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# Viscoelastic and viscoplastic properties of bulk metallic glasses Comparison with oxide glasses and amorphous polymers

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Mechanical behavior of non-crystalline solids is strongly dependent upon temperature: at low temperature they behave like elastic solids whereas at high temperature their behavior is that of a viscous liquid. In an intermediate temperature range, near the glass transition, viscoelastic behavior is preponderant, characterized by strong relaxation effects. In this paper, the viscoelastic behavior of bulk metallic glasses is compared to the one of oxide glasses and amorphous polymers. Both linear and non-linear aspects are considered. A special attention is paid to similarities and differences.

## 1. Introduction

From a very general point of view, mechanical behavior corresponds to the response of a solid to a mechanical stimulus. Viscoelasticity implies behavior intermediate between that of purely elastic solids in which the deformation is proportional to the applied force and of viscous liquids for which the rate of deformation is proportional to the applied force. This introduces a time dependent response [1]. Accordingly, three components of the deformation can be distinguished: (i) the elastic strain: reversible and instantaneously recovered, (ii) the anelastic or viscoelastic component: recovered upon time, (iii) the viscoplastic component: non-reversible. The last component is usually called viscous flow when the viscosity becomes very low. For crystalline materials (metals, crystalline ceramics), the anelastic strain is negligible compared to the viscoplastic strain. In such solids, large viscoelastic effects

can only be observed at temperature near their melting point ( $T_m$ ) but they can be neglected at ambient temperature (i.e. when  $T/T_m < 0.5-0.7$ ). Conversely, for non-crystalline materials, the viscoelastic contribution is a major part of the response. Non-crystalline solids are characterized from a structural point of view by the lack of order at long distance in the atomic arrangement, and from a thermodynamic point of view, by a non-equilibrium state. Non-crystalline solids are characterized by their glass transition temperature, that corresponds to the transition from liquid (super cooled state) to glass (frozen state). Amorphous materials exhibit several relaxation processes, each of them is associated with a more or less pronounced decrease in the storage modulus for increasing temperature or decreasing frequencies [2–7].

This paper deals with the similarities and the differences in the mechanical response of non-crystalline solids. Experimental data concerning three samples belonging to the three different classes of materials, i.e. a bulk metallic glass, an oxide glass and an amorphous polymer are compared in both the linear (viscoelastic) and the non-linear (viscoplastic) regime. The theoretical description of all these data is also addressed.

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## 2. Experimental

Three different samples have been studied: (1) a soda lime glass [SiO<sub>2</sub> (73.2%)–Na<sub>2</sub>O (12.5%)–CaO (11.1%)], supplied by BSN Emballage; (2) two bulk metallic glasses: [Zr<sub>41.2</sub>Ti<sub>13.8</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> (at.%)], commercially available as Vitreloy 1 (Howmet Corp., USA) and [Zr<sub>46.8</sub>Ti<sub>8.2</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> (at.%)] (called Vitreloy 4) manufactured by J.L. Soubeyrioux (CRETA, CNRS, France); (3) an amorphous PET supplied by Sigma Aldrich.

Dynamic mechanical measurements were performed in torsion mode either at a fixed frequency in the range [10<sup>-5</sup>–1 Hz] with a constant heating rate or at a given temperature versus frequency (isotherms). The deformation was chosen in order to study the linear viscoelastic response. Samples were bars with dimensions around 30 × 5 × 1.5 mm<sup>3</sup>. The set-up provides the storage and the loss components of the complex shear modulus ( $G'$  and  $G''$  respectively), and the loss factor  $\tan\phi = G''/G'$ .

The non-linear mechanical behavior of the bulk metallic glass was investigated by compression performed on cylindrical samples ( $\phi = 3$  mm,  $h = 5$  mm). The temperature was close to  $T_g$  ( $T_g = 363$  °C) and the deformation rate between  $2.5 \times 10^{-4}$  and  $5 \times 10^{-3}$  s<sup>-1</sup>. The non-linear response of polymers was investigated by bi-axial compression tests on a Adamel Lhomargy DY25 with a load cell of 20 kN. Tests were performed on rectangular samples (20 × 15 × 0.875 mm<sup>3</sup>) in the range [23–95 °C] and with a constant deformation rate of  $8.3 \times 10^{-3}$  s<sup>-1</sup>.

