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Glass transition in polymers: (In)correct determination of activation energy

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ABSTRACT

The possibility of applying Kissinger-type equations for the evaluation of apparent activation energy in the case of the glass transition phenomenon was investigated. Theoretically simulated data based on the generally accepted Tool–Narayanaswamy–Moynihan model were used to represent all possible cases of structural relaxation behavior. The values of apparent activation energy determined by Kissinger-type equations were in major disagreement with the original values of Δh^* used as the input data for the simulations. In addition, a large dependence of the Δh^* evaluations on the thermal history of the glass was found in the case of all tested equations. The latter points to a significant systematic error in the currently commonly accepted methodology, resulting in a fundamental contradiction with the principle/concept of activation energy as a physico-chemical quantity. In light of these facts, usage of Kissinger-type equations for the evaluation of the "glass transition activation energy" was shown to be incorrect.

1. Introduction

Polymer science dates back to late 1800s and early 1900s, when the first polymeric materials were created. The success of these novel materials led to more intensive research in order to understand the structure of polymers and to synthesize new ones. Since that time, great advances in polymer technology have been made. Polymeric materials are currently an integral part of our lives as well as the subject of intensive continuing research and the source of numerous high-tech technologies [1].

One of the main characteristics of polymeric materials is their glassy or semi-crystalline nature. However, despite the great importance of these materials and the long history of their examination, the actual process of glass-forming is still not fully understood and the true nature of the glass transition phenomenon remains unrecognized. It is well-known that each as-prepared glassy material is in an unstable state and spontaneously changes its structure towards the equilibrium "ideal glass state" represented by the extrapolated undercooled liquid curve. This process of slow reorganization of the atomic structure is called structural relaxation and is often classified according to the property that is being observed (i.e. volume or enthalpy relaxation). Structural relaxation is a very complex process that shows various memory effects, hysteresis and non-linear and non-exponential features. It can take the material from seconds to years to achieve the equilibrium state, depending on the initial state of the structure of the glass at the beginning of the relaxation, as well as on the temperature the glassy material is relaxing at (i.e. how far from the glass transition temperature T_g the system was annealed).

In recent decades, significant effort has been put into the development of various theoretical models and sophisticated concepts describing relaxation behavior [2–7]. Currently, it is the phenomenological four-parameter Tool–Narayanaswamy–Moynihan (TNM) model [8,9] based on Tool's concept of "fictive temperature" [10] that is used most frequently. This model is defined by the following equations:

$$\Phi(t) = \exp\left[-\left(\int_0^t \frac{\mathrm{d}t}{\tau\left(T, T_f\right)}\right)^{\beta}\right] \tag{1}$$

$$\tau\left(T, T_f\right) = A \cdot \exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{2}$$

where $\Phi(t)$ is the relaxation function of the given property, t is time, τ is the relaxation time, β is the non-exponentiality parameter, A is the pre-exponential factor, x is the non-linearity parameter, Δh^* is the apparent activation energy of the structural relaxation, R is the universal gas constant, T is temperature and T_f is the fictive temperature, which is defined as the temperature of the undercooled

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liquid with the same structure as that of the relaxing glass. It can be seen that the TNM model is relatively complex as it accounts for all the main features of structural relaxation behavior. The reward for its complexity and phenomenological character is its very high flexibility, accuracy and prediction ability in the description of experimental data.

However, during the last few years, a new phenomenon occurred in the field of relaxation science, namely that associated with application of simple kinetic equations for the evaluation of (apparent) activation energy for structural relaxation. In this regard, mainly the Kissinger-type equations have been applied:

$$\ln\left(\frac{q^+}{T_p^2}\right) = -\frac{E}{RT_p} + \text{const.} \tag{3}$$

$$\ln\left(\frac{q^+}{T_p}\right) = -\frac{E}{RT_p} + \text{const.} \tag{4}$$

$$\ln\left(q^+\right) = -\frac{E}{RT_p} + \text{const.} \tag{5}$$

$$\ln\left(\frac{q^+}{T_g^2}\right) = -\frac{E}{RT_g} + \text{const.} \tag{6}$$

$$\ln\left(\frac{q^+}{T_g}\right) = -\frac{E}{RT_g} + \text{const.} \tag{7}$$

$$\ln\left(q^+\right) = -\frac{E}{RT_g} + \text{const.} \tag{8}$$

where q^+ is the applied heating rate, T_p is the temperature corresponding to the maximum of the relaxation peak, T_g is the temperature of glass transition and E is the activation energy (which effectively matches Δh^* of the TNM model); the latter quantity is often introduced in the form of the reduced activation energy E/R or $\Delta h^*/R$ in kK. The first three and last three equations are similar, except for the fact that T_g is used instead of T_p. Variation within each set of equations then lies in the different exponent values (equal to 2, 1 and 0, respectively) of the denominator on the left side of the equation. The first three expressions, Eqs. (3)–(5), were in fact originally derived for the description of crystallization behavior (hence the implementation of the maximum of the peak T_p) under the designations of the Kissinger [11], Augis–Bennett [12] and Ozawa [13] equations, respectively. Variations of these equations with respect to the used characteristic temperature are then represented by the second set of the equations (Eqs. (6)–(8)), where the temperature corresponding to the maximum of the relaxation peak was replaced by the symbol T_g that in this case has a rather general meaning (considering various methods of T_g evaluation). Eq. (8) is usually denoted as the Moynihan expression, as it is commonly related to the original work [14] of Moynihan (one of the TNM model authors). Special interest will be paid to this particular equation in the Discussion section.

Argumentation in the sense that the linearity of these equations automatically ensures their applicability or that their usage is already widely accepted in the scientific community often occurs in the literature. The Kissinger-type equations can be, indeed, applied to a variety of kinetic processes, i.e. diffusion as well as boundary reaction-controlled, surface as well as volume-located, processes with any possible dimensionality, single as well as complex overlapping processes, as well as processes such as decomposition, crystallization, degradation, etc. [11,15]. Nevertheless, in all these cases, purely thermally activated processes are in fact being considered. In the case of glass transition kinetics, the physico-chemical background is much more complicated. As was mentioned above, structural relaxation shows very complex behavior, including various memory effects, which the Kissinger-type equations do not take into account. It is the goal of this work was to test the actual applicability of the currently commonly used Kissinger-type equations to the glass transition process. In the first part of the work, the case of glassy polyvinyl acetate (PVAc) will be considered; in the second part of the work, the conclusions will be generalized towards a universal polymeric material.

2. Experimental

In the first part of the work, the data for amorphous polyvinyl acetate [16] will be discussed. The polyvinyl acetate that was used in this study was the granular form of Mowilith 50 (molecular weight $M_w = 260{,}000$). Enthalpy relaxation of the sample was studied using a conventional DSC 822^e differential scanning calorimeter (Mettler, Toledo) equipped with a cooling accessory. Dry nitrogen was used as the purge gas at a rate of 20 cm^3/min. The calorimeter (temperature, heat flow and τ-lag constant) was calibrated through the measurements of melting processes of In, Zn and Ga. The baseline was checked daily. During sample preparation, a thin layer of molten PVAc was spread on the bottom of the standard aluminum pan to improve the thermal conduction and the pan was sealed afterwards. The mass of each batch was approximately 6 mg.

The current work is based on the results of theoretical simulations of relaxation curves. The theoretical background for the simulations was provided by the TNM model, which was incorporated into a computer program as follows [17]:

$$T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{ 1 - \exp\left[-\left(\sum_{k=j}^{n} \Delta T_k / q_k \tau_k \right)^{\beta} \right] \right\} \tag{9}$$

$$T_{f,n} = T_0 + \sum_{j=1}^{n_A} \Delta T_j \left\{ 1 - \exp\left[-\left(\sum_{k=n_A}^{n} \Delta t_{e,k} / \tau_k \right)^{\beta} \right] \right\} \tag{10}$$

where T_0 is the initial equilibrium temperature and t_e is the annealing time. This means that continuous cooling or heating is replaced by a sequence of n temperature jumps ΔT followed by isothermal holds with the duration determined by the cooling and heating rate $\Delta t = \Delta T/q$ as suggested in Ref. [17]. The magnitude of ΔT must be sufficiently small to ensure linearity; $\Delta T = 1$ K was found to be satisfactory. The self-retarding kinetics can be introduced by dividing the aging time into k subintervals and calculating T_f and τ at the end of each. The subintervals are usually determined by dividing the aging time into even logarithmically spaced intervals. The input data are then in the form of normalized heat capacity C_p^N (non-isothermal measurements):

$$C_p^N = \frac{\mathrm{d}T_f}{\mathrm{d}T} = \frac{C_p - C_{pg}}{C_{pl} - C_{pg}} \tag{11}$$

The fictive temperature in this equation is determined on the basis of the Boltzmann superposition integral over time that can also be also replaced by a corresponding integral over temperature.

In the case of all simulations performed within the framework of this study, all isothermal steps were divided into 500 intervals; in the case of non-isothermal steps, the magnitude of the elementary intervals over which the relaxation time and fictive temperature