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Study of poly(L-lactide) using Fast Scanning Calorimetry

Abstract: Fast scanning calorimetry (FSC) is an effective analytical tool to characterize the thermal properties of polymers. Heating rates up to 100 000 K/s allow studies at time scales inaccessible with conventional calorimeters, whose rates are typically less than about 0.5 K/s. Recent studies have successfully demonstrated methods for obtaining quantitative analysis of thermal properties of polymer samples using chip-based FSC. Therefore very small sample sizes, such as particles or nonwovens, can be characterized. In this study, we investigated the thermal properties of poly(L-lactide) PLLA with FSC compared to the results from standard DSC methods. PLLA specimens were fabricated via solution casting and needle electrospinning. The results suggest a significant influence of heating rates on the melting temperature of PLLA. The results show that different fabrication methods lead to changes in crystallinity and that FSC results are not completely comparable with standard DSC measurements.

Keywords: FSC, chip sensor, semi-crystalline PLLA, crystallization, melting

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processes allows the investigation of the resulting material properties [5].

The commercial fast scanning calorimeter Flash DSC 2+ (Mettler Toledo, Switzerland) is based on micro-electromechanical systems (MEMS) sensor technology and allows sampling rates four to six orders of magnitude higher compared to those of conventional DSC systems [6-8]. With scanning rates in the order of 1000 K/s, the FSC have been successfully used to measure the melting point and heat of fusion of silk fibroin, which was impossible with standard DSC [9]. These high scanning rates crucially change the solidification behavior of the material. This is reflected in the variation of the crystallization temperature distribution and characteristic temperatures, such as the peak maximum temperature with the cooling rate of a material during industrial processing. Such information is significant, and if obtained, enables product developers to optimize their production processes [5].

This article focuses on the practical handling of FSC, such as the influence of heating rates on the thermal properties of a model material, here PLLA. For a detailed study, PLLA samples were processed via solution casting and electrospinning and the influence of the manufacturing procedure on the thermal properties was investigated.

1 Introduction

In recent years, the development of fast scanning calorimeters with scan rates in a range of several orders of magnitude (10^{-3} – 10^7 K/s) has significantly extended the field of thermal analysis [1-3].

The development of non-adiabatic chip-based fast scanning calorimetry (FSC) allows complete, degradation-free measurements of polymeric materials, such as polydioxane [4]. The ability to realize the exact temperature-time treatment with FSC as it is employed in real industrial

2 Materials and Methods

2.1 Sample preparation

Semi-crystalline PLLA pellets (RESOMER L210) were provided by Evonik, Germany. The average molecular weight was $M_w = 320.000$ g/mol, as measured by gel permeation chromatography (GPC). The pellets were used for FSC measurements with different heating rates.

For electrospinning, clear and homogenous polymer solution of 4 wt% PLLA was obtained by dissolving the polymer in a solvent mixture of chloroform and 2,2,2-trifluoroethanol (TFE) (1:4 v/v) at 37 °C. Fibrous nonwovens were fabricated from polymer solution by the use of an individually designed electrospinning device ^{xyz}E-Spin as reported in [10].

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Casted films were prepared by solving 1.0 g polymer in 25 ml chloroform and casting the solutions into Petri dishes. After evaporation of the solvent, the films were washed for 2 d in methanol, 2 d in distilled water, and dried for 7 d in a vacuum oven at 40 °C.

The following equation was used to calculate the degree of crystallinity:

$$\chi_s = \frac{\Delta H_s}{\Delta H_{100}} \cdot 100 \quad (1)$$

where ΔH_s is the heat flow. A value of $\Delta H_{100} = 93.7$ J/g for totally crystalline PLLA was used for calculation [11].

2.2 Fast scanning calorimetry

The experiments were performed on a Flash DSC 2+ (Mettler Toledo, Switzerland). In contrast to a standard DSC, the sample for the FSC is not placed in a crucible, as the heat capacity and thermal conductivity of the pan would have a significant influence on the results [5]. Therefore, in FSC the sample is placed directly on the chip sensor. A heating rate q of 2000 K/s was used to measure the heat flow rate. The experiments were carried out under a nitrogen gas flow of 60 mL/min with the basic temperature of the ceramic sensor set to -100 °C.

2.3 Sensor preparation

The MEMS chip sensor MultiSTAR UFS 1 has a total of 16 thermocouples, 8 each on the sample and reference side, arranged in a star shape and symmetrically around the sample and reference surface. The chip is mounted on a specific ceramic base plate MultiSTAR UFS1 chip sensor (24 x 24 x 0.6 mm³) with 14 connection pads and wire-bonded using aluminum, see Figure 1.

Figure 1 Image of a MultiSTAR UFS1 sensor (Mettler Toledo) (left), connection pads (right), based on [5]

Each sensor chip has to be preheated (conditioning) before use to reduce the stress on the sensor wires and avoid

noise during measurements. Therefore, empty Mettler Toledo UFSC1 chip sensors were conditioned three times according to the standard procedure, that means heated between -90 °C and 400 °C at 2000 K/s to receive the signal of the empty sensor.