## 3. Viscoelastic response

Fig. 1 displays the typical viscoelastic behavior of the metallic glass sample studied with a fixed frequency (0.3 Hz) as a function of temperature (3 K min<sup>-1</sup>). Schematically, three temperature domains can be observed:

- At low temperature (1), the material is in the glassy state, i.e. out of equilibrium, the real part of the shear modulus  $G'$  is almost constant and in the order of 28 GPa. The imaginary part of the modulus  $G''$  is low (about 1 MPa). The behavior is mainly elastic.
- At intermediate temperature (2), a strong decay of  $G'$  is observed during the so-called main or  $\alpha$  relaxation. In the same time,  $G''$  and the loss factor  $\tan\phi$  display a maximum. The  $\alpha$ -relaxation is associated to the glass transition of the material [8].
- It approximately separates two different mechanical behaviors corresponding to the glassy state ( $T < T_\alpha \approx T_g$ ) and to the viscous one ( $T > T_\alpha \approx T_g$ ).
- At higher temperature (3), the further increase of  $G'$  can be attributed to the crystallization, as confirmed by DSC or X-rays measurements and microscopy

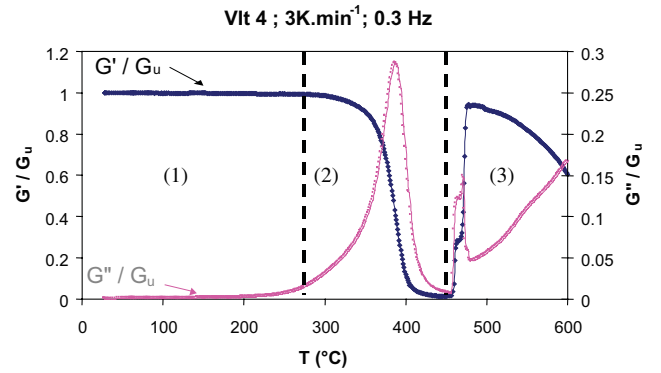


Fig. 1. Normalized  $G'$  and  $G''$  evolution versus temperature for the bulk metallic glass Vitreloy4.

observations [9,10]. This phenomenon results from the metastable nature of the amorphous state and will not be further commented.

The viscoelastic response depends on the frequency, at a given temperature. However, thanks to the time temperature superposition principle, it is possible to plot master curves. The normalized master curves of the bulk metallic glass, the soda lime glass and the amorphous polymer are reported on Fig. 2(a) and (b) using a reference temperature equal to  $T_g$ . The unrelaxed shear modulus is close to 25 GPa for both metallic and oxide glasses, but only of the order of 1 GPa in the case of the polymer. Actually, below  $T_\alpha$ , the stiffness of an amorphous polymer is mainly due to the intermolecular Van der Waals bonds whereas it is due to iono-covalent bonds for the two other glasses. The main observation is the fact that, whatever the chemical nature of the materials, the behavior of the three samples is very similar.

However, several points can be added:

- In the case of amorphous polymers and molecular glasses, secondary relaxations (named  $\beta, \gamma, \dots$ ) are generally observed at temperature below  $T_\alpha$ . They are associated to local molecular motions of few segments of the chains and imply conformational changes.  $\beta$  motions are well described by an Arrhenius relation. The pre-exponential factor is coherent with the Debye frequency, and the activation energy is close to 1 eV. In mineral and metallic glasses, the high interatomic energies and the density limit or even prevent the existence of secondary relaxation. When observed, they can be attributed to either the presence of impurities (such as water molecules in oxide glasses) or the existence of a local order around some metallic atoms in a metallic glass [11] (reported for instance in Pd–Ni–Cu–P).
- The main difference in the behavior of the three samples is observed in the high temperature domain. For polymers, a ‘rubbery plateau’ is observed in the  $G'$  curve.

