Journal of Non-Crystalline Solids 358 (2012) 1710–1715

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

On the frequency correction in temperature-modulated differential scanning calorimetry of the glass transition

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ARTICLE INFO

Article history:
Received 2 April 2012
Received in revised form 2 May 2012
Available online 29 May 2012

Keywords:
Temperature-modulated differential scanning calorimetry;
Frequency correction;
Glass transition;
Glass relaxation

ABSTRACT

Temperature-modulated differential scanning calorimetry (TMDSC) is based on conventional DSC but with a sinusoidally modulated temperature path. Simulations of TMDSC signals were performed for Corning EAGLE XG glass over a wide range of modulation frequencies. Our results reveal that the frequency correction commonly used in the interpretation of TMDSC signals leads to a master nonreversing heat flow curve independent of modulation frequency, provided that sufficiently high frequencies are employed in the TMDSC measurement. A master reversing heat flow curve can also be generated through the frequency correction. The resulting glass transition temperature from the frequency corrected reversing heat flow is thereby shown to be independent of frequency.

1. Introduction

Heat generation or absorption accompanies most chemical reactions and many important physical transitions such as crystallization, melting, phase separation, glass transition, and relaxation. Differential scanning calorimetry (DSC) is an especially useful technique [1] for measuring the evolution of heat in glass samples as a means for understanding important glass transition and relaxation phenomena. In conventional DSC measurements, the most often used temperature program is a linear heating/cooling thermal path with the total heat flow measured as output.

Temperature-modulated differential scanning calorimetry (TMDSC) is a newer and more advanced technique in which the linear temperature path is modulated with a small periodic temperature perturbation, usually from a sinusoidal drive. The thermal profile in a TMDSC can be heat-cool, iso-temperature-scan, step-scan, or quasi-isothermal [2]. The heat-cool profile is typically used in the study of glass transition behavior. The total heat flow from TMDSC is identical to conventional DSC under the same basic linear thermal profile, i.e., for zero amplitude of the modulating tone. The advantage of TMDSC over conventional DSC is argued as the ability to separate overlapping physical phenomena through deconvolution of the signal into reversing and non-reversing components of the total heat flow [3]. For investigation of glassy systems, the reversing heat flow clearly shows the glass transition range while the non-reversing heat flow is a measure of structural relaxation during the TMDSC scan [3]. Fundamental understanding of the system from TMDSC relies on the ability to analyze the reversing and non-reversing signals correctly. Consequently, proper analysis of TMDSC signals has been a very important topic in the development and application of this technique [4,5].

The reversing component of the heat flow signal can be used to determine a modulation-dependent glass transition temperature [6–10], while the non-reversing heat flow has been widely used in the study of Boolchand intermediate phases in Ge-Se [6–9], As-Se [8–10], Na_2O-SiO_2 [11], Na_2O-GeO_2 [12], and several other glass systems. The range of compositions having a zero or near-zero integrated non-reversing heat flow is termed the "reversibility window" and defines the Boolchand intermediate phase for that system [6–12]. Intermediate phase glasses are topologically optimized glass compositions that usually have an average atomic coordination number ($\langle r \rangle$) near 2.4. According to mean-field topological constraint theory [13–16], when the average coordination value reaches $\langle r \rangle$=2.4, the number of rigid two- and three-body bond constraints is equal to the total configurational degrees of freedom. This will result in a rigid but unstressed glass structure which sits at the boundary between an underconstrained floppy phase ($\langle r \rangle$<2.4) and an overconstrained stressed-rigid phase ($\langle r \rangle$>2.4). The discovery of Boolchand is that the optimized (isostatic) glass is not necessarily represented by just a single composition with $\langle r \rangle$ exactly equal to 2.4. The Boolchand intermediate phase consists of a range of compositions, typically centered in the vicinity of $\langle r \rangle = 2.4$, in which the glass structure self-organizes to obtain an isostatic stress-free condition. However, some controversies have arisen regarding the validity of the TMDSC measurement and the

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doi:10.1016/j.jnoncrysol.2012.05.006

existence of the Boolchand intermediate phase. One controversy is in regard to the structure dependence of the intermediate phase in the TMDSC measurement [17]. A second controversy relates to the impact of modulation frequency on the TMDSC results and the resulting physical implications [18]. Here we will focus on the second issue, i.e., the influence of frequency on the TMDSC results and analysis.

The frequency dependence of non-reversing heat flow and glass transition temperature from TMDSC have been noted experimentally [19] and also in simulated experimental scans [20,21]. In Chen et al.'s aging study of selenide glasses, the non-reversing enthalpy is reported as frequency corrected [19]. Generally speaking, in order to do the frequency correction for the non-reversing enthalpy calculation, a cooling scan with the same linear cooling rate overlapped with the same periodic perturbation is required following the initial heating. By subtracting the non-reversing enthalpy in the cooling cycle from the non-reversing enthalpy measured in the heating cycle, a corrected non-reversing enthalpy is obtained. It is expected that we should be able to obtain a universal non-reversing enthalpy after the frequency correction for any frequency of the periodic perturbation in TMDSC. However, the ability to test this hypothesis experimentally is severely limited by the range of frequencies accessible in laboratory TMDSC equipment: at high frequencies the experiment is limited by heat transfer of the sample, and at low frequencies the experiment is limited by the long times required in order to keep sufficient modulation periods in the glass transition range.

