Isoconversional Kinetics of Glass Aging

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Differential scanning calorimetry (DSC) has been applied to study the enthalpy relaxation in maltitol glass at 39−42 °C. Isoconversional kinetic analysis of the data has revealed that the effective activation energy of the process increases significantly upon the conversion from the glassy to supercooled liquid state. For the early stages of aging, the activation energy is found to be ∼117 kJ mol^{-1}, which is considerably smaller than the activation energy of the α-relaxation (413 kJ mol^{-1}). The latter value is reached at the later stages of aging. The temperature dependence of the initial aging rates estimated at 10−30 °C yields activation energies in the range 60−80 kJ mol^{-1}. The obtained results suggest that the effective activation energy for the early stages of aging tends to approach the value characteristic of the β-relaxation.

1. Introduction

Glass is a nonequilibrium state that is driven thermodynamically to relax toward the equilibrium liquid state. The relaxation can occur on heating of a glass through the glass transition temperature as well as on its annealing below the glass transition temperature. In the former case, the process is referred to as the glass transition, whereas in the latter as physical aging. The two phenomena appear to be closely related. Physical aging causes significant changes in a large variety of physical properties of glasses. For this reason, understanding the kinetics of aging and its temperature dependence is important for evaluating the physical stability of amorphous materials. The literature offers different views on the temperature dependence of the physical aging kinetics. For example, the aging kinetics can be treated by using the popular glass transition model of Tool,[1] Narayanaswamy,[2] and Moynihan.[3] According to this model, the temperature dependence of the relaxation time obeys the Arrhenius equation, which includes the temperature independent activation energy of the glass transition. On the other hand, in his classical text, Struik[4] evaluates the aging kinetics by assuming that the temperature dependence of the relaxation time obeys the Williams−Landel−Ferry equation.[5] This equation gives rise to an effective activation energy that is temperature dependent. In addition to the existence of differing models, the situation is complicated by the fact that the theory[6] and related experiment[7] suggest that in the glass transition region the relaxation dynamics changes from Williams−Landel−Ferry to Arrhenius type of behavior so that the latter appears to dominate the kinetics of aging. In this circumstance, it would be of interest and value to have kinetic tools capable of revealing the temperature dependence of the aging kinetics without force-fitting it to a certain type of equation. We suggest that isoconversional kinetic analysis[8] can be such a tool. In this type of analysis, individual Arrhenius equations are applied to evaluate the effective activation energies at different extents of conversion. This allows complex temperature dependencies to be revealed via a variation of the effective activation energies with conversion. As demonstrated in a recent review paper,[9] this type of analysis provides a fortunate compromise in dealing with processes whose kinetics is non-Arrhenius. A relevant example is isoconversional analysis of calorimetric data on heating of various polymeric[10,11] and nonpolymeric[12,13] glasses that has revealed that the effective activation energy of the glass transition varies significantly throughout the process. A smaller but statistically significant variation has also been revealed by Badrinarayanan et al.[14] who applied isoconversional analysis to the glass transition data obtained on cooling of polystyrene. In our recent communication,[15] we have applied isoconversional analysis to probe the kinetics of the rarely explored phenomenon of the heat capacity relaxation that occurs on aging of glass. For aging of maltitol glass, the effective activation energy has been found[15] to increase with conversion so that the final stages of aging demonstrate activation energies similar to those of α-relaxation, whereas the early stages show values about 3 times smaller. The present study is aimed at verifying the intriguing effect by applying for the first time isoconversional analysis to the commonly studied enthalpy relaxation processes as well as at testing the hypothesis that at lower aging temperatures the effective activation energy for the early stages of aging should asymptotically approach the activation energy of the β-relaxation or Johari−Goldstein process.

