tool which makes the evaluation of samples in the laboratory convenient and easy.

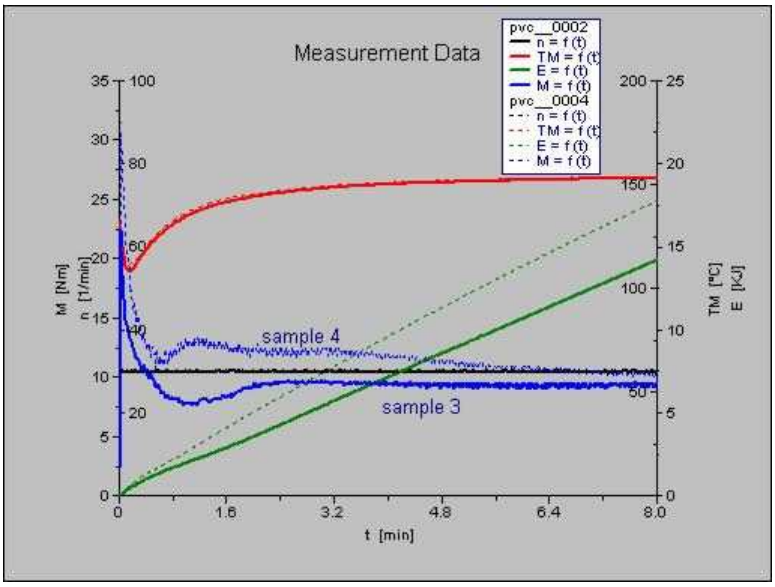


Fig. 5: comparison of sample 3 and 4

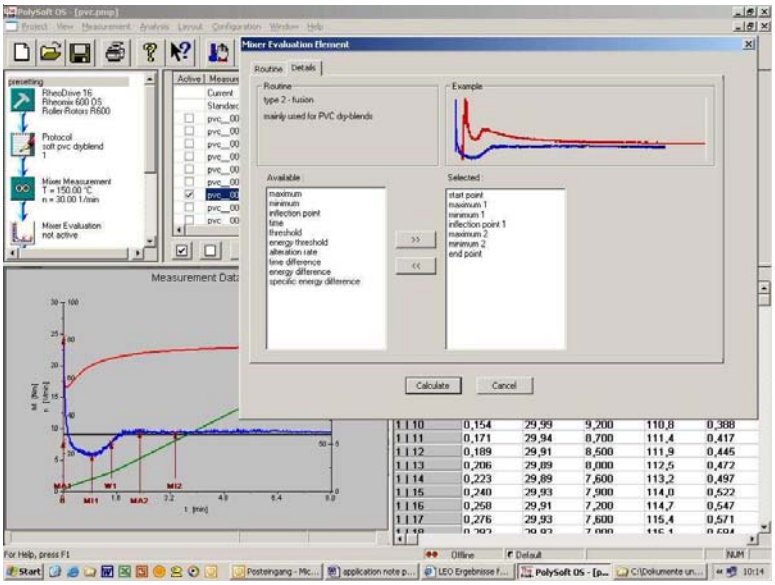
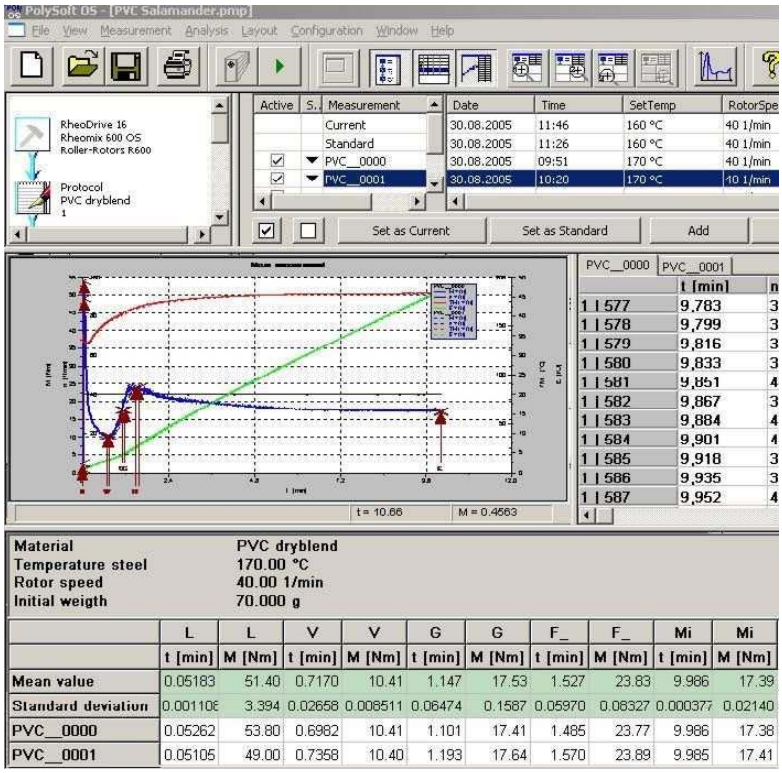


Fig. 6: measurement evaluation with analysis routine for PVC fusion



	L	L	V	V	G	G	F_	F_	Mi	Mi
	t [min]	M [Nm]	t [min]	M [Nm]	t [min]	M [Nm]	t [min]	M [Nm]	t [min]	M [Nm]
Mean value	0.05183	51.40	0.7170	10.41	1.147	17.53	1.527	23.83	9.986	17.39
Standard deviation	0.001108	3.394	0.02658	0.008511	0.06474	0.1587	0.05970	0.06327	0.000377	0.02140
PVC__0000	0.05262	53.80	0.6982	10.41	1.101	17.41	1.485	23.77	9.986	17.38
PVC__0001	0.05105	49.00	0.7358	10.40	1.193	17.64	1.570	23.89	9.985	17.41

Fig. 7: statistic view of evaluation data

Literature

[1] Jährling, Matthias, LR59 - Correlation between mixer tests and extrusion behaviour of dry blends, (Thermo Fisher Scientific KA), (2006)

[2] http://www.euractiv.com/en/food/eu-ministers-agree-banchemicals-toys/article-129891

[3] http://www.plasticisers.org

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