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Non Linearity of Glassy Polymers

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Summary: In this paper the source of non linearity in amorphous materials will be analyzed and verified with phenomenological approaches. A series of simulated results, replicating the relevant experimental data presented in literature along the years, will be reported.

Keywords: glassy polymers; non linearity; viscoelasticty

Introduction

We start recalling that the constitutive equation for linear viscoelastic materials is expressed by the Boltzman superposition principle that in its three-dimensional expression, at constant temperature, takes the following form:

$$\sigma_{ij} = \delta_{ij} \int_0^t K(t-t') \frac{d\varepsilon}{dt'} dt' + \int_0^t G(t-t') \frac{d}{dt'} \left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon \right) dt' \quad (1)$$

In the above form, Equation 1 returns the time-dependent response to an arbitrary deformation history in terms of stress tensor components. K(t) and G(t) represent the bulk and the shear moduli, respectively. A similar expression may be written where the bulk and the shear compliance (B and J, respectively) are required to return the deformation tensor as consequence of an arbitrary stress history. It is worth mentioning that no limits are intrinsically claimed by Equation 1. It simply imply that the bulk and the shear moduli are unique functions of time. However as a matter of fact the experimentalists find the Boltzman superposition principle verified under the condition of ''small'' mechanical perturbations and under very simple loading protocols. It should be also noted that such ''small'' mechanical perturbation acts generally in very narrow time interval in respect to the timescale of the viscoelastic relaxation and Equation 1 is used in its rather simple form under the condition of uniaxial step strain perturbations. For example step shear strain allows the direct determination of G(t) and the whole relaxation timescale can be acquired by invoking the well known time-temperature superposition principle. The master curve can be constructed by shifting the data taken in narrow time intervals, at different temperatures. The latter procedure implies thermo-rheological simplicity (i.e. the relaxation/retardation time spectra do not change their shape and shift horizontally along the time scale with temperature). The classical WLF[1] equation may be used to define the shift factors, a_T, representing the contraction/amplification factor of the timescale at a given temperature in the reduced time domain, t/a_T. WLF equation derives from the linear relationships between viscosity and temperature at equilibrium, and therefore holds above the glass transition temperature, Tg. It is also well recognized that the viscoelastic functions (namely, G and K) should share the same shift factors, under equilibrium. We skip the problematic related to the correct determination of the bulk viscoelastic functions, here. Such argument was recently tackled by our group.[2] It is just to mention that due to the lack of bulk viscoelastic data and the

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relatively small strength of its whole relaxation (i.e. its relatively flat behavior) many authors considered the bulk modulus as a constant when dealing with three-dimensional loadings. Instead, we shall see that the intricacies of viscoelastic responses can be reliably predicted accounting not only for the bulk relaxation strength but also for its relative placement in respect to the remaining viscoelastic functions.

In the glassy state, where normally polymers are used for technological applications, things become more and more complex.[3] First of all the non-equilibrium state means the existence of a latent driving force pushing continuously towards equilibrium. That means that the average interatomic distance between groups sharing secondary bonds does change continuously. Thus the overall polymer stiffness actually changes, so that the viscoelastic functions, in absence of loading, change according to the internal clock of the ongoing aging phenomenon. Actually, any material changing its ‘‘structure’’ (namely, K and G) with its own internal clock is thermoreologically complex, meaning that the whole timescale of viscoelastic phenomena depends on the particular process kinetics in play (spectacular structural changes can be observed in glassy materials in the vicinity of the glass transition temperature or in thermosetting resins during chemical crosslinking, or in materials subjected to environmental degradation and so on). Thus one may ask himself which kind of formalism one should use to treat the viscoelastic response of complex materials.

To illustrate, mechanically loading glassy materials implies accounting for the current time, t, and the internal time clock, τ, of the underlying structural relaxation kinetics. Equation 1 is no longer valid under such conditions (namely, $G = G[t,\tau]$ and $B = B[t,\tau]$) and very sophisticated modelling procedures are required. The above arguments have been largely discussed and theoretically tackled in a series of papers of us.[2,4,5] Here we describe the origin of nonlinear behaviour illustrating the phenomenology of mechanically stimulated glasses.

Phenomenology

In Figure 1 the effect of the sudden application of a tensile stress on a glassy system is reported. In these figure, the full line represents the cooling path that drives the system to a glassy state 1 from an equilibrium state 0. The arrow indicates the effect of stress on the specific volume.

