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THERMAL ANALYSIS OF GLASS

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ABSTRACT

Dynamic thermal analysis is very useful for the characterization of the glass melting process and the thermal behaviour of glasses. In many instances the determination of temperatures of transformation and crystallization is possible by means of DTA/DSC. The limitations of these methods are discussed in connection with the temperature–viscosity function of melts and glasses. The various thermoanalytical methods are not equally suitable for qualitative and quantitative characterization. Selective methods such as EGA provide the possibility of determining single reaction steps by heating a raw material mixture and a glass. Such information is useful for the optimization of the glass melting process and glass properties. Developments in this field are still in the early stages.

INTRODUCTION

As can be seen from special journals [1–3] and conferences [4,5], thermal methods, especially DTA, DSC, TGA and dilatometry, are widely applied for the characterization of raw materials, of the glass melting process and of vitreous organic and inorganic products in nature and technology. There are two main fields of application of these methods: the determination of the "characteristic glass points" and of thermodynamic properties; and the characterization of the glass melting process and the thermal behaviour of glasses and melts.

The interpretation of thermal measurements has a more or less theoretical basis, but the results are frequently contradictory. Several recommendations for the publication and interpretation of thermoanalytical results of glasses have been made [6,7], but with little or no success in the direction of a standardized procedure of analysis. Even now in many publications it is not evident which method and measurement conditions have been used for the determination of data.

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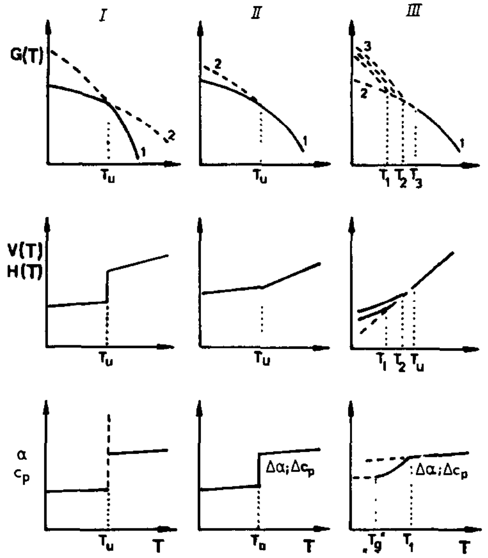

Fig. 1. Schematic diagram of the temperature functions of the free enthalpy $G(T)$, volume $V(T)$ and enthalpy $H(T)$, and the expansion coefficient (α) and specific heat (c_p). I = 1st-order reaction; II = 2nd-order reaction; III = glass transition. T_u = Transformation temperature; T_1, T_2 = quenching temperature; T_g = glass transition temperature. 1, 2, 3 = Stable, metastable and glassy states, respectively.

As the properties of glasses (quenched metastable melts) are dependent on their thermal history, the glasses are considered in terms of the temperature and time required to form and to analyse them. This means that the cooling and heating rates must be stated, and also details of the sample preparation, sample weight and instrumentation.

In the vitreous state can be fixed an infinite number of states and the term "structural relaxation" refers to the kinetically impeded response of extensive properties such as temperature, pressure and composition. As a result, the "glass transition temperature" and other characteristic glass points depend on the heating and cooling history of the sample. Frequently the glass transition is described as a second-order reaction according to Ehrenfest [8,9]. In this instance the glass transition temperature is a function of the extensive properties. However, as demonstrated in many papers, e.g. refs. 10 and 11, the volume or enthalpy of a glass is not an unequivocal function of temperature, pressure or composition. Only in the borderline case that the internal order does correspond to equilibrium on the "quenching line" is the Ehrenfest formalism justified. Generally the glass transition is a range that is controlled kinetically.

Figure 1 shows the typical behaviour of a glass-forming system in comparison with first- and second-order reactions. This description should serve as a basis for further discussion.

A schematic plot of enthalpy versus temperature for a glass-forming system cooled and then reheated is shown in Fig. 2. From this figure DTA and DSC curves are obtained for the same substances, depending on the thermal history (Fig. 3). We can see that the determination of characteristic temperature is uncertain without an accepted convention for sample handling. For practical use it is important to know whether a correlation exists between the "characteristic glass points", e.g., characteristic temperatures in the viscosity function such as "strain point" = $10^{13.5}$ Pa s, "annealing point" = 10^{12} Pa s or "softening point" = $10^{6.6}$ Pa s, and the deflection on the DTA or DSC curves. The change in viscosity in a fixed temperature range is of particular interest in the technology of glass forming. Yamamoto [11] discussed this problem at the 1st ICTA in Aberdeen, and Liska et al. [12] and Hamlik et al. [13] have now focused again on this problem in studies of a complex borosilicate glass. In contrast to Yamamoto and other workers, e.g., ref. 14, it was found by means of a statistical approach that the temperatures of the characteristic points of the DTA curves and the characteristic points of the viscosity curves are almost independent. These results will promote the discussions of this problem considerably, especially with respect to the procedure for the determination of the characteristic points on DTA/DSC curves.

