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SUB T_g ENTHALPY RELAXATION IN GLASSES

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ABSTRACT

A simple model based on the free volume theories as well as on relaxation approximation, has been used to explain the mean features of the sub-Tg enthalpy relaxation in glasses as can be monitored by DSC techniques. The results obtained by means of computer simulation of this model are compared with DSC measurements in metallic, covalent and polymeric glasses.

INTRODUCTION

Sub-Tg structural relaxation towards more stable amorphous structures is a commonly observed phenomenon in all kinds of glasses and is responsible for ageing and changes in many physical properties. The process can be detected by DSC techniques as an apparent specific heat difference, ΔCp, between as-prepared and relaxed samples. Two kinds of microscopical mechanism are currently believed to be involved: topological short range ordering (TSRO), directly related with annihilation of free volume like defects, and chemical short range ordering (CSRO) which implies local redistribution of the atomic species and is more pronounced in multicomponent systems. Although both mechanisms are probably related and free volume controled (ref. 1), TSRO can be considered to be principally responsible for the ΔCp above mentioned (ref. 1).

On the other hand, a broad distribution on the relaxation time is generally needed to take into account all the experimental observations of the relaxation processes in glasses. However, in many practical cases, only a mean relaxation time is necessary for describing the overall kinetic features of the relaxation.

The aim of this paper is to show that a simple model with a single relaxation time related to free volume theories can explain the mean behaviour of sub-Tg relaxation in glasses. Recently this model has been successfully used for interpreting the dielectric relaxation in polar polymer glasses (ref. 2). The procedure which allows to obtain the mean kinetic parameters from experimental DSC data is also outlined.

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THEORY

Glass transition and recovery of glasses are described as a return to the equilibrium state, by means of a structural relaxation time depending of the relative free volume in the sample given by (ref. 2)

$$\tau = \tau_0 \exp\left(\frac{1}{f+\delta}\right) \tag{1}$$

Here f is the relative free volume or configurational enthalpy at equilibrium which is assumed to behave as $f=\alpha_f(T - T_0)$ where α_f is the expansion coefficient of the free volume and T_0 the temperature at which free volume vanishes, δ is the relative excess free volume and τ_0 a preexponential factor. In this model δ is assumed to behave according to (ref. 3)

$$\frac{d\delta}{dt} = -\Delta\alpha\ q - \frac{\delta}{\tau} \tag{2}$$

where $\Delta\alpha$ is the difference between the expansion coefficient or specific heat of the glass and the liquid and q the heating or cooling rate.

Equations (1) and (2) have been solved by numerical integration with adequate parameters (α_f=2.8 $10^{-4}K^{-1}$; $\Delta\alpha$ =8 $10^{-5}K^{-1}$; T_0=500 K and τ_0=10^{-7}s.) in order to simulate standard DSC observations of sub-Tg structural relaxation in glasses. The simulation was carried out in the following steps: 0) formation of glass by cooling from the melt at a formation rate q_f; 1) heating to T>Tg at a rate q_h; 2) cooling at a rate q_c; 3) a second heating at the same heating rate q_h. By this procedure, it is possible to obtain $\Delta Cp=Cp_1-Cp_3$, where Cp_1 and Cp_3 are the apparent specific heats corresponding to steps 1 and 3 respectively. ΔCp shows an exothermal sub-Tg peak in all the cases (see fig. 1). The results obtained by varying the different rates involved (q_f,q_c,q_h) can be sumarized in the following points:

-Fig. 1a shows the influence of formation rate, q_f, on the behaviour of ΔCp peak. As can be seen, a shift of the onset of the peak towards lower temperatures, as well as an enhancement of the ΔCp peak area, occurs when increasing the formation rate. Similar behaviour has been recently reported in the experimental DSC and resistivity measurements for some metallic glasses (ref. 1).

-The cooling rate q_c defines the configurational state of the sample previous to scan 3 which is used as a baseline for drawing ΔCp. When $q_c<q_h$ a second and sharp high temperature peak appears in the ΔCp curve. This new peak is straightforwardly related with the undershoot of the enthalpy with respect to the supercooled liquid, in the reference scan. These trends are illustrated in fig. 1b.

-The whole ΔCp curve shifts towards higher temperatures when increasing the heating rate q_h (fig. 1c). The temperature Tm where ΔCp is maximum, varies with the heating rate following an Ozawa expression ($\ln q_h=A-E/K_BTm$) from which a mean

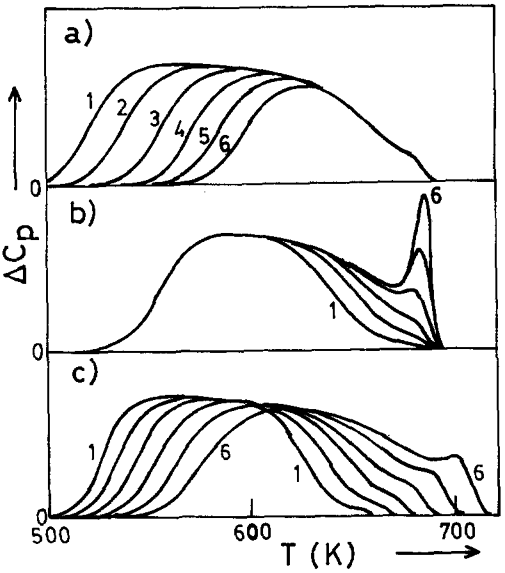

Fig. 1. ΔC_p simulated by means of equations (1) and (2). a) $q_c=q_h=0.1$ K/s and $q_f=10^6$(1), 3 10^5, 10^5, 3 10^4, 10^4 and 3 10^3 K/s (6). b) $q_f=10^5$ K/s, $q_h=0.1$ K/s and $q_c=10^1$(1), 10^0, 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} K/s (6). c) $q_f=10^5$ K/s, $q_c=0.1$ K/s and $q_h=10^0$(1), 3 10^{-1}, 10^{-1}, 3 10^{-2}, 10^{-2} and 3 10^{-3} K/s (6).