To overcome these limitations and study the validity of the frequency correction, here we will present the results of TMDSC "virtual experiments" on Corning EAGLE XG glass. The frequency range in the simulated TMDSC experiment can be much wider than in experiment since there is no limitation on heat transfer from the sample to the environment. The simulated results demonstrate that the frequency correction can produce a universal non-reversing heat flow given that a sufficient number of modulation periods occur during the glass transition range of the sample.

2. Modeling procedure

The simulated TMDSC experiments for EAGLE XG glass are performed using the same approach as used previously in our work on fictive temperature [22]. The enthalpy relaxation follows a stretched exponential decay function [23–25], which is expressed as a Prony series of 12 simple exponential terms for convenience of the numerical solution. The dimensionless stretching exponent is 3/7, which has been demonstrated to be intrinsic for enthalpy relaxation in homogeneous glass in three dimensions [26–29]. The relaxation time is proportional to the nonequilibrium shear viscosity given by the Mauro–Allan–Potuzak (MAP) [30] model, where the equilibrium viscosity contribution is expressed by the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) equation [31]. All of the parameters needed in the model for EAGLE XG glass are published by Mauro et al. [30].

The glass is formed by quenching as a pre-thermal history and is then subjected to two TMDSC upscans with one intermediate downscan. As shown in Fig. 1(a), the starting temperature of the simulated TMDSC scan is 25 °C. The maximum temperature reached during both upscans is 1000 °C, which is well above the glass transition temperature of $T_g = 735.7$ °C (the temperature where the equilibrium viscosity is 10^{12} Pa-s). The linear heating/cooling rate is 1 °C/min, and the amplitude of the periodic sinusoidal perturbation is 5 °C. The modulation frequency is varied from 0.0005 to 0.01 Hz, corresponding to a range of periods from 100 to 2000 s. The as-formed glass has a quenched thermal history as described in Ref. [30]. During the first upscan, this quenched glass is heated to an equilibrium state (1000 °C) and then cooled back to 25 °C. A second, identical upscan is then performed for this "rejuvenated" glass. The output heat flow of the simulated experiment has the same feature as the modulated heat flow signal, $\dot{H}_{TMDSC}$, shown in Fig. A1(b) of Ref. [19]. Then the average

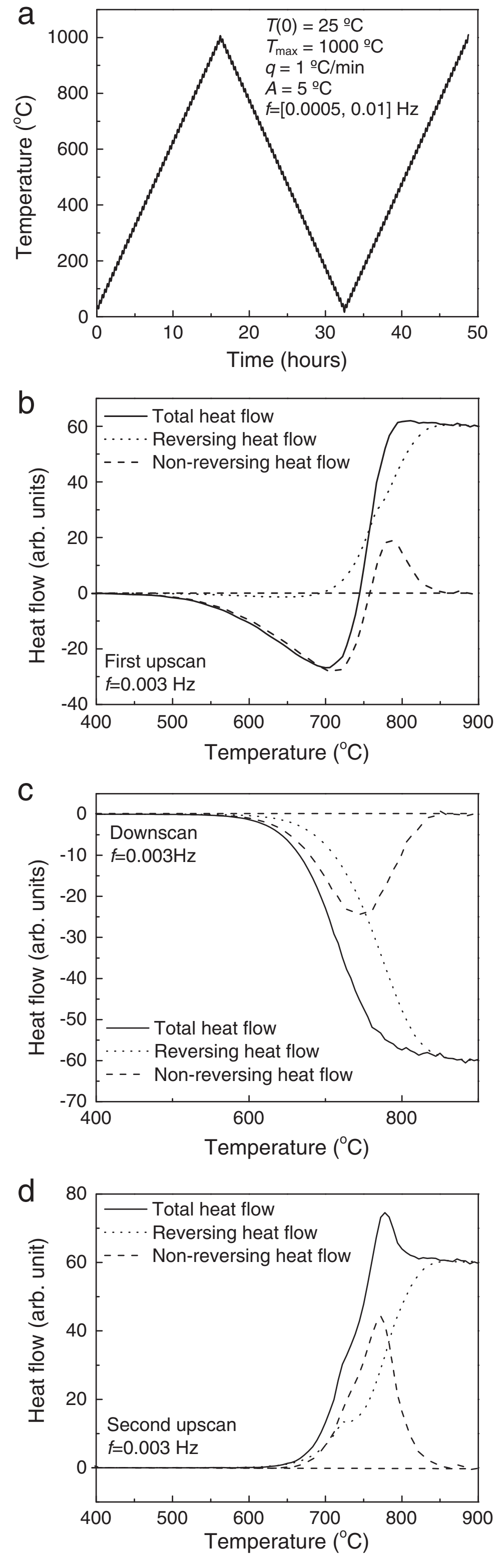

Fig. 1. The thermal path and analyzed total heat flows from the simulation. (a) Thermal path setting up in TMDSC simulation, the starting temperature 25 °C, maximum temperature reached at both upscans 1000 °C, the basic linear heating/cooling rate 1 °C/min, the amplitude of the periodic sinusoidal perturbation 5 °C, and modulation frequencies (f) ranged from 0.0005 to 0.01 Hz; the total heat flow, reversing and non-reversing heat flow for quenched EAGLE XG at $f = 0.003$ Hz: (b) first upscan; (c) downscan; (d) second upscan.

heat flow (total heat flow) and amplitude are generated by Fourier transformation. Then the total heat flow is decomposed to reversing heat flow and non-reversing heat flow for the two upscans and the