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INVESTIGATIONS OF THE GLASS TRANSITIONS OF ORGANIC AND INORGANIC SUBSTANCES
DSC and temperature-modulated DSC

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Abstract

The glass transitions of different materials (a silicate glass, a metallic glass, a polymer, a low molecular liquid crystal and a natural product) were investigated. By means of the temperature-modulated DSC (TM-DSC) mode, the frequency was varied. In the case of DSC, the cooling rate was changed. TM-DSC was shown to be a practicable tool for the acquisition of dynamic parameters of glass transitions for all kinds of materials.

Keywords: glass transition, metallic glass, silicate glass, temperature-modulated DSC

Introduction

In general an undercooled melt crystallizes. If the free enthalpy of nucleation is large enough, extensive undercooling results. In this case, the crystallization rate is determined by the small molecular movement. At low temperatures, the crystallization rate is practically zero. The melt is then in a metastable thermodynamic equilibrium. On further cooling, the cooperative movement of the liquid freezes. The glass transition is measured. The glass is in a thermodynamic non-equilibrium state.

If a glass is heated, a cold crystallization process may take place above the glass transition temperature.

In this paper, the glass transitions of different glasses have been investigated by means of DSC and temperature-modulated DSC (TM-DSC). The substances were a silicate glass (duran), a metallic glass ($Zr_{65}A_{17.5}Cu_{17.5}Ni_{10}$), an amorphous polymer (polystyrene), a low molecular liquid crystalline glass (3,3'-sulphonyl-bis[methyl 4-(4-n-pentyloxy-benzoyloxy)benzoate] (short name: 3,3SMB; characterized in [1]), and honey.

Glass transition – thermodynamic aspects

The enthalpy temperature curve reveals a change in slope in the glass transition region. The temperature of the point of intersection is the glass transition

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temperature, T_g. It depends on the cooling rate, β_o [2]. The glassy state is a time-dependent non-equilibrium state. The processes that occur are irreversible. In such a case, the second law of thermodynamics is

$$\mathrm{d}S > \frac{\delta Q}{T} \tag{2}$$

$$\mathrm{d}S = \mathrm{d_e}S + \mathrm{d_i}S \tag{3}$$

where $\mathrm{d_e}S$ is the change in entropy by the exchange of heat, and $\mathrm{d_i}S$ is the change in entropy due to processes which occur inside the system. To describe the entropy change, one needs an additional macroscopic variable, $\zeta(t)$ [3]. The enthalpy change reads:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_{\mathrm{T},\zeta} \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_{\mathrm{p},\zeta} \mathrm{d}T + \left(\frac{\partial H}{\partial \zeta}\right)_{\mathrm{T,p}} \mathrm{d}\zeta \tag{4}$$

The generalized isobaric heat capacity, C_p, can be defined as:

$$\begin{aligned} C_\mathrm{p} = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_\mathrm{p} = &\left(\frac{\partial H}{\partial T}\right)_{\mathrm{p},\zeta} + \left(\frac{\partial H}{\partial \zeta}\right)_{\mathrm{p,T}} \left(\frac{\mathrm{d}\zeta}{\mathrm{d}T}\right)_\mathrm{p} \\ &\quad\downarrow \qquad\qquad\quad \downarrow \\ = &\quad C_\mathrm{st} \qquad + \qquad C_\mathrm{dyn}(t) \end{aligned} \tag{5}$$

The heat capacity is a function of time because ζ and T are independent. C_{st} is the heat capacity of the system in an inhibited non-equilibrium state.

Glass transition – dynamic aspects

It is well known from relaxation spectroscopy (e.g. dielectric or mechanic) that the glass transition is time or frequency-dependent. If the frequency f is increased, then the glass transition temperature shifts to higher temperatures (temperature – time superposition). For several years, spectroscopic measurements of the specific heat capacity have been known [4]. In general, spectroscopic measurements are carried out on the melt (thermodynamic equilibrium).

In terms of thermodynamics, one distinguishes between two different types of glass transitions: thermal glass transitions (freezing of the cooperative movements on coolings, as a transition from an equilibrium to a non-equilibrium) and thermal relaxation glass transitions (frequency-dependent transition in the equilibrium).

