

THE STUDY OF THE GLASS TRANSITION BY THE STEPSCAN DSC TECHNIQUE

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The glass transition has been studied by novel StepScan DSC technique (Perkin-Elmer). This one allows separate by way of equilibrium steps fast reversible processes from slow kinetic ones. The reversible part of the glass transition has been the subject of this study. It was found that this part could be regarded as a temperature dependence of equilibrium glass \leftrightarrow undercooled melt conversion, α . Two-parametric semi-empirical model $\alpha=1-\exp(-(T/T_g)^n)$ was proposed. Parameter T_g corresponds to the inflection point of S-shaped α vs. T curve. The steepness parameter, n , depends inversely on the glass transition temperature. The results obtained means that untransformed glass and undercooled melt coexist in the glass transition region.

(Received July 14, 2005; accepted September 22, 2005)

Keywords: Non-crystalline materials, StepScan DSC, Glass transition

1. Introduction

The glass transition, one of the characteristic features of glasses, was firstly observed during the thirties of the last century, see e.g. [1] and references cited in, and since that time, it has been the subject of the intensive study. The glass transition was originally observed during the melt cooling and for this reason, it is very often associated with gradual freezing of the melt structure during cooling. According to this approach, it is generally assumed that when a melt is sufficiently quickly cooled to avoid crystallization, an abrupt increase of structural relaxation time occurs and a melt gets into the structural non-equilibrium. Such a material, denoted as a glass, is still regarded as a melt. Until recently the glass transition is thus frequently considered to be a pure kinetic effect [2,3]. This view is commonly supported by the following findings: the value of the glass transition temperature depends on both applied technique of measurement and the process by which the glass is formed, it means on its thermal history [2-6].

New experimental DSC techniques allow taking a new view on the glass transition. In this study a new type of DSC method called StepScan DSC (Perkin-Elmer) was used. This method enables to split the glass transition into two kinds of processes (parts) – the temperature dependent one (denoted as thermodynamic or reversible part) and the time dependent one (kinetic or irreversible part). In our previous work [7,8], we have found that the reversible part of the glass transition, which is the temperature dependence of the heat capacity (C_p vs T), is completely independent on both experimental conditions (especially on heating or cooling rate) and thermal history of glass. It means that this part depends only on the chemical composition of material under study. It follows very interesting conclusion that the glass transition temperature, T_g , determined from the reversible part, depends also only on the chemical composition and hence, it could serve as

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a material constant [7,8]. Boolchand and coworkers, who studied the glass transition by means of TMDSC [9], obtained very similar results.

This study is a follow-up to our previous works [7,8]. The main goal of present work is aimed at the more detailed study of the reversible part of the glass transition (C_p vs T curve) obtained by StepScan DSC measurement of various kinds of non-crystalline materials with different chemical composition.

2. Experimental

New stepwise DSC technique StepScan (PerkinElmer) based on the measurement between states close to thermal equilibrium of a glass was used. This method facilitates the taking of accurate specific heat capacity data and allows separating C_p (reversible or thermodynamic) part from slow irreversible kinetic events. The temperature modulated DSC (TMDSC) permits also similar separation [2,10], but the advantage of the StepScan DSC approach is that it provides a direct heat capacity measurement using traditional and time-proven means without the need for deconvolution. Contrary to TMDSC, StepScan DSC results are not plagued with some experimental difficulties, e.g. phase lag. The C_p can be obtained over wide temperature range to better than a percent using this technique [11].

In comparison with conventional DSC, the StepScan DSC C_p measurement close to thermal equilibrium removes completely both hysteresis of heat capacity and shape difference between cooling and heating scans, see our previous work [8].

StepScan DSC technique is based on repeatedly measured heat flow, Q , of a known amount of sample at a constant heating or cooling rate, q^\pm , compared to that of the heat flow in an adjacent isotherm. The duration of isotherm at each step depends on the response of sample and is software controlled. Hence, the equilibration time is minimized during temperature region where the sample response is rapid, and extended when more time is required.

