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Size of the cooperative rearranging regions vs. fragility in complex glassy systems: Influence of the structure and the molecular interactions

E. Bouthegourd [a], A. Esposito [a,*], D. Lourdin [b], A. Saiter [a], J.M. Saiter [a]

[a] AMME-LECAP EA 4528 International Laboratory, Institute for Material Research FED4114, Université et INSA de Rouen, Faculté des Sciences, Avenue de l'Université BP 12, 76801 Saint Etienne du Rouvray, France
[b] INRA, UR1268, Unité Biopolymères Interactions et Assemblages, 44300 Nantes, France

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ABSTRACT

By using Donth's model, the size of the Cooperative Rearranging Regions (CRR) at the glass transition was determined from TM-DSC measurements on two glassy biopolymers with different molecular structures (amylose and amylopectin) as well as on starch, which is the mixture of amylose and amylopectin as it is obtained during its biosynthesis. For these materials, the ΔC_p values at T_g and the values of the fragility index (m) were determined by conventional DSC. The fragility concept was then analyzed by taking into account the existence of two contributions: m_{isoV} (the so-called isochoric fragility, which is a pure thermal contribution) and $m_{\Delta v}$ (which incorporates the effects due to volume and density fluctuations). Whenever the molecular structure of a glass-forming liquid involves non-linear sequences of rigid and sterically hindered repeating units with high densities of hydrogen bonds, the fragility is found to be governed only by the temperature; the contribution of the volume (density and pressure contribution) has a quasi-nil effect.

1. Introduction

A liquid cooled at a rate high enough to avoid phase transformations (crystallization) will see a drastic increase of its viscosity in a temperature domain that is called glass transition and is defined by a temperature (T_g) which is not a constant but depends on the thermal history, including the cooling rate. At temperatures below T_g, the material is in a solid-like state called the glassy state. The glassy state is by definition a non-equilibrium state from a thermodynamic point of view and could be also described as a frozen liquid state [1]. The lack of thermodynamic equilibrium implies that all the properties are time-dependent and thermally activated (this condition is generally referred to as physical ageing [2]). At temperatures above T_g, the relaxation time τ_α (or, similarly, the viscosity) characterizing the molecular dynamics depends on the temperature and a non-Arrhenius behavior is often observed. The concept of fragility [3] has been previously proposed to analyze this deviation from the Arrhenius behavior through the calculation of a behavior steepness at $T=T_g$, also called fragility index m [4], as

$$m=\frac{\partial \log\tau_\alpha}{\partial (T_g/T)}\Big|_{P;T=T_g} \tag{1}$$

Under isobaric conditions, the fragility index includes two contributions: one exclusively associated to energy (a pure thermal contribution also called isochoric fragility) and one associated to volume and density fluctuations [5,6]. Hong et al. [7] suggested to rewrite m as:

$$\begin{aligned} m&=\frac{\partial \log\tau_\alpha}{\partial (T_g/T)}\Big|_{V;T=T_g}+\frac{\partial \log\tau_\alpha}{\partial P}\Big|_{T;T=T_g}\frac{\partial P}{\partial (T_g/T)}\Big|_{V;T=T_g}\\ &=m|_{V;T=T_g}+\frac{\Delta V^*}{\ln 10 k_B}\frac{\alpha_T}{\kappa} \end{aligned} \tag{2}$$

The two terms correspond to the isochoric fragility (m_{isoV}) and to the contribution taking into account the volume (thus density) and pressure dependence of the molecular dynamics at the glass transition ($m_{\Delta v}$), as κ is the compressibility, α_T is the thermal expansion coefficient, ΔV^* is the activation volume per relaxation unit and k_B is the Boltzmann constant.

The second most important property of a liquid in the glass transition domain concerns the nature of the molecular movements, which become cooperative as the temperature decreases. This cooperativity has been first presented by Adam and Gibbs [8],

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* Corresponding author. Tel.: +33 2 32 95 50 85; fax: +33 2 32 95 50 82.
E-mail addresses: emilie.bouthegourd@etu.univ-rouen.fr (E. Bouthegourd), antonella.esposito@univ-rouen.fr (A. Esposito), denis.lourdin@nantes.inra.fr (D. Lourdin), allison.saiter@univ-rouen.fr (A. Saiter), jean-marc.saiter@univ-rouen.fr (J.M. Saiter).

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who defined a Cooperative Rearranging Region (CRR) as the smallest subsystem that, upon a sufficient thermal fluctuation, can undergo conformational rearrangements independently of its environment. Following the idea of Adam and Gibbs and dividing the total volume into subsystems of equal elementary sub-volumes ($V_{sv}=\xi^3$), the standard statistic thermodynamic relationships allow the calculation of the mean square fluctuations of density $\langle\Delta\rho^2\rangle$, temperature $\langle\Delta T^2\rangle$, entropy $\langle\Delta S^2\rangle$ and energy $\langle\Delta E^2\rangle$ [9]. When the sample geometry or structure is modified in such a way that a modification of the cooperative movements is also expected, the Gibbs distribution approach for the treatment of the characteristic length ξ must be replaced by the von Laue treatment [10,11]; as proposed by Donth [12] and confirmed by Schröter [13], an analysis of the dynamic heterogeneity of the glass transition with a distribution including a term of temperature fluctuation must be done. So, each sub-volume is considered as a metastable thermodynamic system with fluctuating variables following Gaussian distributions, having its own glass transition and its own relaxation time. According to Donth [12], the characteristic volume of cooperativity at the glass transition temperature (ξ^3_{Tg}) can be obtained as follows:

$$\xi^3_{Tg} = \frac{\Delta(1/C_p)}{\rho(\delta T)^2} k_B T_g^2 \tag{3}$$

where T_g is the glass transition temperature, ρ is the density, k_B is the Boltzmann constant, δT is the average temperature fluctuation related to the dynamic glass transition of an average CRR, $\Delta(1/C_p)=[1/C_{pglass}-1/C_{pliquid}]_{T=Tg}$.