2.4 Sample loading

The sample was brought into direct contact with the sensor. To ensure optimal thermal contact between both, the material is cut with a scalpel blade under an optical microscope (Leica Microsystems, Germany) and transferred to the centre of the sensor using a brush hair. As good thermal contact of the sample with the sensor (see Figure 2) is essential for fast scanning measurements, a preheating step with a low heating rate, e.g. 100 K/s, up to temperatures above the glass transition temperature or the melting point of the investigated material is required. It is necessary to permanently check whether the sample is still in the correct position. If heating is too fast during this preheating step, any water content of the material will suddenly evaporate and displace the sample from its original position, the middle position, making the data useless.

Figure 2 Macrophotographical image of the UFS1 sensor loaded with a PLLA pellet sample (point middle)

2.5 Calculation of the sample mass

Because the sample mass is in the sub-microgram range, it cannot be determined gravimetrically. Therefore, we need the standard DSC method with scanning rates to overlap with FSC, in a way that the same crystallinity can be achieved by using the same cooling history to calculate the sample mass from the heat energy using equation 2. With this first-order approach, the material under investigation is expected to be homogeneous and isotropic. Furthermore, it is assumed that the sample dimensions do not lead to different crystallization behavior. If the crystallinities are equal, by definition both specific melting enthalpies are also the same [5]. The mass of the sample, measured by FSC, is calculated by:

$$m_{FSC} = \frac{\Delta H_{FSC}}{\Delta H_{DSC}} \cdot m_{DSC} \quad (2)$$

where ΔH_{FSC} and ΔH_{DSC} are the melting enthalpies in units J, measured by the Flash DSC 2+ and DSC, respectively, and m_{DSC} and m_{DSC} are the corresponding sample masses.

3 Results and Discussion

3.1 Influence of heating rate on the thermal properties of PLLA

To investigate the influence of the different heating rates on the thermal properties of PLLA, a pellet sample was heated up at heating rates between 50 and 10000 K/s and then cooled down at the same rate of 0.016 K/s to ensure crystallization of the sample. In Figure 3 the glass transition T_g of PLLA can be found. This transition shifts to higher temperatures as the heating rate q increases. Compared to the standard DSC method, where T_g is at 60 °C, it increases to 109 °C ($q = 10000$ K/s) in the FSC method.

Figure 3 Heat flow rate of PLLA pellets using FSC as a function of temperature at different heating rates (500 - 5000 K/s), shown in the temperature range near the glass transition T_g .

Figure 4 Heat flow rate of PLLA pellets using FSC as a function of temperature at different heating rates (500 - 5000 K/s), shown in the temperature range of the melting temperature T_M .

Figure 4 shows the change in shift of the melting temperature of PLLA pellets with increasing heating rate. We also see an increase of the melting temperatures from $T_M = 163$ °C for $q = 50$ K/s up to $T_M = 231$ °C for $q = 10000$ K/s. This is due to superheating [12].

If the mass of the sample is calculated from equation 2, for PLLA pellet a degree of crystallinity of 36% is obtained.

3.2 Influence of sample preparation on crystallization rates

Table 1 shows the mass of the differently processed PLLA samples, using equation 2 and the resulting crystallinity values. Similar values were calculated for the pellets ($m = 232$ ng) and the cast films ($m = 281$ ng). As expected, the nonwoven exhibited with $m = 96$ ng a significantly lower mass in comparison to the other two samples.

Table 1: PLLA sample properties: mass, heat of fusion and crystallinity, measured with DSC and FSC.

PLLA sample	calculated mass (ng)	heat of fusion (mJ)	cryst. DSC (%)	cryst. FSC (%)
granulate	232	8.16×10^{-3}	36	37
solvent cast film	281	9.90×10^{-3}	28	11
nonwoven	96	3.37×10^{-3}	36	45

In comparison to the pellets, the crystallinity using FSC of cast film is a factor 3 lower due to the possible residual solvent in the film, which acts as a plasticizer. Therefore, the crystallinity using FSC is reduced. Crystallinity using FSC is also much smaller compared to the DSC method. This is due to the low heating rate, measured with standard DSC, which allows melting and reorganization processes to be performed simultaneously. In contrast, the crystallinity of the nonwoven is significantly higher compared to the pellets. This could be caused by the manufacturing process. Due to the fibre formation, the molecular chains are much more aligned in equal direction, which leads to an increase in the degree of crystallinity.

4 Conclusion

Fast scanning calorimetry to investigate differently prepared PLLA samples has been performed with FSC, in respect to sample preparation, mass calculation and performance. The

results were compared to standard DSC methods. PLLA samples were prepared with different methods and thermally investigated to show the impact on crystallinity. PLLA pellets were also heated up with different heating rates to investigate the thermal properties of the polymer. It was shown that FSC is capable of suppressing reorganization processes and therefore the resulting properties of the material could be investigated. Further investigations need to be conducted.

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