It has been assumed that the mechanical loading alters the thermodynamic state of the system through the isotropic part of the stress tensor, $\sigma = \frac{1}{3}\sum_{i=1}^{3}\sigma_{ii}$, that acts as a pressure.

From Figure 1 one can readily see that the stress actually alters the kinetics of volume relaxation as the controlling parameters (i.e. δ and T_f) are altered. Therefore, even if only qualitatively showed, the influence of stress on the underlying structural relaxation should be accounted in a theory dealing with the prediction of the response of mechanically stimulated glasses.

Thus mechanical stresses do perturb the structural relaxation kinetics so that, the viscoelastic relaxation process, even under the smallest mechanical perturbation,

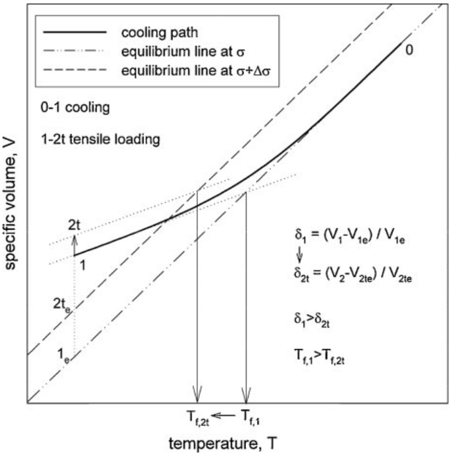

Figure 1.
The volumetric effects generated by the isotropic part of the stress tensor. The full line indicate a specific thermal history at a given point within the sample that drives the point to the ‘‘state’’ 1 from an equilibrium state 0. The mechanical loading perturbs the volume driving the system in the state 2t and consequently alters its relaxation behaviour.

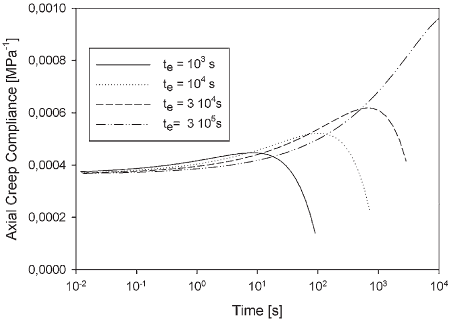

Figure 2.
"Small stress" creep compliance responses at different elapsed times, as indicated. (T = 115 °C, $\sigma = 10^{-3} MPa$). Simulations refers to samples cooled at a rate $q = 1°C/s$.

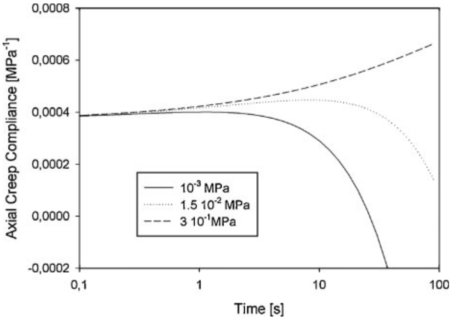

Figure 3.
The viscoelastic response subsequent to the application of "small stresses", as indicated, at a given aging time (T = 115 °C, aging time $t_{ei} = 1500$). Simulations refers to samples cooled at a rate $q = 1°C/s$.

would be nonlinear due to the non linear character of the structural relaxation, i.e. the viscoelastic response would depend on the sign and magnitude of the applied stress (pressure). In fact, polymers show significant pressure dependence of the glass structure, and therefore their response, under arbitrary loading histories can be reliably modelled if the viscoelastic and the volume relaxation phenomena are intimately linked.

The mathematical formalisms and the numerical routines used to describe the viscoelastic response of mechanically stimulated glasses have already reported. Here, we only report a series of results highlighting the reliability of our approach.

Creep

The spectacular non linear behaviour of glassy polymers is illustrated in Figure 3. Simulations based on our approach refer to Polycarbonate (LEXAN GE) at 115 °C and different times elapsed from quenching from above Tg. Creep compliance curves are nonmonotonic and possibly may reach negative values. Our group experimentally reported this behaviour in a previous paper.[5] The stress in play is very "small" and the nonmonotony arises from the competition of viscoelastic and volume relaxations acting simultaneously in opposite direction.