The experiments were carried out with following parameters. The scanning step 1°C was used and heating or cooling rate in the scanning step was selected $\pm 1^\circ\text{C}/\text{min}$ and/or $\pm 100^\circ\text{C}/\text{min}$. The maximal allowed heat flow difference during isotherm before next step was $\Delta Q = \pm 0.1 \mu\text{W}$. The measurements were performed on Pyris 1 DSC (Perkin-Elmer) because this technique is feasible only with the power compensated DSC.

Chalcogenide and oxide bulk glasses and some polymers were used in the study. The chalcogenide glasses (As_2Se_3 , As_2S_3 , GeS_2 , $\text{Ge}_4\text{As}_4\text{S}_{92}$ and Se bulk glasses) were prepared by conventional method of direct synthesis from high-purity elements (5N) in evacuated silica ampoules in a rocking furnace and quenched in air or in water. The oxide glass LiPbPBO ($40\text{Li}_2\text{O}:10\text{PbO}:10\text{B}_2\text{O}_3:40\text{P}_2\text{O}_5$) was prepared by melting of oxides and melt was consequently cooled on cold copper plate. The lead-silica glass NBS 711 is a commercial product [12]. The poly(styrene-*co*-acrylonitrile), 75/25, PSA, from BASF and commercial product based on poly(ethylen terephthalate), PET, were used as a polymer samples. Samples of weight around 10 mg were measured into sealed aluminum pans.

3. Results and discussion

The As_2Se_3 bulk glass was measured repeatedly over the glass transition region by the StepScan DSC using considerable different heating/cooling step rates $q^\pm = \pm 1$ and $\pm 100 \text{ K}/\text{min}$. Kinetic effects were separated and sigmoidal-shaped curves corresponding to the changes of isobaric heat capacity in the glass transformation region (reversible part) are shown in Fig. 1. It is evident that the identical temperature dependence of C_p was obtained regardless of both the rate and the direction of the temperature change. Hence also the values of the glass transition temperatures, obtained both in the heating and cooling regime, are always the same. The experiment confirms our previous result that T_g determined from the reversible part of StepScan DSC depends only on the chemical composition of glass and therefore it can be used as a material constant, see [7,8].

On basis of above-mentioned experiment it can be further concluded that the temperature T can be considered to be the equilibrium transformation temperature. It means that the reversible part of the glass transition (C_p vs. T) may be referred to the temperature dependence of glass \leftrightarrow undercooled melt equilibrium. This dependence after normalization represents the temperature dependence of glass \rightarrow undercooled melt conversion $\alpha(T)$.

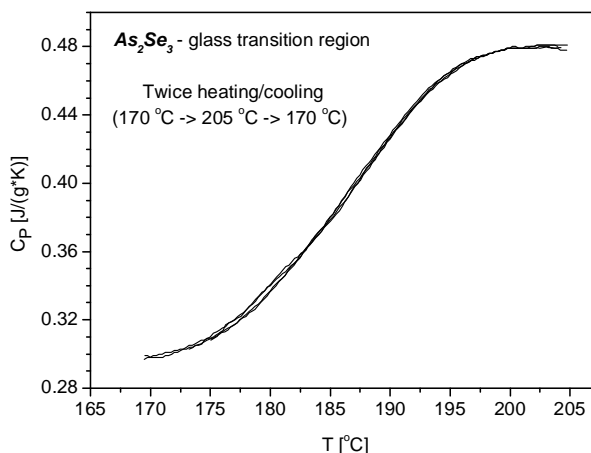


Fig. 1. Reversible parts of the glass transition of As_2Se_3 glass (C_p vs. T , StepScan DSC). The measurement was done in two heating/cooling cycles (four curves) with different rates of the temperature step, for details see text.

