

Determination of the thermal short time stability of polymers by fast scanning calorimetry



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ABSTRACT

Thermogravimetric analysis (TGA) is a standard technique to measure the thermal stability of polymeric materials. This technique is not sensitive for degradation steps which are not related to mass loss. However, such reactions can significantly influence the mechanical behavior of material. In this contribution we introduce the technique of stability estimation by crystallization analysis (SECA) and pseudo TGA which uses differential scanning calorimetry (DSC).

SECA measures the influence of decomposition on crystallization kinetics. This technique is very sensitive to decomposition. Using fast scanning calorimetry, SECA determines the short time thermal stability of semi-crystalline polymers. This property is essential for fast polymer processing like selective laser sintering or welding.

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1. Introduction

Knowledge about the thermal stability of the materials is an important key for the optimal use and processing of polymers. Usually the thermal stability of polymers is characterized using thermogravimetric analysis (TGA) eventually combined with a dedicated evaluation of the reaction kinetics [1–4]. However, especially in polymers the degradation is usually a very complex reaction, which contains several reaction steps like chain scission, molecular growth (e.g. crosslinking), cyclization reactions and elimination of side chains and side groups [4]. These reactions are not necessarily associated with mass loss due to production of gaseous components. Consequently the TGA is in many cases not sensitive for the early degradation steps, which significantly influence the material properties. Therefore, stability predictions based on conventional TGA measurements are often not relevant for fast heating processing techniques like fused filament fabrication, selective laser sintering or polymer welding.

Also the practical use of polymeric materials, for instance in electrical applications, requires knowledge of the short term stability at high temperatures. It was suggested to study the changes

of material behavior by short thermal stress exposure by fast scanning calorimetry [5,6]. Recently Starostin et al. [7] introduced a heat pulse technique to study the thermal short time stability of amorphous polymers due to changes of thermal transport properties.

It is frequently shown on differently stressed semi-crystalline polymers, that the crystallization behavior changes sensitively with molecular modifications due to the stresses [8–17]. Principally the DSC technique allows the study of the modification in the crystallization behavior due to thermal stress. However, for investigation of fast technical processes the heating and cooling rates are not sufficient. We therefore introduce a novel analytical method for short time stability investigation based on fast scanning calorimetry (FSC). This estimation method is called SECA: stability estimate by crystallization analysis. The use of FSC enables the extrapolation to fast heating rates because the time constants of the instruments are in the millisecond range and the measurements can be performed at heating and cooling rates in the order of several thousands of Kelvins per second [5]. At such scanning rates the degradation can be prevented by shifting to high temperatures. This is shown on the example of biopolymers [18].

The aim of this contribution is the introduction of SECA and pseudo TGA with FSC for polymer stability investigations. These methods are used for analyzing polymer materials developed for selective laser sintering (SLS).

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2. Experimental

2.1. Samples

The materials of investigation are developed for selective laser sintering. There are four different polymer powders:

- Thermoplastic polyurethane (TPUS) supplied and developed for SLS within a project between BMW AG and Freudenberg Forschungsdienste SE & Co. KG. The TPU is an aliphatic, ester-based block copolymer without ether linkages.
- Rolaserit® (TPUR) is a thermoplastic polyurethane (thermoplastic elastomer) supplied by ROWAK AG.
- DuraForm®Flex (DFF) is supplied by 3D Systems (Rockhill, USA). According to Ref. [19] this material is a block copolymer based on aromatic ester blocks (building the hard segment) and aliphatic ether blocks (building the soft segment).
- PA2200 is a polyamide 12 (PA12) supplied by EOS (EOS GmbH, Krailling, Germany). It is a common used semi-crystalline polymer for laser sintering.

2.2. Conventional thermal analysis

The TGA analyses were performed using a TGA/DSC3+ from METTLER TOLEDO with DTA Sensor. The instrument was calibrated with indium, zinc, aluminum and gold. The gas used was nitrogen and the heating rate was 30 K/min. Typically 5 mg samples were placed in a 30 μ l alox-crucible.

2.3. Fast scanning calorimetry

The measurements were performed using a METTLER TOLEDO Flash DSC1 with UFS1 sensor. The performance of this instrument is discussed in Refs. [5,6]. The sample support temperature was set to -90°C , -40°C or 20°C , respectively. The measurements were performed in nitrogen atmosphere. To reduce the remaining oxygen concentration the measuring cell was covered with a glass plate [6] and the nitrogen flow was set to 55 ml/min. A typical sample size of 50 ng was selected.

