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Hard and soft methods for prediction of antioxidants' activity based on the DSC measurements

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Abstract

Testing of antioxidants' activity in polyolefin is considered. It is proposed to substitute the conventional Long Term Heating Aging (LTHA) test for the method of Differential Scanning Calorimetry (DSC). Values of the Oxidation Initial Temperature measured by the DSC method (X data) are calibrated using the values of Oxidation Induction Period obtained in the LTHA tests (data Y). This data is further processed applying both soft and hard modeling. The hard method is the Non-Linear Regression approach with the traditional confidence interval estimation. The soft method combines the Partial Least Squares regression and the method of Simple Interval Calculation. We compare the results of soft and hard prediction based on the same data set and point out which approach is better in various cases.

Keywords: Anitioxidant activity; Differential Scanning Calorimetry; Long Term Heating Aging; Interval estimations; SIC; PLS; Fitter

1. Introduction

Testing the activity of *antioxidants* (AO) in polyolefin is a long and costly process, which requires 1–3 months of heating up the samples in an oven. This laborious procedure is called Long Term Heating Aging (LTHA). This paper considers an alternative chemometric approach that makes the process of the AO development more effective. The proposal to use the Differential Scanning Calorimetry (DSC) method and to construct a calibration model that can predict AO activity has been studied earlier [1,2]. These works describe the hard (NLR) [1] and the soft (PLS) [2] approaches to modeling, but use short data sets, different for each case. In this paper we study a representative AO sample set that enables us to explore two important issues. The first one is a practical question regarding feasibility of the suggested DSC alternative method. The second one is the comparison of the hard and the soft modeling being applied to the same data set.

The hard method is based on the Non-Linear Regression (NLR) approach [4], while the soft method employs the Projection on Latent Structures (PLS) technique [5]. Both methods give point estimates for a predicted value. To make the prediction more comprehensive for each predicted value we provide an interval that represents the uncertainty in prediction. For the hard method it is a traditional confidence interval calculated by statistical simulation. For the soft method a novel approach called Simple Interval Calculation (SIC) [6,7] is used. There are many alternative methods for calculation of uncertainty in PLS [8,9] and the literature references listed herein. Though these methods are still under discussion, we neither criticize them, nor compare them with the SIC approach. That might be an interesting

Abbreviations: AO(s), Antioxidant(s); CI(s), Confidence interval(s); DSC, Differential Scanning Calorimetry; LTHA, Long Term Heating Aging; MED, Maximum Error Deviation; NLR, Non-Linear Regression; OIP, Oxidation Induction Period; OIT, Oxidation Initial Temperature; OSP, Object Status Plot; PI(s), Prediction interval(s); PLS, Partial Least Squares; PP, Polypropylene; RMSEC, Root Mean Square Error of Calibration; RMSEP, Root Mean Square Error of Prediction; SIC, Simple Interval Calculation.

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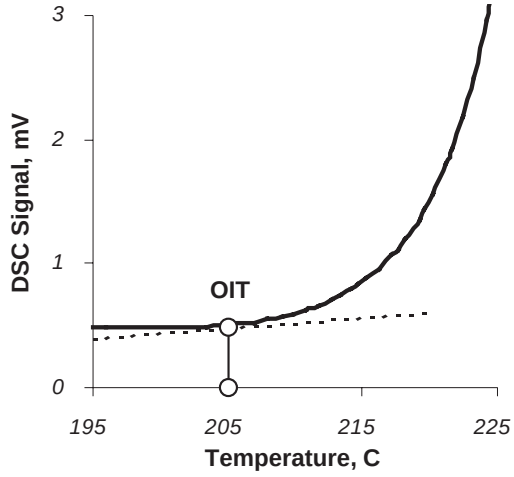

Fig. 1. Example of the DSC curve and the OIT value.

topic for the future papers, but in the present work we concentrate on comparison of the SIC method with the well-known technique of the confidence estimators in the Non-Linear Regression [10].

