Fundamental thermal properties of polyvinyl alcohol by fast scanning calorimetry

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ABSTRACT

Polyvinyl alcohol (PVA) is a synthetic, semi-crystalline polymer with a wide array of commercial uses ranging from textiles and packaging to medicine. Despite the fact that PVA is in common use, several important thermal properties have not been measured including: 1. temperature dependent liquid state specific heat capacity, $c_p^{Liquid}(T)$; 2. specific heat capacity increment of amorphous PVA at the glass transition temperature, $\Delta c_p^{amor}(T_g)$; and, 3. fraction of rigid amorphous phase in semi-crystalline PVA, ϕ_{RA}. Two rate-dependent effects have prevented these measurements: PVA thermally degrades at temperatures just in excess of 200 °C which is often within the onset of melting, and PVA crystallizes from the melt so rapidly that it is difficult to obtain fully amorphous polymer. To prevent degradation, and measure these fundamental thermal properties, we have used fast scanning calorimetry at rates ranging from 1000 K/s up to 600,000 K/s. The Mettler Flash DSC1 and a custom-built calorimeter were used to cover this range of heating and cooling rates. We determine the critical cooling rate, β_c, needed to quench PVA into an amorphous glass as $|\beta_c| = 20,000$ K/s. Using FSC in combination with conventional differential scanning calorimetry, we find $c_p^{Liquid}(T) = ((0.0016 \pm 0.0002)^*T + (2.3 \pm 0.2))$ J/(gK). The specific heat capacity increment for fully amorphous PVA is $\Delta c_p^{amor}(T_g) = (1.01 \pm 0.05)$ J/(gK). For the semi-crystalline samples used in this study, PVA obeys a two phase model in which ϕ_{RA} ~0. The approaches used in this work are applicable to any semicrystalline polymer or biopolymer which degrades upon heating, or crystallizes so rapidly from the melt that a fully amorphous material cannot be realized.

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1. Introduction

Polyvinyl alcohol (PVA) is a synthetic, linear, semi-crystalline polymer which can be synthesized by hydrolyzing polyvinyl acetate, a polymer which does not have to be sourced from petroleum. PVA is also a hydrophilic polymer which is non-toxic, biocompatible, biodegradable, and water soluble at temperatures above its glass transition ($T_g = 85$ °C). In addition, PVA also possesses favorable mechanical properties and has excellent resistance to organic solvents and vapors. The combination of chemical resistance and mechanical properties has led to its widespread industrial uses in applications such as: adhesives [1,2], textile coatings [3], and sterile packaging materials [4–6]. The biodegradability [7] and non-toxicity [8] of PVA have led to various biomedical and

pharmaceutical applications including but not limited to: fibrous meshes and membranes for wound dressings [9,10], drug delivery systems [11,12], interventional radiology embolization particles [13], and hydrogels used in orthopedic medicine [14] and contact lenses [15].

The wide range of applications for PVA has resulted in many investigations over the past four decades into both its fundamental thermal [16–25] and structural [26–28] properties as well as the crystallization behavior of PVA hydrogels [17,29], PVA nanofibers [9,11,12,30,31], and PVA blends and composites [22,23,25,32,33]. A critical challenge to overcome when investigating the thermal properties and nucleation and crystallization behavior of PVA is that, at high temperatures, PVA will undergo thermal degradation within its melting range. This was recognized in some of the earliest studies on PVA [16,28] and there have been conflicting reports [16,17,20,22–25,29] as to the impact degradation will have on the crystallization kinetics and fundamental thermal properties of PVA. Furthermore, PVA is also used to generate the force field used for computer simulation of polymer crystallization. A

simplified version of a model for poly(vinyl alcohol) (PVA) was derived by a systematic coarse-graining procedure from fully atomistic simulations [34] and is still in use [35]. However, the applied cooling rates in these simulations are orders of magnitude larger than the critical cooling rate determined here.

Since the development of non-adiabatic chip based fast scanning calorimetry (FSC) [36–38] it has become possible to make complete, degradation free measurements of polymeric materials which are not possible in conventional differential scanning calorimeters (DSC). Both custom-made FSC systems [38,39] and the commercial Mettler Flash DSC1 [40–42] allow for scanning rates four to six orders of magnitude greater than those accessible to conventional DSC systems [40]. The ultra-fast scanning rates accessible to these instruments have provided new insights into the crystallization kinetics of polymers such as: polyamide 6 [43,44], polyethylene terephthalate [45,46], polybutylene terephthalate [46,47], polyvinylidene fluoride [48], isotactic polypropylene [49], and poly(ε-caprolactone) [50,51], polyethylene and its copolymers with 1-octene [52], and polymers in the presence of nucleating agents [46,51]. With scanning rates on the order of 1000 K/s these instruments have been successfully utilized to measure the melting point and heat of fusion of silk fibroin [53–56], measurements which were not possible by standard DSC as silk fibroin, like PVA, undergoes thermal degradation within its melting range [16,20,22–24].