The measurements were performed using USF1 sensor up to 500°C . At this temperature we have not found significant drawbacks at higher temperatures for our measurements.

3. Measuring procedure

3.1. The general idea of SECA

The stability of semi-crystalline polymeric material is analyzed by a new technique based on fast scanning calorimetry. We denote this as “stability estimation by crystallization analysis” (SECA). This technique based on the fact that relatively small molecular changes due to degradation significantly influence the crystallization behavior of polymers [8–17]. For the identification of the beginning of degradation the change in crystallization or melting behavior is more sensitive than TGA.

In SECA we define first a program for the thermal stress. After defined time periods this stress is interrupted and the influence of the applied thermal stress to the crystallization and subsequent melting behavior of the sample is analyzed. As it is shown in Fig. 1, the temperature program of SECA is a sequence of steps of the thermal stress exposure and analysis steps. To identify the changes in the crystallization and melting behavior, the program starts with an initial analysis step. The program of the thermal stress exposure can simulate a heating or an isothermal process. The thermal stress exposure steps are interrupted after a define time, Δt , by fast

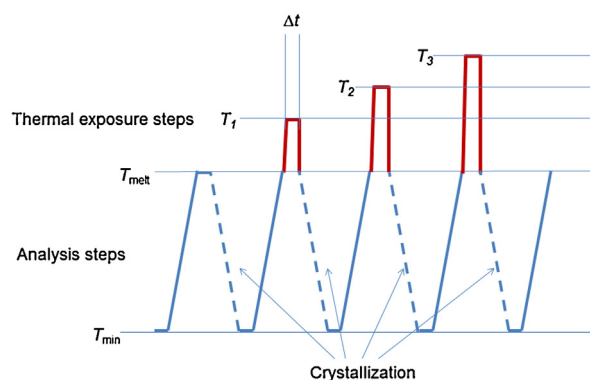


Fig. 1. The first three exposure steps of a temperature program with increasing thermal exposure temperature T_i ($i = 1, 2, 3, \dots$) and constant thermal exposure time for each step Δt .

cooling. For re-initiation of the thermal stress the sample is heated rapidly.

In the example, shown in Fig. 1, the thermal stress simulates a heating program in the molten state. T_{melt} is a temperature at which the sample is totally molten, but relatively stable.

Principally SECA measurements can be also performed using conventional DSC, however the thermal exposure time, Δt , for a single step has to be relatively long (minimum on the order of 10 s) and the degradation rate has to be slow, because fast reactions cannot be sufficiently interrupted at the possible cooling rates. Flash DSC however enables exposure times in the order of 10 ms and cooling rates much faster than 1000 K/s. Also the analysis of the melting behavior is more sensitive at fast heating because of the suppression of reorganization.

3.2. The thermal exposure steps

The program of the thermal stress is divided in suitable segments with the segment length Δt_i . Each segment starts and finishes at the temperature T_{melt} (Fig. 1). At this temperature the material is practically stable and no significant crystallization occurs. The temperature at the end is again T_{melt} and the next thermal exposure step starts. To prevent eventually overshoot the sample temperature due to thermal inertia we recommend the heating to the exposure temperature with a defined rate of 1000 K/s or 10000 K/s. The cooling down at the end of the exposure step can be ballistic by programming of a temperature jump to reach the maximum possible rate.

As an example the temperature program in Fig. 1 simulates a thermal exposure with a fast heating process. In each step the sample is stressed at a selected exposure temperature T_i for a defined time interval, Δt_i . At the subsequent step the exposure temperature is increased to T_{i+1} . The actual exposure time after the n th step is $t_e(n) = \sum_{i=1}^n \Delta t_i$ and the actual heating rate during the exposure process is $\beta(t_e) = (T_n - T_{n-1}) / \Delta t_n$. To simulate, for instance, a heating process of 1000 K/a constant time interval $\Delta t = 10$ ms and temperature increment between subsequent exposure steps of $\Delta T = T_i - T_{i-1} = 10$ K can be selected.

Similarly thermal exposure programs with non-constant heating rates or isothermal exposure can be generated.

3.3. The analysis steps

In the initial SECA step the crystallization and melting behavior of a virgin sample is analyzed. All subsequent analyses steps indicate the change of the material due to the thermal exploration.

The analysis steps include crystallization and melting. The conditions for the crystallization have to be selected carefully. The

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