Thermal relaxation glass transition (linear case)

Equation (5) shows that the heat capacity is a function of time. At close to equilibrium, one can describe time-dependent processes by using the superposition principle [5]:

$$\partial H(t) = H_o \int_o^t \dot{C}(t - t')\partial T(t')\mathrm{d}t' \tag{6}$$

In frequency-dependent terms, the equation reads ($\omega = 2\pi f$):

$$\partial H(\omega) = C(\omega)\partial T(\omega) \tag{7}$$

where

$$C(\omega) = C'(\omega) - iC''(\omega) = C_{st} + \int_o^\infty \dot{C}(t)e^{-i\omega t}\mathrm{d}t \tag{8}$$

In general, the complex heat capacity is described by means of the retardation function, $L(\omega)$:

$$C(\omega) = C_{st} + \Delta C_p L(\omega) \tag{9}$$

A relationship for L is given by Harvrilak and Negami [6]:

$$L(\omega) = \frac{1}{(1 + (i\omega\tau)^\alpha)^\gamma} \tag{10}$$

The real part C' (storage heat capacity) describes the degree of mobility of the molecular movements, and the imaginary part C'' (loss heat capacity) is proportional to the work of dissipation (this means Td_iS).

Thermal glass transition (non-linear case)

During the freezing of the cooperative movements, the system leaves equilibrium. The linear relationship in Eq. (6) is inadequate to describe this phenomenon. Introduction of a new time scale $u(t)$ allows a linearization:

$$\partial H(t) = \int_o^{u(t)} C(u(t) - u')\frac{\mathrm{d}T(u')}{\mathrm{d}u'}\mathrm{d}u' \tag{11}$$

u characterizes the actual state of the molecular movement. It depends on the fictive temperature and an empirical parameter to describe the non-equilibrium [7].

Donth proposes a relationship to calculate the characteristic frequency for a thermal glass transition [8]:

$$f = a\frac{\beta_o}{2\pi\Delta T} \tag{12}$$

where ΔT is the half-width of the glass transition and *a* is an experimental factor (a~1).

In the low-frequency range, the thermal relaxation glass transition is influenced by the thermal glass transition. Due to the mode coupling, the still frozen modes influence the still available ones. This effect is discussed in [9]. It causes the difference of the heating and cooling TM-DSC run (Fig. 1).

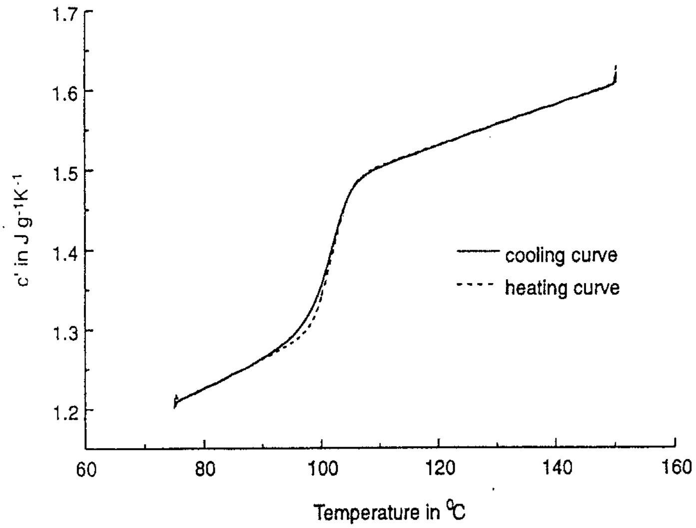

Fig. 1 Storage heat capacity of Polystyrene measured in the cooling and heating mode (T_a=1 K, f=40 mHz, β_o=0.5 K min^{-1}, m=6.818 mg)

Experimental

The measurements were carried out in standard DSC mode and in temperature-modulated DSC (TM-DSC) mode. In the case of TM-DSC, the conventional temperature program (linear heating or cooling and isothermal measurements) is superimposed by a periodic temperature change. The difference heat flow rate between sample and reference is measured. This heat flow rate has a phase shift to the temperature change. After calibration, we obtain the complex heat capacity of the sample at different frequencies. The theoretical background of the data evaluation is described in [10, 11].

The measuring device used was a modified Perkin-Elmer DSC 7 (DDSC). For all measurements, the furnace surrounding temperature was –90°C.

Depending on the sample material, the DSC measurements were carried out at different cooling and heating rates (between 80 and 0.5 K min^{-1}). The data measured with scanning rates above 5 K min^{-1} were desmeared [12]. The glass transition temperature was determined by using the fictive temperature method [2]. The characteristic frequency was calculated from the cooling curves by use of Eq. (12). The parameter a was set to 1. The procedure to evaluate ΔT is shown in [13].