If temperature dependent transformation occurs randomly in the material and the fraction dx of glass is transformed to undercooled melt we can write:

$$d\alpha = (1 - \alpha)dx, \quad (1)$$

where α varies from zero to unity (the end of the transformation). Integration of this equation yields to:

$$\alpha = 1 - \exp(-x). \quad (2)$$

In case of the glass transition, the temperature dependence of the conversion α can be expressed by the measurable values as $\alpha = (C_p(T) - C_{pg})/\Delta C_p$. $C_p(T)$ is the actual value of isobaric heat capacity at temperature T , ΔC_p is its total change during the glass transition and C_{pg} is the heat capacity of glass at the lowest temperature of the glass transition region. We have found that substituting x by $(T/T_g)^n$ yields to the following equation:

$$\alpha = 1 - \exp\left(-\left(\frac{T}{T_g}\right)^n\right) \quad (3)$$

describing well the experimentally obtained data. In this equation T'_g is the temperature of inflexion point of α vs. T dependence, and n is a steepness parameter. The α vs. T form is more suitable for computer fitting than C_p vs. T because the use of degree of conversion instead of isobaric heat capacities eliminates their temperature dependencies out of glass transition region.

The applicability of Eq. (3) at the description of reversible part of the glass transition was tested on many non-crystalline materials of a different chemical nature: bulk chalcogenide glasses (Se, As_2Se_3 , As_2S_3 , GeS_2 , $Ge_4As_4S_{92}$), the oxide glasses (LiPbPBO, NBS 711) and polymers (PET, PSA), see Experimental section. The reversible parts of the glass transformation process were normalized and then fitted by Eq. (3). It was found that this equation fits the glass transition region fairly well in all cases. As an example the result for bulk selenium is presented in Fig. 2.

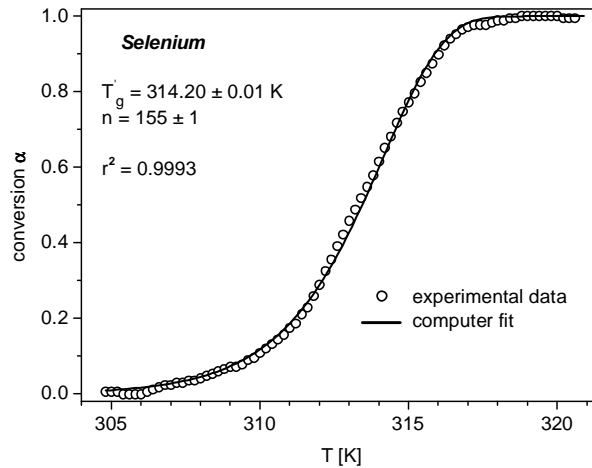


Fig. 2. Normalized reversible part of the glass transition (conversion α) of glassy Se and its computer fit obtained by using Eq. (3).

From the Eq. (3) it arises that in the inflection point ($T = T'_g$) the conversion must always be $\alpha = (1 - 1/e) = 0.632$, where e is the base of natural logarithm. Therefore when reduced temperature, T/T'_g , is used, the conversion curves of all glasses studied must intersect within an experimental error at $\alpha \sim 0.63$. Experimental results are in the excellent agreement with this presumption, see Fig. 3.

It is evident that the reversible parts differ in the shape. The steepness of curves is determined by the value of parameter n in Eq. (3). By differentiation of this equation for $T = T'_g$ the parameter n is obtained as $n = e \cdot d\alpha/d(T/T'_g)$ and it is the slope of the glass \leftrightarrow undercooled melt conversion curve in the inflexion point. Values of n calculated for all materials studied are included along with values of T'_g in Table 1.