Figure 4 shows schematically DTA and DSC curves from glass and the problem of their unambiguous interpretation.

Independent of these problems, the expansion of the transformation range is an important factor to be considered in the discussion of the slope of DTA/DSC curves. If the slope of the viscosity curve is small, the

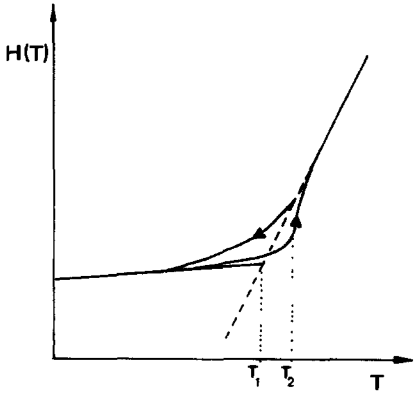

Fig. 2. Schematic plot of enthalpy [$H(T)$] versus temperature for glass cooled and then reheated through the transition region. T_1 = "Fictive temperature"; T_2 = "maximum temperature".

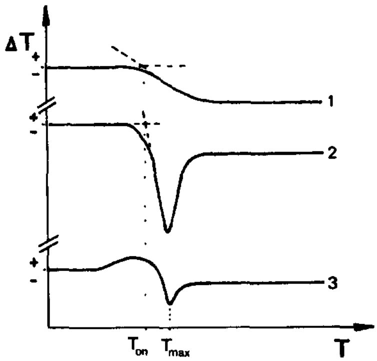

Fig. 3. DTA/DSC curves of a glass showing the different thermal histories of the sample. 1 = Slow cooling and slow heating; 2 = slow cooling and fast heating; 3 = fast cooling and fast heating.

temperature difference in the DTA measurements decreases to a critical value and then a deflection is not observable on the DTA curve.

For phase separation in glass we can observe several deflections on the DTA curve (Fig. 5). The relationship between $T_{g(\text{matrix})}$ and $T_{g(\text{droplets})}$ does not influence the determination. By means of dilatometric measurements this effect is observable only when $T_{g(\text{matrix})} > T_{g(\text{droplets})}$.

A comparison of different thermoanalytical methods requires the consideration of the different relaxation rates such as enthalpy, volume, refractive

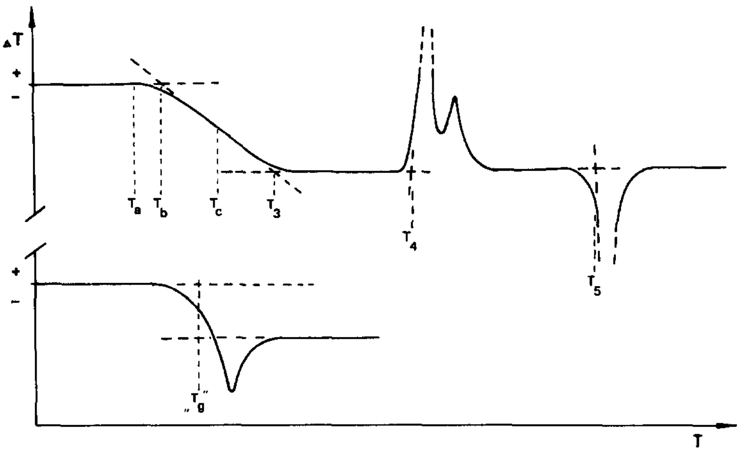

Fig. 4. Schematic plot of DTA/DSC curves and the evaluation of the characteristic glass transition temperatures by different procedures. ICTA procedure: T_a = first significant deviation from the baseline (initial deflection); T_b = extrapolated onset temperature; T_c = inflection point temperature; T_3 = extrapolation end-temperature; T_4 = extrapolated crystallization temperature; T_5 = extrapolated melting temperature; "T_g" = "glass transition temperature" ($1/2T/1/2c_p$).

