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APPLICATION OF THERMAL ANALYSIS FOR THE INVESTIGATION OF POLYMER DEGRADATION PROCESSES

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Abstract

A short description of the thermal analysis methods used for the investigation of polymer degradation processes is given. The fields of application of TG, DTA and DSC for polymers are presented. A kinetic approach to the thermal degradation processes is also given.

Keywords: kinetics, polymer degradation processes

Introduction

Thermal methods of analysis of polymers can provide information about the thermal stability of the polymers, their lifetime or shelf-life under particular conditions, phase changes occurring in the polymers and the influence of additives on the polymers. The main thermal analysis techniques used for polymer investigation are listed in Table 1.

For the investigation of polymer materials (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have proved particularly useful. In TG, measurements of changes in sample mass with temperature are made by using a thermobalance. This should be done in a suitably enclosed system so that the atmosphere can be controlled.

Perhaps the greatest number of applications of TG during recent years have been in the characterization of polymeric materials. These studies have been useful not only in applied areas, but also in the theoretical aspects of high polymers. Applications of TG include comparisons of the relative thermal stability, the effects of additives on the thermal stability, moisture and additive content, studies of degradation kinetics, direct quantitative analysis of various copolymer systems, oxidation stability, and many others. In studies of thermal oxida-

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tive degradation, TG can reveal the molecular structure and arrangement of repeating units, the existence of cross-links between chains, side-groups in homopolymer and copolymer chains, and so on. Rate constants, activation energies and reactions orders can also be obtained.

DTA and DSC are also methods of thermal analysis often used in the area of polymeric materials. DTA is the simplest and most widely used thermal analysis technique. The difference in temperature, ΔT, between the sample and a reference material is recorded while both are subjected to the same heating programme. Alumina, Al_2O_3, and carborundum, SiC, have been extensively used as reference substances.

In power-compensated DSC, the sample and a reference material are maintained at the same temperature ($\Delta T = T_s - T_r = 0$) throughout the controlled temperature programme. Any energy difference in the independent supplies to the sample and the reference is then recorded against the programme temperature. Thermal events in the sample thus appear as deviation from the DSC baseline, in either an endothermic or an exothermic direction, depending upon whether more or less energy has to be supplied to the sample relative to the reference material. The fields of application of DTA and DSC that are of greatest potential, or actual interest, for plastics comprise:

1. polymerization, together with the characterization of raw materials;
2. physical characterization of raw and compounded plastics in terms of crystalline – amorphous (melt) transitions;
3. chemical modification of polymers;
4. measurements of heats of solution;
5. degradation and ageing processes under both inert and oxidative conditions, including the evaluation of anti-degradants;
6. qualitative and quantitative analysis of plastics.

Table 1 The main thermal analysis techniques used for polymer examination

Property	Technique
Mass	TG, DTG
Temperature	DTA
Enthalpy	DSC
Dimensions	TD
Mechanical properties	TMA
Optical properties	Thermooptometry
Magnetic properties	TM
Acoustic properties	TS
Electrical properties	Thermoelectrometry

The degradation of polymers involves a whole range of chemical and physical processes leading through destruction to the simple products. These are pure monomers, low molecular organic compounds, and also carbon dioxide and water. The additives also contribute to the overall mechanism.

In our research we are dealing with the modelling of the processes of thermal degradation of some polymeric materials, in order to determine the mechanisms and decomposition products. The partial reactions of thermal degradation of a polymer, depending on its structure and degree of degradation, can be divided into three groups. They can be characterized as follows:

- disruption of the main chain
- detachment of substituents from the main chain
- breaking of cross-linking bonds.

The kinetic equation taking into account such partial reactions can be written in a simple form:

$$r = k_1c_1 + k_2c_2 + k_3c_3 \tag{1}$$

where k_i is the rate constant, and c_i is the concentration of the corresponding bonds.

This is related to the general mathematical model which describes the kinetics of a system undergoing chemical change:

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{2}$$

where α is the fractional reaction,

For polymer degradation, the simplest, most widely used representation of $f(\alpha)$ is

$$f(\alpha) = (1 - \alpha)^n \tag{3}$$

where n is the order of reaction.

The Arrhenius equation is the model generally used to express the temperature-dependence of rates of reaction:

$$k(T) = A\exp(-E/RT) \tag{4}$$

where R is gas constant, A is the pre-exponential factor, and E is the activation energy.

Substituting for $f(\alpha)$ and $k(T)$ in Eq. (2) gives

$$\mathrm{d}\alpha/\mathrm{d}t = (1 - \alpha)^n A\exp(-E/RT) \tag{5}$$

In cases where the change in temperature of the specimen with time is $\beta = dT/dt$, we have

$$d\alpha/dt = \beta d\alpha/dT\,(1-\alpha)^n A\exp(-E/RT) \tag{6}$$

On the basis of Eq. (6), the approaches may be classified as either differential or integral methods and, within each group, as either single-run or multiple-run methods. Differential methods are based on the above equation.

A direct approach has been to measure a series of α, T and $(d\alpha/dT)$ values at a giving heating rate β (with the practical problems of integration or differentiation and their associated errors, depending upon the initial form of the experimental data). If a form of $f(\alpha)$ is assumed, then

$$y = \ln[(d\alpha/dT)/f(\alpha)] = \ln(A/\beta)-(E/R)(1/T) \tag{7}$$

so that a plot of y against $(1/T)$ leads to values of E and A.

Mass-loss experiments measure processes which are heterogeneous by definition and which as a matter of course are complicated by chemical and physical processes taking place in the condensed phase. The degradation processes generally consist of several steps, each with its own set of kinetic parameters, so one must assume that identical or average values are sufficient to represent the overall process well. For example, in the representation of the radical chain depolymerization models for vinyl polymer degradation, whole series of reactions involving homologous species are given the same rate constant. However, it can be accepted that the values obtained under the known conditions yield an acceptable estimation, especially when many data points are available for evaluation.

The thermal degradation of polymers remains a significant area of polymer science and an important subject of current research. The stability of polymers under a variety of conditions, and methods of determining such stability quantitatively, are of great importance for successful application of these materials. New importance is being gained by methods of thermal analysis in connection with other techniques, e.g. mass spectrometry. These allow identification of volatile products and therefore permit investigation of degradation mechanisms. A fundamental understanding of degradation process is essential for improving all aspects of the stability of polymers and recycling problems.

Zusammenfassung — Vorliegend wird eine kurze Beschreibung der thermoanalytischen Methoden zur Untersuchung von Zersetzungsprozessen von Polymeren gegeben. Dabei werden die Anwendungsbereiche für TG, DTA und DSC aufgezeigt. Eine kinetische Annäherung zu thermischen Zersetzungsprozessen wird ebenfalls gegeben.