The CRR concept has recently been used in a wide range of polymeric systems to describe the molecular dynamics at the glass transition [14–26] and successfully extended to other temperatures above T_g [27]. On the other hand, the CRR concept has been confronted to the fragility concept through the originally suggested index (m) and it has been demonstrated that the higher the fragility of the liquid-like system at T_g, the higher the CRR size at T_g [28,29]. In spite of all these results and as claimed by Ngai [30], many other experimental data arose to point out a lack of clear evidences for a correlation between the values of ξ^3 and the values of m [6,31]. This problem was partially solved by Hong et al. [7], who showed that a correlation can actually be highlighted if the discussion is not driven around m as a global index, but around $m_{\Delta V}=m-m_{isoV}$ (i.e. by referring uniquely to the contribution which is volume, density and pressure dependent).

The experimental determination of m_{isoV} is relatively difficult, whereas m and ξ^3 can be directly inferred from DSC and TMDSC measurements. As a consequence it is proposed, here, to use the CRR size obtained by Donth's model [12] and the results reported by Hong et al. [7] to deduce the $m_{\Delta V}$ component of the fragility for a series of glasses having different molecular architectures (see Table 1) and then to infer, from the experimental determination of m, their isochoric fragility as $m_{isoV}=m-m_{\Delta V}$. The series of selected samples includes an inorganic glass (glassy selenium, g-Se), an organic glass (α-poly lactic acid, PLA) and a much more complex glass-forming system (amorphous potato starch). g-Se macromolecular chains can only interact with each other through the lone pairs in the outermost electron shell of Se atoms, whereas biopolymer chains (such as PLA and any polysaccharide) can develop a particularly high density of hydrogen bonds. Both g-Se and PLA could be considered as linear polymers, formed by repeating units that are extremely (g-Se) or reasonably (PLA) flexible with no (g-Se) or very low (PLA) steric hindrance, whereas amorphous potato starch is the result of a biosynthesis leading to an intimate mixture of amylose and amylopectin. Amylose and amylopectin result from the same sterically hindered and rigid repeating unit (glucose) but are linear and highly branched, respectively. As the results obtained on g-Se and PLA have already been published [32,33], only the results concerning starch and its structural components will be presented here, but the discussion will include a comparison with the previous results.

2. Materials and methods

Native potato starch was purchased from Roquette (Lestrem, France) and destructured by extrusion at 110 °C with 25 wt% of water, then ground under liquid nitrogen to obtain an amorphous powder. As starch and starch-based materials are highly hydrophilic, all the samples were stored in conditions of controlled relative humidity (57% RH). The final water content of destructured starch was 13 wt%. Potato starch consists of 80 wt% of amylopectin and 20 wt% of amylose. Amylopectin (waxy maize) was purchased from Roquette (Lestrem, France) and has the structure of a hyperbranched polymer, as illustrated in Table 1. Amylose was extracted from pea starch (as explained in details in Ref. [34]) and has the structure of a linear polymer with high levels of steric hindrance. The water content of amylose was 11 wt%. Before any measurement, the water content of each sample was measured by thermogravimetry (isothermal mass recording during 90 min at 130 °C under nitrogen). Hermetically sealed aluminum pans were used for all DSC measurements. The morphology of all samples was checked to be entirely amorphous by X-Ray measurements.

To determine the CRR size, the samples were characterized by Temperature Modulated Differential Scanning Calorimetry (TM-DSC Q100, TA Instruments). The calorimeter was calibrated in temperature and energy with the standard values of zinc and indium melting points. The specific heat capacity for each sample was measured using sapphire as reference. All the samples weighed approximately 20 mg except amylose samples, whose mass was always comprised between 4 and 5 mg. The experimental parameters for the temperature modulation were set at 1 °C for the oscillation amplitude, 60 s for the oscillation period and 0.5 °C/min for the cooling rate. These parameters gave the best signal-to-noise ratio. The measurements were performed under nitrogen. The procedure of Weyer et al. [35] was used to correct the experimental phase angle for each measurement. According to the procedure previously described by Donth et al. [12], the C'' curves obtained by TM-DSC for each sample were fitted with a Gaussian peak to estimate the values of $\langle\delta T\rangle$, whereas the C_p and T_g values were determined straightaway from the C curves (Fig. 1). TM-DSC provided indeed all the values to be injected into Eq. (3) to calculate ξ.

The global fragility index is easily obtained by Eq. (1) and, as shown in previous works [36,37], can also be obtained from standard DSC measurements. The standard DSC measurements were performed on the same calorimeter used for TM-DSC. For standard measurements, the calorimeter was calibrated in temperature and energy by using the melting points of zinc and indium. All the measurements were performed under nitrogen with an heating rate of 10 °C/min. Accurate values of the fragility index can only be obtained by accurately measuring the glass transition temperature T_g, as demonstrated in previous works [38–40]. Once T_g accurately measured, the value of m was obtained according to

$$m = \frac{\delta h*}{RT_g \ln 10} \tag{4}$$

where δh^* is the apparent activation energy, defined in the Tool-Narayanaswamy-Moynihan equation [41–43].

δh^* was obtained experimentally from DSC measurements by exploiting the T_g shift observed, at the same heating rate, for any