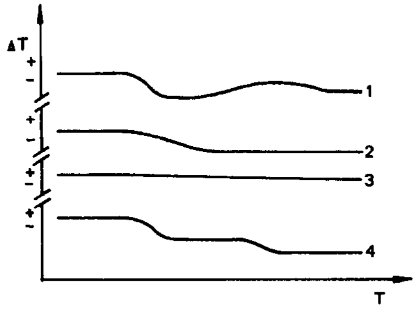

Fig. 5. Illustration of possible DTA/DSC curves of glasses with different viscosity–temperature functions and phase separation in the transition range. 1, The viscosity varies considerably with temperature; 2,3, slow variation of viscosity with temperature; 4, heterogeneous glass through phase separation.

index or shear viscosity. Therefore, temperatures such as T_g for the same state assessed from different properties are not necessarily identical. Usually the dilatometric transformation temperature is determined between the DTA_{onset} and $DTA_{inflection}$ temperature. However, differences of more than 20 K have been observed, as was demonstrated with a sodium calcium silicate glass (Fig. 6).

The characterization of the molecular configurations by means of a "fictive temperature" [15,16] is uncommon in glass manufacture. Principles of approaches to the structural relaxation phenomena in liquids and glasses in connection with macroscopic behaviour such as the viscosity were discussed by Eichhorn and Kluge in terms of the non-equilibrium thermodynamics [17].

The characterization of the crystallization behaviour of glass by means of DTA/DSC measurements is very empirical. The problem of the quantitative analysis of the crystallization of glasses has been widely studied. Malek et al.

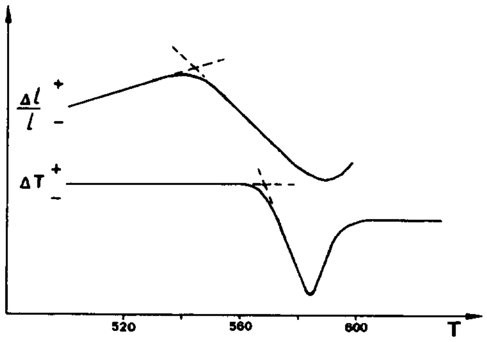

Fig. 6. Dilatometric and DTA curve of sodium calcium silicate glass.

[18], Rysava et al. [19] and Mitkova and Boncheva-Mladenova [20] used the Kissinger first-order reaction approximation or the Avrami equation to determine the "activation energy of crystallization" as a function of the chemical composition. They all used equations that are under discussion with respect to both their theoretical basis and their statistical significance. A discussion of such an interpretation is necessary not only on the borders of glass chemistry; also the determination of the crystallization rate by means of the exothermic effect on the DTA curve is typical for glass investigations.

More details are necessary for a critical review of the experimental conditions and procedures of data evaluation.

CHARACTERIZATION OF THE GLASS MELTING PROCESS AND THE THERMAL BEHAVIOUR OF GLASSES AND MELTS

Dynamic thermal analysis is very useful for the characterization of the glass melting process and the thermal behaviour of glass-forming melts. By means of investigations in the laboratory we can obtain guidelines for technological applications with respect to the melting behaviour of different raw material mixtures [21,22]. As has been shown in different papers (e.g., refs. 23 and 24), it is possible to investigate the glass-forming process especially by means of EGA in combination with TGA and DTA. It was shown that the effects of different kinds of additives, fining compounds, etc., on the decomposition of carbonates in the batch are quite different. The change in CO_2 partial pressure obtained on heating a batch of glass is not always a suitable control value for the silicate-forming process. Analysis of the gaseous content of glasses assists the glass technologist in understanding

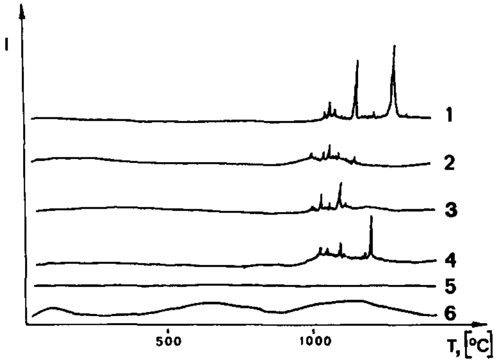

Fig. 7. Gas release profiles of container glass (heating rate, 10 K min^{-1}). 1, $m/e = 32$ (O_2^+); 2, $m/e = 28$ (CO^+,N_2^+); 3, $m/e = 64$ (SO_2^+); 4, $m/e = 44$ (CO_2^+); 5, $m/e = 14$ (N^+); 6, $m/e = 17$ (OH^+).

the melting and fining reactions and diagnosing production problems. Mass spectrometric analysis of volatiles extracted from the glass by programmed heating is a successful thermoanalytical method in the field of glass technology. Especially the gas-release temperature profile gives information on the amounts of gas that are dissolved in the silicate melt (Fig. 7).

Moreover, thermal investigations are helpful for the determination of the history of natural glasses. Variations in the gas-release temperature profile are produced by changes in the glass structure on heating. The gas-release temperature profile reflects the different glass-forming processes in nature, such as volcanic processes, lightning and meteor impact [25].

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