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Novel method for fast scanning calorimetry of electrospun fibers

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ABSTRACT

Fast scanning chip-based calorimetry allows for the study of challenging polymers, for example, those which have rapid nucleation and crystallization kinetics, or which degrade within their melting range. Heating rates up to 4000 K/s allow for studies of hetero- and homogeneous nucleation at time scales inaccessible with conventional calorimeters, whose rates are typically less than about 0.5 K/s. Recent studies have successfully demonstrated methodologies for obtaining quantitative measurements of thermal properties of polymer samples using fast scanning calorimetry (FSC). However, these studies have been restricted to thin films or small flakes cut from bulk samples. Fibrous samples present extreme challenges due to their fluffy nature, which prevents good thermal contact for FSC. Here we present a new methodology to obtain quantitative fast scanning thermal data from electrospun nanofibers using the Mettler Flash DSC1. The technique is demonstrated using polyethylene terephthalate (PET) whose fundamental thermal properties are available in the literature, and provide a good test for the accuracy of FSC on micron- to nano-scale fibers. The structure of nanofibers requires special methods to load nanogram-sized samples onto a UFSC1 sensor. Fibers were directly spun onto copper TEM grids which provide a durable substrate to support bundles of nanofibers and possess excellent thermal conductivity allowing for a strong, repeatable signal and ensure good sample-to-sensor contact. As spun amorphous samples were held isothermally at temperatures ranging from T_g (69 °C) to T_m (280 °C) then heated at 2000 K/s to assess their melting behavior after cold crystallization. Results show that this sample preparation technique provides quantitative data, comparing favorably to that achieved with conventional calorimeters.

1. Introduction

Fast scanning calorimetry (FSC) has become a powerful technique in the study of semicrystalline polymers [1]. The commercial Mettler Flash DSC1 enables measurements on chip-based sensors to be conducted at scanning rates spanning five orders of magnitude [2]. This instrument, along with custom built chip calorimeters [3,4], allowed for experiments which resulted in deeper understanding of the nucleation and crystallization kinetics of polymers such as: polyethylene terephthalate, PET [5,6], polybutylene terephthalate [5,7,8], polyamide 6 [9–11], poly(ε-caprolactone) [12–14], polyvinylidene fluoride [15], isotactic polypropylene [6,16], and polyethylene and its 1-octane copolymers [17]. The range of heating and cooling rates accessible to fast scanning calorimeters has enabled new experiments probing glass transition properties [18–22]. Ultra-fast scanning rates provide a unique advantage by enabling measurements of thermal properties of small molecules [23,24] and polymers like silk [25–28] and polyvinyl alcohol [29] which undergo degradation within their melting range as

well as volatile [30] or fragile ionic liquids [31].

Despite the advantages provided by this technique, chip-based calorimeters present unique challenges for both sample preparation and data analysis. While there has been recent success in developing experimental protocols yielding quantitative data [23,25,27,32], sample preparation remains a challenge that limits the systems which can be studied. Common approaches have relied on the manual deposition of a cut section of thin film initially prepared by spin coating or compression molding [10,11,13,28], or samples cut from bulk [13].

Electrospun nanofibers have been widely studied as the basis for new functional materials [33], tissue scaffolds [34–37], drug delivery systems [38–40], and the means of studying the effects of confinement on polymer crystallization [41–47]. To date there have been few studies on electrospun fibers using chip-based calorimeters [48] or other fast scanning techniques [49]. The unique difficulty lies in the nature of such nanofibers which are light, fluffy, and delicate; these features prevent manual deposition onto sensors. While it possible to electrospin onto sensors, the control over fiber orientation is poor and is highly