2. Experimental Section

Maltitol was purchased from MP Biomedicals, Inc., and used without further purification. About 15−20 mg of the substance was placed in 40 μL Al pan, melted in an oven, and hermetically sealed. The oven temperature was set at 160 °C, i.e., ∼10 °C above the melting of maltitol (mp = 149 °C) to ensure quick and complete melting. The nominal glass transition temperature, T_g, was ∼47 °C, which was determined as the midpoint of the heat flow step in a differential scanning calorimetry (DSC) run at 10 °C min^{-1}. The resulting samples were annealed at the aging temperatures: 39, 40, 41, and 42 °C. The temperatures were taken to be identical to those used in our previous work[15] on the heat capacity relaxation. Each aging run followed the following protocol. A sample was first heated in DSC to 160 °C and held for 2 min. Without removing it from the DSC cell, the liquid sample was cooled at 30 °C min^{-1} to a given aging temperature and held at this temperature for different aging times that varied from 2 to 1410 min. Once a selected aging time

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passed, the sample was cooled to −5 at 30 °C min⁻¹ to stop the aging process and reheated to 90 at 10 °C min⁻¹ to measure a DSC curve for the aged sample. Immediately after that, the same cooling−heating program was repeated to obtain a DSC curve for an unaged sample. The aging or relaxation enthalpy, $\Delta H(t)$, was determined according to Petrie,[16] i.e., as the difference in the integrals of the DSC curves for aged and unaged samples. It was made sure that the resulting DSC curves of unaged samples can be superimposed regardless of the aging time, indicating that the aged sample always restored its original structure after heating to equilibrium. A single sample was used throughout all aging runs at each aging temperature. In addition, two series of aging experiments were performed at lower temperatures. The first series of low temperature runs was conducted in the range 10−30 °C. At each chosen aging temperature, the runs were performed for four short periods: 5, 10, 15, and 20 min. The respective values of the aging enthalpy were determined following the aforementioned protocol. The second series of lower temperature runs was carried out at 30, 32, 34, and 36 °C for periods of time ranging from 1 h to 26 days. The experiments followed the same protocol, except that all of the isothermal aging segments were carried out on different samples placed in an oven. To shorten the total experimental time, four ovens were used. The ovens maintained the respective aging temperatures within a ±0.5 °C range. All calorimetric measurements were performed by using a heat flux DSC (Mettler-Toledo, 822e). Indium and zinc standards were used to perform temperature, heat flow, and tau-lag calibrations. The experiments were performed in the atmosphere of nitrogen flow (80 mL min⁻¹).

3. Results and Discussion

A dependence of the effective activation energy, E_α, on conversion, α, can be revealed by using various isoconversional methods.[8,9] For runs conducted under isothermal conditions, E_α can be evaluated straightforwardly by eq 1

$$E_\alpha = R \frac{d \ln t_\alpha}{dT^{-1}} \quad (1)$$

i.e., as the slope of a plot of the natural logarithm of the time, t_α, to reach a given conversion, α, against the reciprocal temperature of the run. By repeating this procedure for a series of the conversions, one obtains a dependence of E_α on α. Although eq 1 is based on the Arrhenius temperature dependence, the latter is assumed only for a given conversion. That is, the isoconversional method represents each conversion by its own Arrhenius equation. An advantage of such an approach is that it affords establishing whether the whole process obeys a single Arrhenius law. If this is the case, then the E_α value should demonstrate independence of conversion. However, revealing a systematic dependence of E_α on α would be indicative of the occurrence of several processes having significantly different activation energies.

The application of an isoconversional method requires experimentally measured curves of the relaxation enthalpy vs aging time to be converted to the curves of the conversion vs time. At any given aging time, the conversion can be defined as
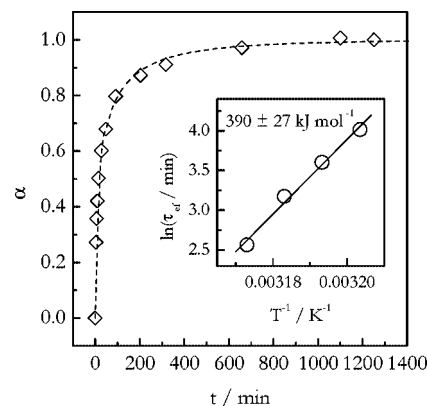
$$\alpha = \frac{\Delta H(t)}{\Delta H_\infty} \quad (2)$$

Figure 1. Progress of maltitol aging at 40 °C (diamonds, actual values; dashed line, KWW fit). The inset shows the temperature dependence of τ_{ef} (Table 1) fitted to the Arrhenius equation and the respective value of activation energy.

