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Plastiques — Analyse calorimétrique différentielle (DSC) ou analyse thermogravimétrique (TGA) — Analyse cinétique sans modèle basée sur la méthode isoconversionnelle incrémentale non-linéaire

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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Introduction

Conventional thermoanalytical methods for the characterisation of reaction kinetics, such as those described in ISO 11357-7, ISO 11358-2[1] or ISO 11358-3[2], are applicable only for constant values of the activation energy. Furthermore, a reaction model has to be assumed. In case of, for example, competing or side reactions, the assumption of a constant activation energy is not applicable. Furthermore, the description of a chemical reaction can also include processes, such as diffusion or evaporation.

Another method is specified in IEC/TS 60216-7-1[3] in which the thermal endurance of electric insulating materials is predicted based on thermal analysis methods for the evaluation of the activation energy and a lifetime test. However, this method is limited to ageing reactions where one single reaction is predominant.

To cope with these fundamental limitations, model-free kinetics have been proposed. Instead of a reaction model and a constant activation energy, it makes use of an activation energy which depends on the extent of conversion. This conversion-dependent activation energy is not an activation energy in the traditional sense but rather an apparent activation energy describing the chemical reaction(s) as well as any transport processes. This approach is based on the isoconversional principle which assumes that the reaction rate at a certain conversion depends only on the temperature[4][5][6]. For the temperature dependence of the reaction rate the Arrhenius approach can be applied. Thus, the activation energy as a function of the conversion can be calculated from several DSC or TGA measurements of a reaction done at different temperature programs. The determination of the apparent activation energy as a function of the conversion is sufficient to make predictions, i.e. there is no need for an explicit reaction model[6].

More advanced methods of the model-free kinetics approach can be applied to any temperature program, i.e. constant scan rate, isothermal or arbitrary temperature variation measurements[4][8][9].

However, model-free kinetics is not an all-purpose tool. Misleading results can be obtained especially for more complex reactions. In this case, the results and in particular the predictions should be checked for plausibility and verified.