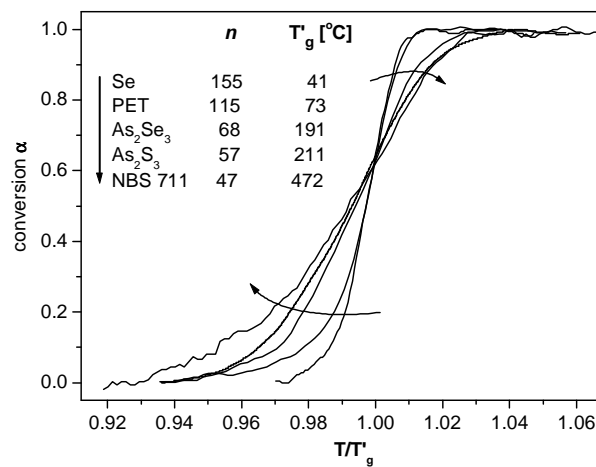


Fig. 3. Normalized reversible parts of the glass transition of some studied samples. All curves intersect close to $\alpha \sim 0.63$ for T/T'_g . Some results have been omitted in order to avoid cluttering in the figure.

Table 1. Parameters of Eq. (3): the glass transition temperature, T'_g , and the steepness parameter n . For compositions see Experimental.

Sample	T'_g [°C]	n
Ge ₄ As ₄ S ₉₂	23	160
Se	41	155
PET	73	115
PSA	109	64
As ₂ Se ₃	191	68
As ₂ S ₃	211	57
LiPbBO	344	60
NBS 711	472	47
GeS ₂	507	43

From this table it follows that n decreases when T'_g increases regardless of the chemical composition of glass. It means that if glasses of different chemical composition have close values of T'_g than the shape of reversible part of glass transition will be very similar.

The physical meaning of parameter n is not still clear. The dependence of n on T'_g can be divided into two regions, see Fig. 4.

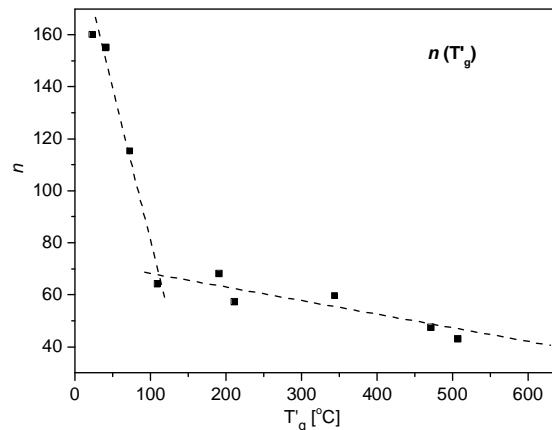


Fig. 6. The dependence of the glass transition steepness parameter, n , on the glass transition temperature, T'_g , for all studied non-crystalline materials. The lines are only for eye guidance.

Straight lines with markedly different slopes can approximate these dependencies and they cross at approx. 110 °C. We suppose that the parameter n , probably relates to the various types and energy of chemical bonds in material studied. However, further experiments are needed for detailed explanation.

5. Conclusions

The glass transition of various kinds of non-crystalline materials was studied by StepScan DSC technique. This one allows separate reversible processes from slower kinetic events taking part in the glass transition region. Attention was focussed on the study of the reversible part of the glass transition, e.g. on the temperature dependence of C_p . Experimental results confirmed previously published findings [7,8] that reversible part does not depend on both the glass thermal history and measurement conditions. In other words reversible part of glass transition is insensitive to both isothermal and non-isothermal enthalpic relaxation. From it follows that the glass transition cannot be considered as only kinetic effect.

From experimental results follow that the glass transition can be regarded as a temperature dependence of a glass \leftrightarrow undercooled melt equilibrium. The semi-empirical two-parametric equation was proposed to describe the temperature dependence of glass \leftrightarrow undercooled melt conversion. One of the parameters, T'_g , determines temperature of inflexion point of sigmoidal shaped curve and the second one, n , is the steepness at T'_g . Applicability of proposed equation was tested using various non-crystalline materials with very different chemical composition. All experimentally obtained reversible parts were fitted fairly well and in agreement with the proposed equation an inflection point at $\alpha \approx 0.63$ was found in all cases. The steepness, n , was found to be inversely proportional to the glass transition temperature.

The temperature of inflection point, T'_g , should be used as unambiguously defined glass transition temperature.

Acknowledgements

This work was supported by The Ministry of Education of Czech Republic under the projects MSM 0021627501.

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