The specific heat capacity of the liquid phase, $c_p^{Liquid}(T)$, and the specific heat capacity increment at the glass transition for 100% amorphous material, $\Delta c_p^{amor}(T_g)$, are two fundamental thermal properties of polymers. These properties have been difficult to measure for PVA. First, concerning the measurement of $c_p^{Liquid}(T)$, thermal degradation can set in at temperatures as low as 200 °C, a temperature which is typically within the melting range of semi-crystalline PVA [16,20,22–24]. To the best knowledge of the authors there are no accepted values for $c_p^{Liquid}(T)$. Second, measurement of $\Delta c_p^{amor}(T_g)$ relies on ability to obtain PVA in its fully amorphous state, which is difficult to achieve because PVA crystallizes extremely rapidly upon cooling from the melt. To our knowledge there is no $\Delta c_p^{amor}(T_g)$ value for PVA in literature. To make complete, degradation free measurements of these important properties, we use both fast scanning and conventional DSC to provide thermal data on PVA over a range of heating rates from 5 to 20 K/min (DSC), 2000 K/s (FSC, using the Mettler Flash DSC1), and 1000 K/s-600,000 K/s (FSC, using a custom–built chip based calorimeter [38,39]). The fast scanning experiments provide insights into the thermal degradation of PVA under fast scanning conditions to determine the range over which degradation free measurements could be made, and allow measurement of $c_p^{Liquid}(T)$.

Within the range over which degradation free measurements can be made, isothermal melt crystallization experiments were performed using the Mettler Flash DSC1. Over a wide range of crystallinities, obtained by varying the isothermal crystallization temperature and time, the mass fraction crystallinity and heat capacity increment at the glass transition could be measured. These experiments, combined with slow scan rate DSC experiments, allowed for the measurement of both $c_p^{Liquid}(T)$ and $\Delta c_p^{amor}(T_g)$ using an extrapolative method developed previously [57].

The manuscript is organized as follows: Section 2 provides experimental details of PVA sample preparation and FSC measurements; Section 3 presents results of thermal stability, crystallinity, liquid state heat capacity, and glass transition behavior of PVA under conditions of fast scanning; Section 4 presents the fundamental thermal properties obtained by FSC, including $c_p^{Liquid}(T)$, $\Delta c_p^{amor}(T_g)$, and the rigid amorphous fraction of PVA, φ_{RA}. Conclusions are summarized in Section 5.

2. Experimental section

2.1. Materials and sample preparation

Semi-crystalline pellets of polyvinyl alcohol (PVA), with weight average molecular weight, M_w, of 78,000 and 98 mol% hydrolyzed, were obtained from Polysciences, Inc. (Warrington, PA) PVA was dissolved at 3.0 wt% in deionized water at 90 °C with continuous stirring for 2 h resulting in a homogeneous solution. The solution was spun onto substrates with a Headway (Garland, TX) research grade spin caster. To obtain thin film samples, 10 droplets of PVA solution were passed through a 0.8 μm PTFE filter and sequentially deposited onto a PTFE coated slide spinning at 2000 rpm for 60 s. This resulted in films approximately 3 μm thick which were easily removed from the PTFE coated slides prior to mounting on chip sensor membranes. This will be referred to as the "thicker film" and served as the parent film for one group of 9 samples. A second film was prepared by passing the PVA solution through a 0.8 μm PTFE filter and depositing 10 droplets on a PTFE coated slide at rest. This slide was then spun at 2000 rpm for 60 s resulting in a film approximately 1 μm thick. This film will be referred to as the "thinner film" and was used as the parent film for one experiment. All films were placed in a vacuum oven at approximately 30 °C for 24 h for drying.

2.2. Fast scanning calorimetry, FSC

A Mettler Flash DSC1 (Mettler-Toledo, Switzerland) was used to measure heat flow rate vs. temperature for PVA at a scanning rate, β, of ±2000 K/s. Experiments were performed under a nitrogen gas flow of about 50 mL/min with the ceramic sensor base temperature set to −100 °C. Empty Mettler Toledo UFSC1 chip sensors were conditioned following the manufacturer's procedure four to five times then cooled and reheated between −90 °C and 270 °C at 2000 K/s to obtain the baseline empty sensor signal. Samples from the parent films were hand cut with a surgical scalpel, with the assistance of a binocular microscope, carried on a fine wire and then placed onto the sensors.

A custom nano-calorimeter [38,39] was used to achieve faster rates, up to 600,000 K/s. A sample was cut from the thicker parent film and loaded, in the same manner described above, onto sensor XI-390. The sample and sensor were sealed in a helium environment both to improve cooling performance and to mitigate sample degradation. The sensor was placed into the fast scanning power compensated differential scanning nano-calorimeter [38,39] with a sensor support cooled by liquid nitrogen to a temperature of approximately −196 °C. PVA was heated to the melt at 280 °C and cooled to −170 °C at rates between 1000 Ks/s and 600,000 K/s and then reheated at a fixed rate of 10,000 K/s.

Empty sensor and sample scans were collected and exported for further analysis via Mettler Toledo STARe© software [58]. Data analysis was performed with custom programs written in MATLAB© [59].

2.3. FSC experiments

PVA films contain bound water from processing [24] and, along with wrinkles and folds from handling, require an initial heating ramp to the melt to eject bound water and flatten the film. This optimizes the sample-to-sensor thermal contact, and as such, all methods begin with an initial heat-cool-heat cycle. This cycle brings the sample between −80 °C and 270 °C at 2000 K/s with 0.01 s holding time between heating and cooling segments. A schematic of the temperature vs. time profile can be found in the Supplemental Information Fig. S1. Furthermore, this initial thermal