TABLE 1: Results of Fitting the Enthalpy Relaxation Data to the KWW Equation

T/°C	τ_{ef}/min	β	ΔH_∞/J g⁻¹
39	55.4	0.46	5.4
40	36.7	0.46	4.7
41	23.9	0.54	3.9
42	13.0	0.60	3.3

where $\Delta H(t)$ is the aging enthalpy measured at the aging time, t, and ΔH_∞ is the final (plateau) value. Of course, the variable α does not uniquely represent the glass structure, which also depends on the aging temperature, so that E_α obtained by eq 1 is associated with some temperature averaged structure. This, however, appears to be a general issue of the glass relaxation kinetics that stems from the fact that any experimentally derived activation energy is unavoidably a value averaged over an experimental temperature region.

Figure 1 displays an example of the resulting α vs t data. In order to use eq 1, one needs to determine the time to reach a given extent of conversion at different aging temperatures. This is readily accomplished by fitting (interpolating) the actual experimental data to the Kohlrausch−Williams−Watts (KWW) equation

$$\alpha = 1 - \exp\left[-\left(\frac{t}{\tau_{ef}}\right)^\beta\right] \quad (3)$$

Equation 3 has two parameters: τ_{ef} is the effective relaxation time, and β is the stretch exponent. The reciprocal value of the latter characterizes the width of the relaxation time distribution. Note that the extent of conversion reached at the time τ_{ef} equals $1 - e^{-1} = 0.63$, where e is Euler's number. The τ_{ef} and β parameters obtained by fitting the experimental aging data are collected in Table 1. Although relaxation processes in glasses typically demonstrate the KWW dynamics, it is commonly found that[17] the parameter β varies systematically with temperature and that[18] τ_{ef} depends on temperature in a non-Arrhenius manner. Our results (Table 1) clearly demonstrate that the stretch exponent increases with temperature as frequently is the case in glass aging studies.[19] The non-Arrhenius temperature dependence of τ_{ef} is not obvious (Figure 1) which is not surprising considering the narrow temperature region used in this study. A plot of $\ln \tau_{ef}$ vs T^{-1} seems quite linear (correlation coefficient 0.995) and yields an effective activation energy of 390 ± 27 kJ mol⁻¹. The use of the τ_{ef} values reported by Bustin and
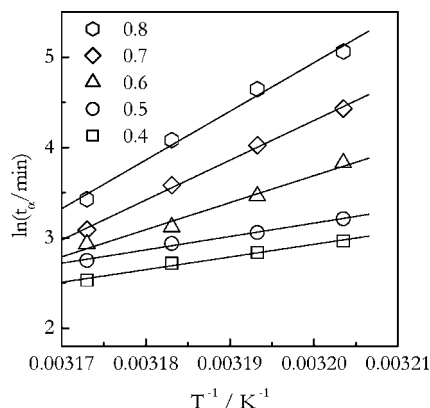
Figure 2. Isoconversional plots for different extents of conversion (shown as numbers by the point types).
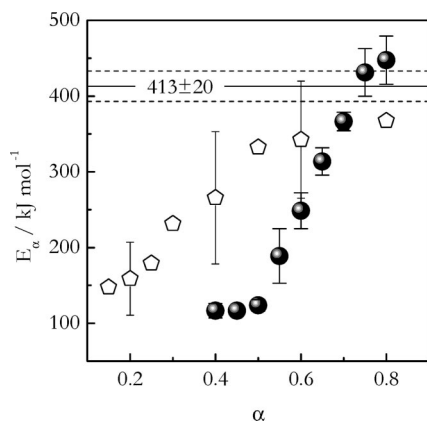

Figure 3. Variation in the effective activation energy with the extent of conversion (spheres, enthalpy relaxation data; pentagons, heat capacity relaxation data[15]).

Descamps[20] yields a comparable value (326 kJ mol^{-1}) of the activation energy for aging of maltitol glass. The obtained value agrees well with our previously reported[15] value 413 ± 20 kJ mol^{-1} determined by temperature modulated DSC for the glass transition in maltitol. The respective literature values for the glass transition and α-relaxation are 457[20] and 439[21] kJ mol^{-1}.

