Activation energies derived from the pre-glass transition annealing peaks

Sergey Vyazovkin *, Ion Dranca

Department of Chemistry, University of Alabama at Birmingham, 901 S. 14th Street, Birmingham, AL 35294, USA

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Dedicated to Professor Wolfgang Hemminger on the occasion of his 65th anniversary.

Abstract

The paper explores the use of the DSC annealing peaks for estimating the activation energies of the β-relaxation in low and high molecular glassy systems. For the four studied systems that include D-glucose (dextrose), maltitol, poly(methyl methacrylate) and poly(ethylene terephthalate) the estimated values of the activation energy are 59 ± 10, 71 ± 6, 73 ± 12 and $75 \pm 7 \, kJ \, mol^{-1}$. These values together with the activation energies determined earlier from the annealing peaks of polystyrene (PS), PS–clay nanocomposite, indomethacin, ursodeoxycholic acid and poly(vinylpyrrolidone) have been compared against the literature values of the activation energies of the β-relaxation. It is concluded that the DSC estimates typically do not deviate for more than 20% from the reference values obtained by the standard dielectric and mechanical methods.

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1. Introduction

It was originally reported by Illers [1] that reheating of polyvinyl chloride annealed significantly below the glass transition temperature, T_g, results in detecting a small endothermic DSC peak that may occur before the glass transition step. A similar effect was later reported for several metallic glasses by Chen [2,3] and for several polymers by Bershtein et al. [4,5]. Chen explained this effect as the partial enthalpy relaxation (during annealing) and recovery (during reheating) that occur at the expense of the faster part of a broad relaxation spectrum of the glassy state. On the other hand, Bershtein et al. [4,5] linked this effect specifically to the β-relaxation process that is normally detected by dynamic mechanical [6] and dielectric techniques [7]. Chen as well as Bershtein et al. suggested using the shift in the annealing peak temperature, T_p, with the heating rate, q, to determine the effective activation energy, E, of the underlying process as follows:

$$E = -R \frac{d \ln q}{d T_p^{-1}} \tag{1}$$

where R is the gas constant. The resulting E values were consistently found [2–5] being several times smaller than the respective activation energies of the main glass transition (i.e., α-relaxation) event, i.e., as it is typically reported [6,7] for the respective β- and α-relaxations in polymers. Conversely, Hodge and Berens [8] showed that one can simulate the annealing peaks by substituting the activation energy of the α-relaxation in the Tool–Narayanaswamy–Moynihan (TNM) model and then varying other parameters of the model. Note that this result does not actually prove that the activation energy of the process that causes the annealing peak is similar to that of the α-relaxation for several reasons. Firstly, accurate applications of the TNM model are limited "to systems in which viscosity obeys an Arrhenius dependence within and above the glass transition range" [9] or, in other words, to so-called "strong" [10] glass forming systems. However, most liquids show a "fragile" behavior, which is characterized by the VTF/WLF temperature dependence [9,11] and, therefore, by a temperature dependence of the activation energy that is especially profound in the most fragile liquids such as polymers [12]. Secondly, the TNM model is known [13,14] being incapable of predicting annealing in the temperature region significantly below T_g. However, regardless of the limitations and a physical meaning, the four parameter TNM model has enough computational flexibility to fit simultaneously the glass transition event and an annealing peak. Thirdly,

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* Corresponding author. Tel.: +1 205 975 9410; fax: +1 205 975 0070.
  E-mail address: vyazovkin@uab.edu (S. Vyazovkin).

according to the substantial array of experimental data [15], the process of annealing at temperatures far below T_g has an activation energy that is several times smaller than that of the α-relaxation. In addition, as the temperature falls below T_g, the cooperative α-process fades away very quickly giving way to the local β-process that becomes the major contributor to the relaxation that occurs on annealing glasses well below T_g, i.e., during the so-called physical aging [15–17]. In this circumstance, it does not seem unreasonable that a fair approximation to the activation energy of the β-relaxation, E_β, can be obtained as an activation energy estimated from the annealing peaks produced well below T_g, as was originally found by Bershtein et al. [4,5] for several polymers. This has also been the case of our previous work on polystyrene (PS) and PS–clay nanocomposite [18], indomethacin (IM) [19], ursodeoxycholic acid (UDA) and poly(vinylpyrrolidone) (PVP) [20]. In the present paper we explore this issue further by combining our previous results with a study of the four new systems that include two polymers (poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET)) and two low molecular compounds (glucose (Gl) and maltitol (Mt)). For all four systems, the activation energies of the β-relaxation have been determined by using either dielectric or mechanical spectroscopy and reported in the literature that affords a straightforward comparison with values derived from the annealing peaks. In addition to testing the obtained values against the literature data, we also test them against the empirical correlation, $E_\beta = (24 \pm 3)RT_g$ reported by Kudlik et al. [21].