The TM-DSC measurements were carried out at frequencies from 200 to 2 mHz. The temperature amplitude was varied from 0.5 to 2 K, and the underlying heating rate β_0 was lower or equal to 2 K min^{-1} (determination of the optimal measuring parameters is described in [14]). The non-crystalline substance honey, polystyrene and duran were measured in the cooling mode. The TM-DSC measurements on the others were performed by heating. The temperature range was from –60°C (honey) to 700°C (duran).

Results

Figure 2 shows the complex heat capacity and the related heat flow rate from the standard DSC curves of a metallic glass. In the glass transition region, c'

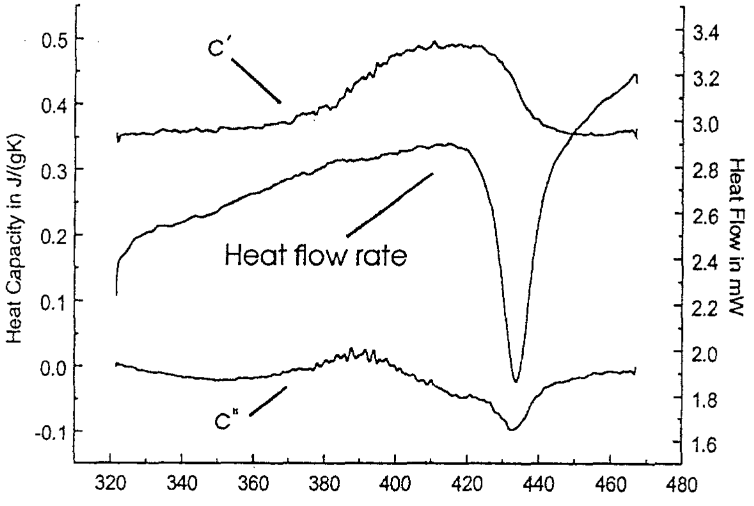

Fig. 2 Complex heat capacity and heat flow rate of the metallic glass in the region of glass transition and cold crystallization (T_a=1 K, f=18 mHz, β_0=1 K min^{-1}, m=11.156 mg)

depicts a step and *c*″ a characteristic peak. The peak maximum temperature is correlated to the flexing point temperature of the *c*′ step and is defined as a dynamic glass transition temperature. In the cold crystallization region, *c*′ decreases and *c*″ shows a negative peak. This behaviour is discussed in [15] on

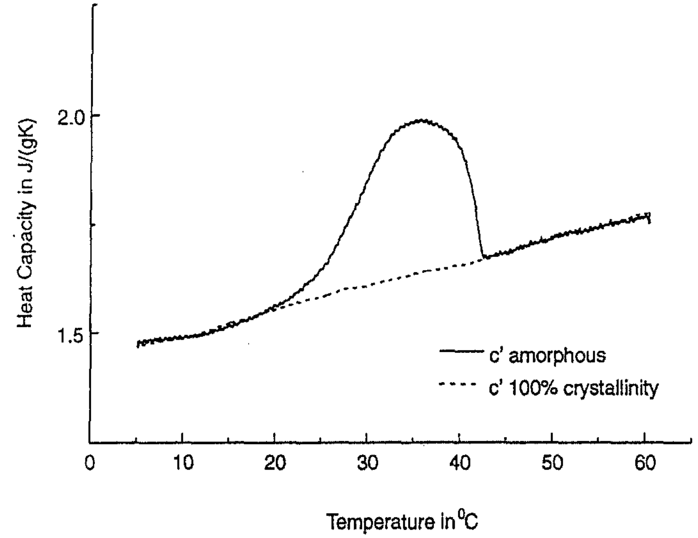

Fig. 3 Storage heat capacity of 3,3SMB in the region of glass transition and cold crystallization (T_a=0.5 K, f=36 mHz, β_o=0.4 K min^{-1}, m=2.870 mg)