Figure 2 presents a series of isoconversional $\ln t_\alpha$ vs T^{-1} plots whose slopes increase markedly with increasing conversion value. This obviously means that the effective activation energy of aging increases throughout the aging process. A dependence of the isoconversional value of E_α on α is presented in Figure 3. The lower boundary of conversions is limited by 0.4 because the aging rate is the fastest in the initial moments so that the smallest values of conversion experimentally detected after only a few minutes of aging have typically been larger than 0.3. The observed E_α dependence is statistically significant, as confirmed by the nonparametric u-test and Spearman's coefficient of rank correlation.[22]

As seen in Figure 3, only the later stages of aging demonstrate activation energies similar to the value found for the glass transition process. This effect can explain why the effective activation energy of aging derived from the temperature dependence of τ_{ef} is similar to the activation energy of the glass transition. As mentioned above, theoretically, τ_{ef} represents the time to reach the conversion value 0.63. As can be found from Figure 3, the value of E_α at this conversion is only ~25% smaller than the activation energy of the glass transition. On the other hand, the fact that different aging times have different effective activation energies prompts us to question the use of the concept of single effective relaxation time as an adequate

estimate of the kinetic stability of glassy systems. Similar concerns have recently been raised by Mao et al.[23]

It is noteworthy that the E_α dependence obtained in the present study from the enthalpy relaxation data demonstrates a notable similarity with the E_α dependence derived earlier[15] from the heat capacity relaxation data. Although some of the numerical values of E_α related to the same conversion differ significantly, for both dependencies, the E_α values at the later stages of aging are similar to the activation energy of the glass transition. Also, for both dependencies, the E_α values at the early stages are about 3 times smaller than the value for the glass transition. Therefore, both dependencies are consistent in at least a semiquantitative sense.

As mentioned above, revealing a systematic dependence of E_α on α indicates the occurrence of several processes of different activation energies. Apparently, the early stages of physical aging are dominated by a faster process having smaller activation energy and the later stages by a slower process of larger activation energy. Since at conversions approaching 1 the E_α value approaches the activation energy of the glass transition, it is reasonable to assume that the slower process of larger activation energy is the cooperative α-relaxation. Then, the faster process of lower activation energy is likely to be associated with relaxations of low cooperativity. For instance, Perez and Cavaille[24] distinguish three types of relaxation processes in the glassy state: the nonequilibrium mode of α-relaxation and α'- and β-relaxation. These have progressively smaller activation energies, each of which being smaller than the typical values found for α-relaxation in the metastable equilibrium sate. Maltitol is known[25] to demonstrate the nonequilibrium α-mode. The α'-relaxation has been observed in metallic[26] and polymeric[27] glasses and linked to the "frozen-in relaxation sites". The β-relaxation is usually associated with mobility islands.[28] Various relaxation processes of different degrees of cooperativity and, thus, of different activation energies can coexist in spatially heterogeneous glassy structures. The spatially heterogeneous dynamics of physical aging reveals itself, for example, in experiments by Thurau and Ediger,[29] who demonstrate that translational diffusion associated with low density regions occurs faster and has a smaller temperature coefficient than rotational diffusion associated with high density regions.

It is reasonable to expect that in spatially heterogeneous glass the initial stages of aging occur predominantly via collapse (densification) of low density mobility islands. This is driven by faster relaxation processes of lower cooperativity and lower activation energy. As glass becomes denser and more homogeneous with aging, the molecular mobility becomes more cooperative, which causes the energy barrier to increase continuously toward the value characteristic of cooperative α-relaxation. This phenomenological picture appears to well explain the increase in the effective activation energy observed in the present study.

The coexistence of relaxation processes of different activation energies suggests that their relative contributions to the overall aging rate should change with temperature. As temperature is lowered, a cooperative process of greater activation energy should be slowed down to a larger degree than a noncooperative one, having a smaller energy of activation. For this reason, the initial stages of physical aging should tend toward the activation energy of the noncooperative β-relaxation with decreasing aging temperature. To test this hypothesis, we have conducted a large series of long-term aging experiments at 30, 32, 34, and 36 °C that regrettably have shown too much sample-to-sample variation at each of the aging temperatures and have, therefore, been
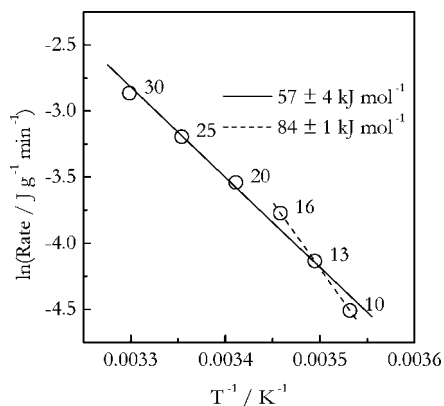
Figure 4. Fitting the temperature dependence of the initial aging rates to the Arrhenius equation (numbers by the points represent the aging temperature in °C).

deemed unsuitable for isoconversional analysis. To get around the problem associated with using multiple samples, a series of short (up to 20 min) aging runs has been conducted at six temperatures from 10 to 30 °C. The resulting data have been used to determine and analyze the temperature dependence of the initial aging rates.