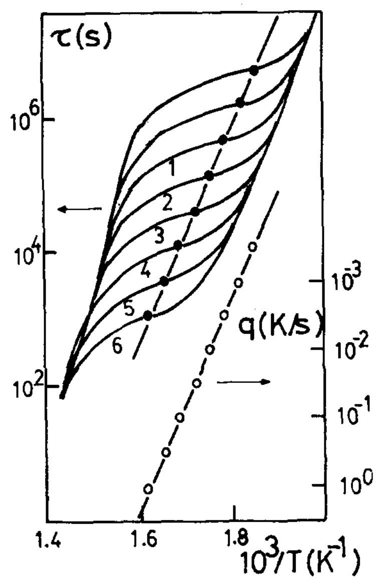

Fig. 2. Evolution of $\ln\tau$ during the first scan (see the text). Figure also include Ozawa plot for the ΔC_p maxima.

apparent activation energy, E, for the relaxation process can be evaluated. The value of E obtained by this procedure is close to the corresponding one for the structural motions in the isoconfigurational as-recived state of the glass (see fig. 2). This figure shows the behaviour during the first scan of the relaxation time given by (1) at different heating rates. The full circles correspond to the Tm values in fig. 1c and the empty ones to the Ozawa plot.

EXPERIMENTAL

DSC measurements have been performed on different kinds of glasses: covalent semiconductor ($Al_{20}As_{40}Te_{40}$), polymeric (Poly-Arylate (PAr)) and metallic ($Fe_{40}Ni_{40}P_{14}B_6$). Comparison between experimental results and theoretical simulations are shown in fig. 3.

The parameters used in the simulation are:

-Covalent:$\alpha_f=1.1\ 10^{-4}K^{-1}$, $\Delta\alpha=3\ 10^{-5}K^{-1}$, $T_0=200$ K, $\tau_0=2\ 10^{-13}$s. (deduced from kinetic behaviour of Tg (ref. 4)), $q_f=10^2$K/s,$q_c=q_h=20$K/min. The activation energy E obtained from both experimental and simulated ΔCp shift was 1.2 eV.

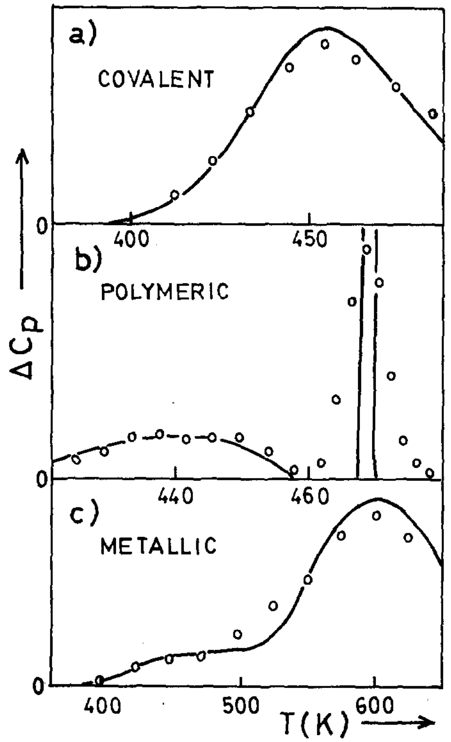

Fig. 3. Comparison between experimental (o) and simulated (——) ΔC_p behaviour.

-Polymeric: α_f=5.3 10^{-4}k^{-1}, $\Delta\alpha$=4.
T_o=399K, τ_o=6 10^{-13}s. (close to tl
tained parameters from dielectric
rements of ref. 2), q_f=40K/min.,
K/min. and q_h=20K/min.

-Metallic: In this case the simul
has been carried out by superposi
of two processes which can be ass
ted to the metal and metalloid at
the sample. The ratio of both pro
was estimated from chemical compo
and metal-metalloid volume ratio
as 85:15. Common parameters are:
T_o=500K, τ_o=10^{-6}s., q_f=3 10^4 K/
q_c=q_h=20 K/min. Metal parameters
α_f=2.55 10^{-4} K^{-1} and $\Delta\alpha$=8.5 10
Metalloid parameters are: α_f=3.5
and $\Delta\alpha$=1.8 10^{-4} K^{-1}. The average
of α_f as well as T_o and τ_o values
in good agreement with the report
ones in ref. 5. On the other har
energy values for the two simulat
cesses (1 and 2 eV) are close to
experimental ones reported in ref

As a conclusion, the model reported accounts for the overall features of sub-Tg enthalpy relaxation in glasses by using a single relaxation time. Di tion between TSRO and CSRO is needed in metal-metalloid glasses by allowing two different relaxation times. A wide distribution in relaxation times is ver necessary for the description of the glass transition in most glasses.

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