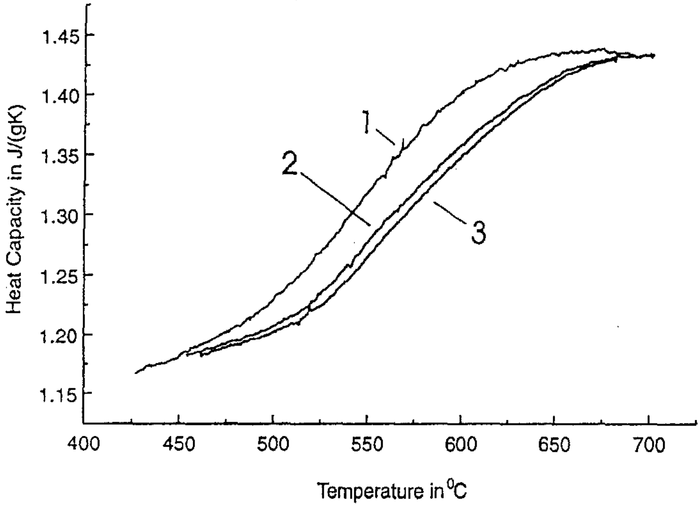

Fig. 4 Storage heat capacity of duran (m=59.72 mg) at different measuring conditions (1:DSC cooling curve, β_o=40 K min^{-1}, 2: TM-DSC curve, f=42 mHz, T_a=2 K, β_o=2 K min^{-1}; 3: TM-DSC curve, f=21 mHz, T_a=2 K, β_o=2 K min^{-1})

the example of poly(ethylene terephthalate). For amorphous and crystalline 3,3SMA, in the region of cold crystallization the storage heat capacity shifts from the liquid to the solid-state value (Fig. 3).

On the example of duran, the frequency dependence of the dynamic glass transition is shown in Fig. 4. Despite the temperature difference between the

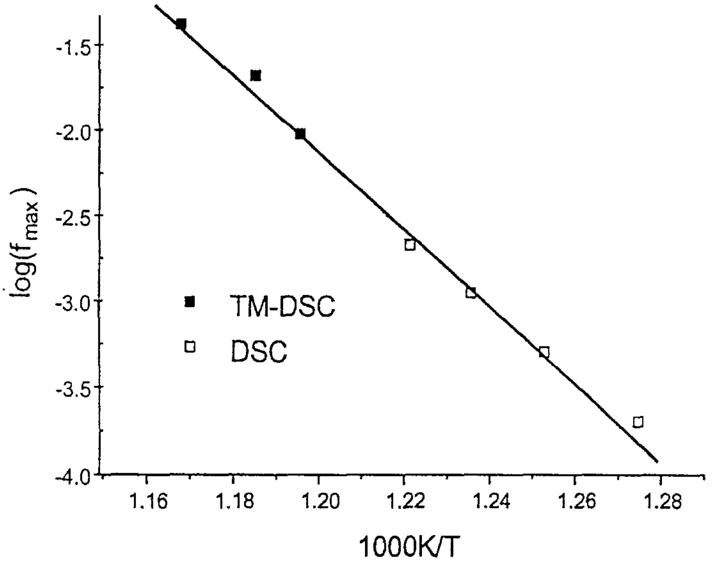

Fig. 5 Activation plot of duran

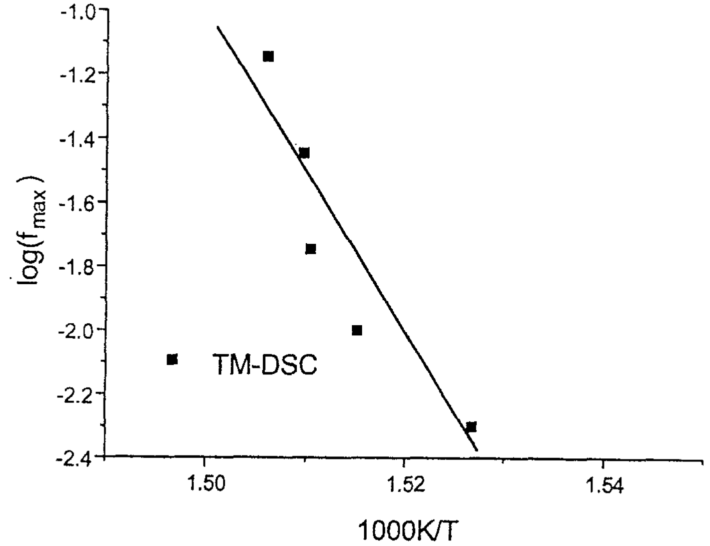

Fig. 6 Activation plot of the metallic glass

surroundings and the furnaces of approximately 800 K, the signal to noise ratio for the TM-DSC measurements is good. The activation plots of all substances are shown in Figs 5 to 9. Characteristic glass transition parameters are listed in Table 1. Although the parameters are different, the phenomenological behaviour is the same for all substances.