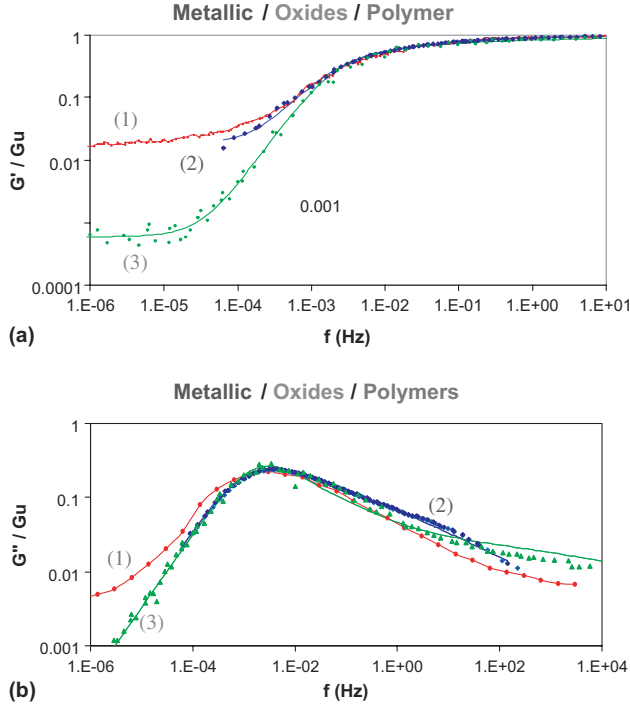


Fig. 2. (a)  $G'$  master curves ( $T_{ref} = T_g$ ): (1) amorphous PET, (b) (2) Vitreloy 4, (3) soda lime glass. Dots: experiments; curve: calculated:  $G'$  master curves ( $T_{ref} = T_g$ ) (1) amorphous PET, (2) Vitreloy 4, (3) soda lime glass. Dots: experiments; curve: calculated.

This rubbery plateau is due to the presence of entanglements between polymer chains. Actually, above  $T_\infty$ , the thermal agitation makes the Van der Waals bonds negligible. When polymers are uncrosslinked, the length of the plateau depends on the molar weight, which controls the time necessary for the disentanglement. In the case of crosslinked polymers (thermosets, elastomers) chemical crosslinks prevent the chain flow (Fig. 3). The modulus in the rubbery plateau is proportional to the entanglement or crosslink density. In mineral glasses, the existence of a residual modulus is observed. The residual modulus  $G'$  is only observed for very low applied stress. The physical mechanisms at the origin of this phenomenon are still under discussion [12]. In metallic glasses, the existence of a residual modulus can not be observed due to morphological evolutions (crystallization, phase separation) of the specimen.

- The time and temperature dependence of the  $\alpha$  relaxation corresponds to a non-arrhenian behavior. Several theories have been proposed to analyze dynamics of liquids and glass. In most of these approaches, the complex nature of the molecular motions in the glass transition range has been regarded as either simultaneous elementary molecular motions [13] or correlated motions [8, 14]. In the later case, the concept of hierarchically correlated motions yields the following expression for the relaxation time,

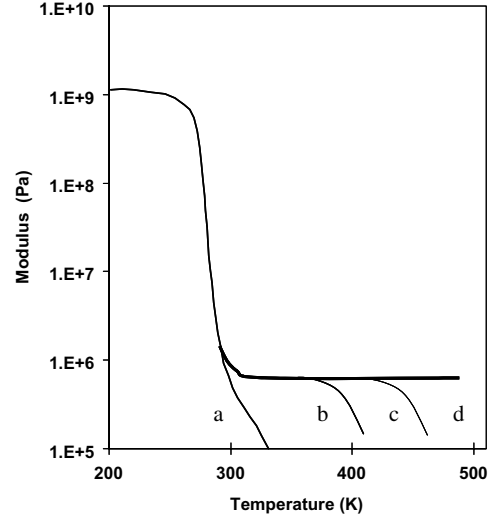


Fig. 3. Schematic evolution of  $G'$  versus temperature : (a-c) amorphous polymers with increasing molecular weight, (d) cross-linked elastomer.

$$\tau_{mol} = t_0 \left( \frac{\tau_1}{t_0} \right)^{1/\chi}, \quad (1)$$

where  $t_0$  is a scaling parameter,  $\tau_1$  corresponds to the characteristic time of the fastest or elementary molecular motion.  $\chi$  is a measure of the effectiveness of the correlation effects and varies from 0 (fully constrained situation, with an infinite value for  $\tau_{mol}$ ) to 1 (constraint free situation where  $\tau_{mol} = \tau_1$ ).

Whatever the chemical nature of the material, a unique physical model can be used to describe the variation of the complex modulus [8]. A formulation available to describe the curves is the well known biparabolic equation:

$$G = G_{res} + \frac{G_u - G_{res}}{1 + \delta(i\omega\tau_{mol})^{-\chi} + (i\omega\tau_{mol})}, \quad (2)$$

where  $G_u$  is the unrelaxed modulus, i.e. the value before the  $\alpha$  relaxation,  $G_{res}$  the rubbery or residual modulus (when exists);  $\delta$  is a parameter close to 1. The calculated curves have been reported on Fig. 2(a) and (b) (full lines). The numerical values of the parameters have been discussed considering the chemical nature of the material [15]. The most noteworthy feature is the wide distribution (over more than 10 orders of magnitude) of characteristic times.