Antioxidant is a special additive which inhibits polymers thermo-aging, protecting polymers from oxidation during processing as well as at the end-use application. Reacting with free radicals, AO terminates chains and exhausts. The oxidation is completely suppressed as long as the concentration of AO exceeds some critical value. Therefore, it is very important to estimate Oxidation Induction Period (OIP)—the time during which the concentration of AO is high enough. The more effective is an antioxidant the longer is the OIP. In practice, the AO effectiveness is measured by the OIP value in days. A generally adopted testing procedure involves keeping polymer samples in ovens at a standard temperature like 140 °C for some time: from 1–2 days for poor AOs, up to 40 days for the AO of the best composition. Twice a day a qualified tester examines the samples and checks for apparent signs of degradation: brittleness, crumbling, yellowing. Needless to say this type of testing is very erratic and time-consuming.

An alternative to the LTHA testing is the DSC measurement and further data processing. Differential Scanning Calorimetry is a method of testing in which a sample is heated at a constant heating rate using special instruments. The measured signal represents a heat flow as a function of growing temperature T, Fig. 1. For a chemical reaction with a thermal effect, the DSC signal is proportional to the rate of the reaction. While the AO concentration in a sample is sufficient, the signal remains constant; at some specific temperature it starts growing. This temperature is called Oxydation Initial Temperature (OIT) and it is used in our example here. The DSC approach has an apparent advantage of being a fast and well-automated method without strong requirements to the size and form of specimens.

2. Experimental

The experiment is conducted using 25 AO samples marked AO-1, . . . , AO-25. Some of them (e.g. AO-1, AO-2 and AO-3) are the standard additives used in production. Other AOs are the trial agents that are expected to be effective. All samples are added to polypropylene (PP) powder in concentrations of 0.05% (500 ppm), 0.07%, and 0.1%. After blending the additive and the polymer, the mixture is added to the pre-heated extruder at the temperature of 250 °C. The product of extrusion is converted into the 0.25 mm film, which serves as a base material for the LTHA and the DSC testing.

The LTHA tests are performed at the temperature of 140 °C and result in a set of the corresponding OIP values (in days). The DSC measurements are conducted at the temperature range of 150 °C to 300 °C, where an exothermic maximum related with polymer oxidization is observed. We use five different heating rates: 2, 5, 10, 15, 20 (degree per min). The OIT values are calculated applying Fitter software [3] to the raw DSC curves as it is explained in Ref. [4].

The obtained data are shown sketchy in Fig. 2. X are the OIT values resulting from the DSC experiment. They form a 3D block: 25 AO samples × 3 AO concentrations × 5 heating rates. Y are the OIP values obtained in the LTHA tests. They form a 2D matrix: 25 AO samples × 3 AO concentrations.

3. Soft modeling

This dataset is processed using a soft approach that combines the PLS method [5] for calibration and the SIC method [6] for an interval prediction, which is explained bellow.

The raw X data are unfolded over five heating rates as it is shown in Fig. 3. This simple method of a 3-way data modeling was applied for the reason that more complicated approaches (i.e. PARAFAC [11]) did not provide us with an

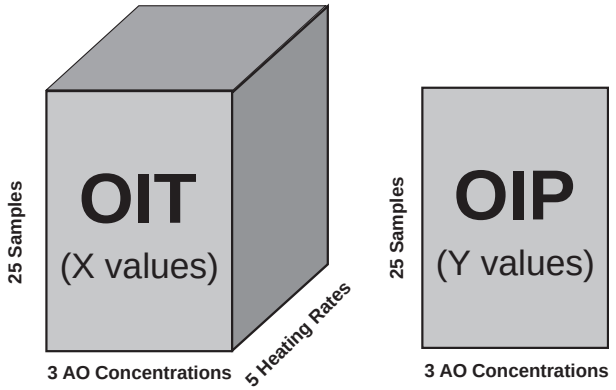

Fig. 2. Scheme of data.