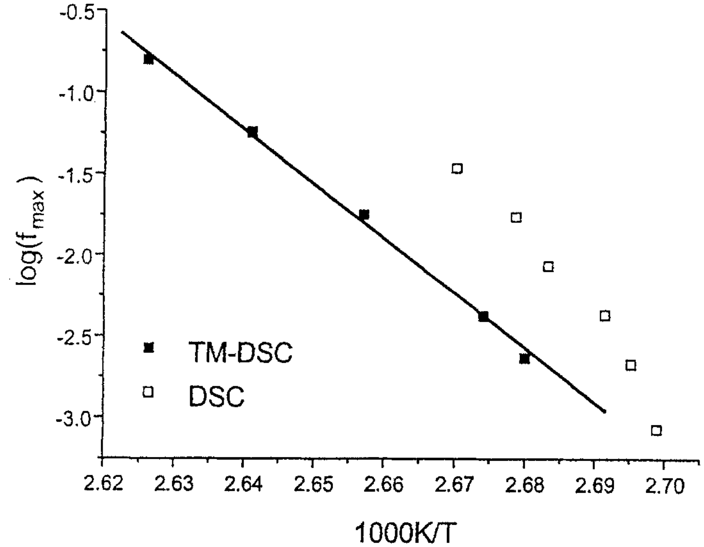

Fig. 7 Activation plot of polystyrene

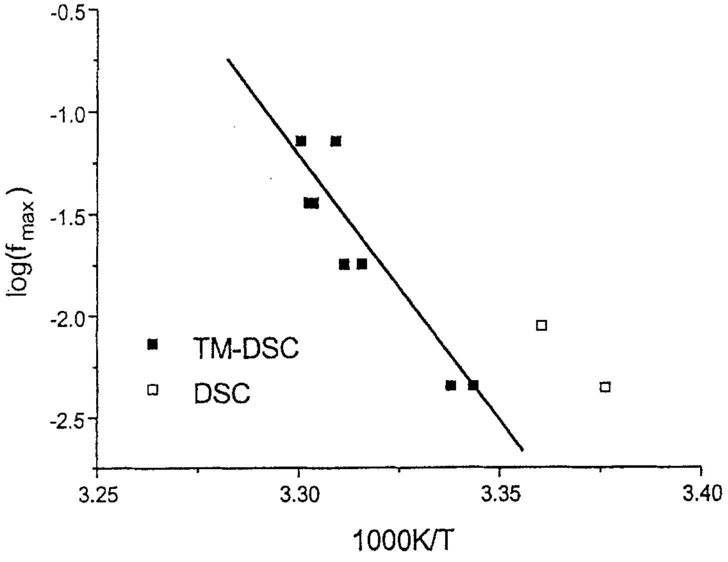

Fig. 8 Activation plot of 3,3SMB

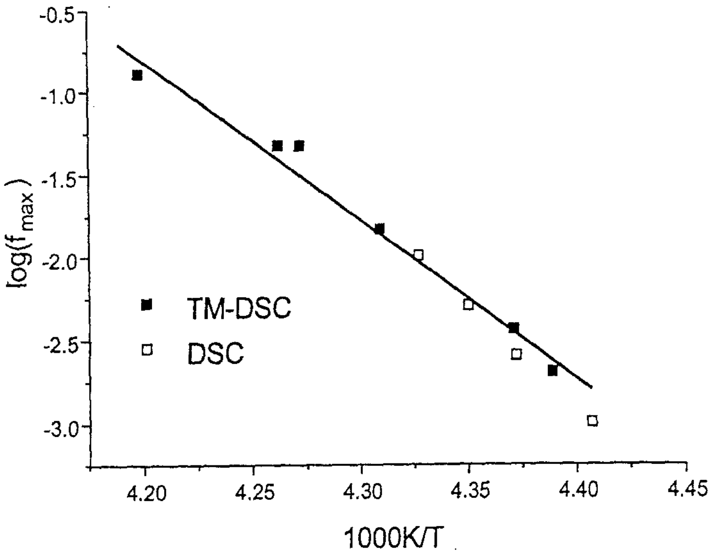

Fig. 9 Activation plot of honey

Table 1 Some characteristic properties of glass transition: T_g is the glass transition temperature at 0.01 Hz, ΔT is the half-width of the glass transition, a_f is the slope in the activation plot, and Δc the step height of the specific heat capacity

Substance	T_g /°C	ΔT/K	a_f/1000 K^{-1}	Δc/J(g K)$^{-1}$	cold crystallization
duran	562.7	52	–23	0.23	no
met. glass	385.3	15.2	–52	0.32	yes
PS	102.4	6.1	–34	0.30	no
3,3SMB	27.4	5.4	–27	0.31	yes
honey	–41.9	8.9	–10	0.80	no

The results reveal that TM-DSC is a good method to acquire dynamic information on glass transitions, independently of the nature of the sample material.

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