#### 4. Viscoplastic response

Fig. 4(a) presents the stress strain curves of the metallic glass Vitreloy1 at different temperatures near the glass transition. Similar results are presented for the

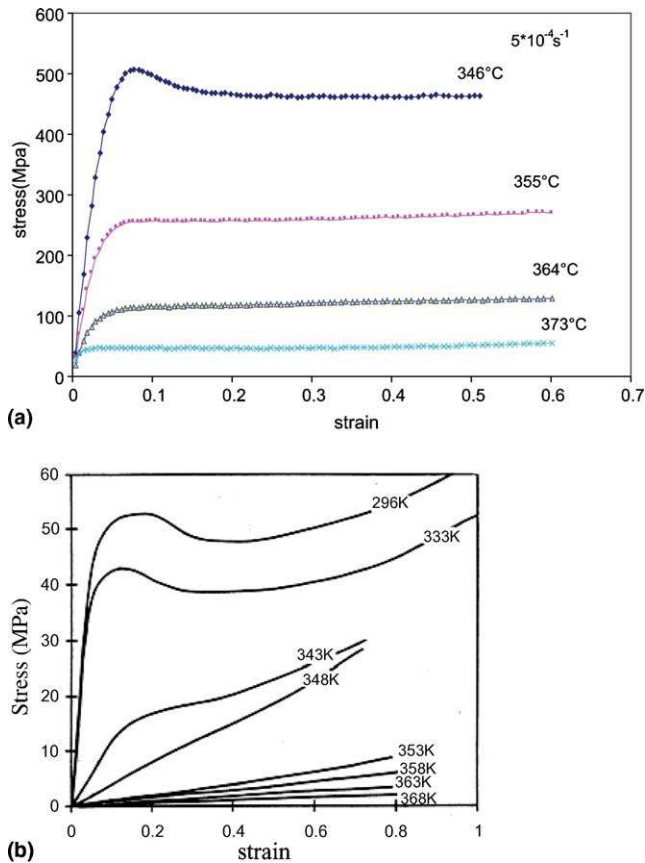


Fig. 4. (a) Compression curves for bulk metallic glass Vitreloy 1 (strain rate:  $5 \times 10^{-4} \text{ s}^{-1}$ ). (b) Biaxial compression curves for amorphous polymer (strain rate:  $8.3 \times 10^{-3} \text{ s}^{-1}$ ).

polymer in Fig. 4(b). For both samples, a yield point is observed, that is more pronounced for lower temperatures (or for higher deformation rate). The yield phenomenon is followed by a viscoplastic flow where the stress is minimum and more or less constant versus deformation. The level of stress in this plateau is strongly dependent on temperature.

The main difference between polymer and metallic glass stands in the strain hardening observed at higher strain. This phenomenon, observed only for the polymeric sample, is due to macromolecular orientation leading to (i) entropic processes and (ii) a decrease of molecular mobility due to a higher degree of organization in the specimen [4]. For all the other types of glasses (molecular, metallic, oxide) the absence of strain hardening is attributed to the lack of obstacles to molecular motions when stress increases.

In literature, different models have been proposed to describe the influence of temperature and deformation rate on the non-linear response of non-crystalline solids. In the theory developed by the group of Perez, the anelastic part of the deformation is associated to the nucleation and the growth of shear micro domains whereas the viscoplastic flow corresponds to the equilibrium between nucleation and coalescence of these do-

main [8]. The main advantage of this model is that it provides a unique description of both linear and non-linear response, i.e. with a unique set of parameters. In the case of polymers, the hardening phenomenon has been introduced taken into account the rubbery elasticity and the chain orientation effects on molecular motions [4]. This model can be used for metallic glass [16], it has also been applied with success for oxide glasses [17].

## 5. Conclusion

The main aspects in the mechanical response of metallic glasses are (i) a viscoelastic linear response characterized by a strong decrease of the storage modulus and a maximum in the loss modulus in the domain of the main relaxation, (ii) a stress strain curve with a yield phenomenon preceding the viscoplastic flow. These aspects are specific of amorphous state since they are common to all types of non-crystalline solids. For instance, similar dependencies of the yield stress and the plastic stress versus temperature and strain rate are observed. Moreover, a unique theoretical description is able to reproduce the main aspects of the mechanical behavior of non-crystalline solids. However, the specificity of polymers is the presence of long chains that leads to the existence of a rubbery modulus above the main relaxation and a strain hardening limiting the viscous flow.

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