The rate of relaxation of a given physical property (e.g., enthalpy, volume, entropy, etc.) of a glass is typically assumed to be first order with respect to departure of this property from its equilibrium value.[30-32] By replacing the property with dimensionless conversion, the rate takes the following form

$$\frac{d\alpha}{dt} = \frac{(1 - \alpha)}{\tau_{ef}} \qquad (4)$$

It follows from eq 4 that, at the initial stages when conversion is small, the value of the rate can serve as a reasonable approximation of $1/\tau_{ef}$. Therefore, the slope of a plot of the natural logarithm of the initial rate against the reciprocal aging temperature should yield the effective activation energy for the early stages of aging. The initial rates have been estimated as a slope of the aging enthalpy vs time data obtained within the first 20 min of aging at five temperatures from 10 to 30 °C. Figure 4 presents an Arrhenius plot for the temperature dependence of the initial rate. The complete plot yields an activation energy of 57 ± 4 kJ mol⁻¹ and a coefficient of linear correlation of −0.991. Of course, the reliability of this estimate depends on how valid the basic assumption about the rates is. Ideally, it would be desirable to have the rate for small values of α which also are about the same for different aging temperatures. Unfortunately, this condition cannot be tested without knowing ΔH_∞, i.e., without aging the samples all the way to equilibrium. On the other hand, some indirect testing can be done by evaluating the activation energy for different temperature regions of the plot in Figure 4. Apparently, the basic assumption is more likely to fail for higher aging temperatures that are associated with faster aging. However, eliminating the data for 30 °C does not practically change the value of E that becomes 60 ± 6 kJ mol⁻¹. The use of the data for the three lowest temperatures (10, 13, and 16 °C) yields a somewhat greater value of 84 ± 1 kJ mol⁻¹. Nevertheless, all of these values compare well with experimental activation energies for the β-relaxation in maltitol. According to the literature, dielectric spectroscopy yields the values 57[21] and 61[25] kJ mol⁻¹, mechanical spectroscopy, 62[25] kJ mol⁻¹, and DSC, 71 ± 6[33] kJ mol⁻¹. The result is obviously consistent with our anticipation that as

the aging temperature is lowered the effective activation energy of the early stages of aging should approach the activation energy of the β-relaxation. This effect appears to be in agreement with the results of Nemilov[34] and Nemilov and Johari[35] for silicate glasses, of Cangialosi et al.[36] for polycarbonate, and of Hu and Yue[37] for hyperquenched GeO₂ that demonstrate that at temperatures markedly below T_g the overall aging kinetics is controlled by processes whose activation energy is approaching the values characteristic of the β-relaxation process.

Naturally, the question arises of whether the observed increase in the effective activation energy throughout the process of physical aging is unique to maltitol. Although our present experience is yet limited to the application of isoconversional analysis to aging of this material, we believe it should be common in other glassy systems. Analysis of the literature indicates that an increase in the effective activation energy of physical aging has been noticed by other workers who monitored the process by measuring nonthermal physical properties. The effect has been observed[38,39] in metallic glasses when measuring the squared velocity of sound that is proportional to Young's modulus. However, the observed effect[38,39] was not correlated with the α- or β-relaxation processes in the respective glasses.

4. Conclusions

The application of isoconversional kinetic analysis to physical aging data demonstrates that the effective activation energy of the process increases upon the conversion of the system from the glassy to supercooled liquid state. It is proposed that the early stages of aging are associated with the mobility islands that age (densify) at the expense of relaxation processes of low cooperativity and, thus, of low activation energy, whereas the later stages occur via the regular cooperative α-relaxation. The use of lower aging temperatures indicates that the activation energy of the initial aging stages tends to approach the activation energy of the β-relaxation. Overall, the effective activation energy of physical aging has a rather complex structure, being a function of both conversion and aging temperature. Isoconversional analysis appears to be an effective tool for revealing and exploring the structure of the temperature dependence of the physical aging kinetics.

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