2. Experimental

Gl (dextrose), Mt, PMMA (Mw $\sim$ 75,000) and PET (Mw $\sim$ 18,000) were, respectively, purchased from Fisher, MP Biomedicals, Polymer Scientific Products and Aldrich and used without further purification. In order to produce amorphous (glassy) samples, 10–20 mg of a sample was placed in 40 μL closed Al pans and heated to ~10 °C above their respective melting points, 161 °C (Gl), 149 °C (Mt), 280 °C (PET) or ~70 °C above its T_g (PMMA). Shortly after heating the samples were quenched into liquid nitrogen. The glass transition temperatures of the amorphous samples were estimated as midpoint temperatures of the DSC glass transition steps measured at 10 °C min⁻¹. The resulting values were 36 °C (Gl), 48 °C (Mt), 75 °C (PET) and 105 °C (PMMA). For annealing measurements, freshly quenched samples were quickly placed into the DSC cell (Mettler-Toledo DSC 822^e) that was maintained at −40 °C. The temperature and heat flow calibration of DSC were performed by using an Indium standard. From −40 °C the samples were heated to an annealing temperature, T_a, and held at it for 30 min. The annealing temperatures were −30, −25, −20 and −10 °C for Gl, −20, −10 and 0 °C for Mt, 20, 30 and 40 °C for PET, and 10, 15, 20, 30 and 40 °C for PMMA. After completion of the annealing segment, the samples were cooled down to −40 °C and immediately heated above T_g. The heating rates were 15, 20, 25 and 30 °C min⁻¹. The resulting endothermic peaks observed on heating were used to determine the peak temperature, T_p, by using the standard DSC soft-

ware that subtracts an extrapolated baseline and finds the peak position.

3. Results and discussion

The annealing peaks are easily produced by annealing a glassy material at $T_a \sim 0.8T_g$. Recall that the dielectric and mechanical loss peaks for β-relaxation in polymers are commonly found at temperatures around $0.75T_g$ [22]. The glass annealed in this region relaxes lowering its enthalpy. The lost enthalpy is recovered on reheating producing a small endothermic effect that is observed in DSC as a very broad and shallow "annealing peak", which starts to evolve above the annealing temperature. While broad and shallow, the peaks are readily noticeable when comparing DSC traces for annealed samples with those for not annealed samples which demonstrate a monotonic behavior before the glass transition step (cf. Figs. 1–4). Increasing annealing temperature increases the size of the peak and shifts it to higher temperatures (Fig. 1). As a result, the peak may appear not only before the glass transition step, but also during and after the step, ultimately emerging as the large enthalpy overshoot that is typically observed in the glasses aged not far below T_g [18,19]. At any given annealing temperature the peak increases in size and shifts to higher temperatures with increasing the heating rate (Figs. 2–4) that is used for estimating the effective activation energy by Eq. (1). As discussed earlier [19], the use of the lowest feasible T_a gives rise to better estimates for the activation energy of the β-relaxation.

3.1. Gl sample

Fig. 1 shows the effect of the annealing temperature on the annealing peak. For Gl, T_g is 36 °C so that $0.8T_g$ is around −25 °C. It is seen that annealing at −30 °C barely produces any
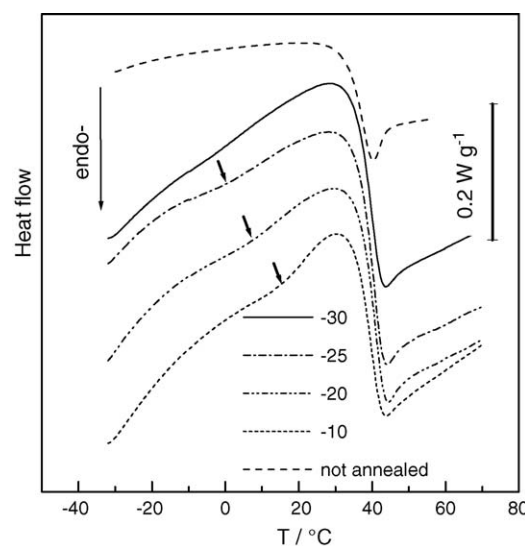

Fig. 1. DSC curves obtained on heating of Gl at 20 °C min⁻¹ after annealing for 30 min at different T_a. The values of T_a (°C) are shown by respective line types. "Not annealed" denotes a curve produced without annealing at 10 °C min⁻¹. Arrows show the location of the annealing effect.