Similar arguments may be treated for what concerns Figure 3. Here different stress levels are probed at a given elapsed time. Again the stress in play is very "small". At the lowest stress the volume relaxation behaviour rapidly prevails and the overall response appears in its non monotonic behaviour resulting in a negative creep compliance!

Stress Relaxation

Nonlinearity is not strictly associated with the glassy state. In Figure 4 we report the volumetric response in tension and compression on "equilibrated" samples. It can be readily observed that the response is clearly non-symmetric that means that the

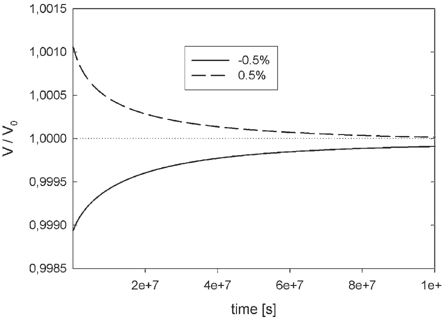

Figure 4.
Volumetric response in tension and compression on "equilibrated" samples.

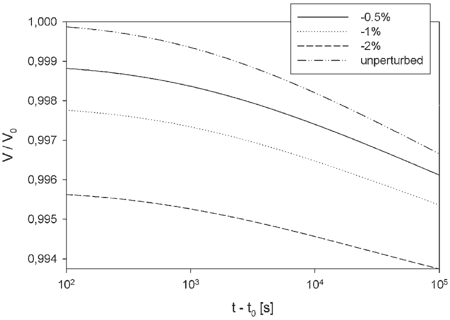

Figure 5.
Time dependent volume changes as a function of axial strain in compression for GE PC Lexan. Numbers in the legend refer to the applied strain level.

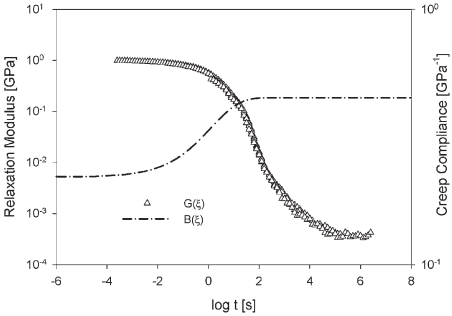

Figure 6.
The relative placement of viscoelastic functions. Symbols: experimental data, line: derived function.

viscoelastic response depends on the sign of the perturbation, a direct manifestation of non-linearity.

Different considerations arise looking at Figure 5 where the volume relaxation resulting from the application of different strains in compression in a classical stress relaxation experiment, is reported.

One may see that after the elastic, instantaneous jump, the volume continues to decrease even if the (compressive) stress is relaxing. This phenomenon is referred to as "volume implosion" and experimentally verified.[6] Our approach accounts for the fact that, deep in the glassy state, during stress relaxation experiments in compression the volumetric strain depends on the volumetric viscoelastic strain, ε_V^{σ}, and the natural contraction strain associated with the structural relaxation, ε_V^{nc}. Actually, in both tension and compression, ε_V^{nc} is a decreasing function of time because of the non-equilibrium state, i.e. $\delta > 0$. But, due to stress relaxation, ε_V^{σ} decreases with time (the stress varies from a positive value towards zero) in tension and increases in compression (the stress varies from a negative value towards zero). So that while in tension, the two phenomena (viscoelasticity and structural relaxation) act in the same direction (leading to a volume decrease – please, note that the opposite occurs when tensile creep tests are of concern), in compression the two phenomena act in the opposite direction. Therefore, while in the former case the volumetric strain is a monotonic decreasing function of time, in the latter case one cannot "a priori" predict any functional form for the volumetric strain. In fact, the volumetric strain in compression depends on both the relative strength of the two competing phenomena (viscoelasticity and the structural relaxation) and their relative timescale placement. Thus, densification in compression can occur if the rate of the stress-induced volume variation, which depends on the rate of stress relaxation (a relaxation modulus-related behaviour), is slower than the rate of the structural relaxation-induced volume variation (a bulk compliance-related behaviour). In other words, the time dependent densification in compression takes places because the characteristic time of the tensile relaxation modulus is slower than the characteristic time of the bulk compliance. This occurrence was verified by us and illustrated in Figure 6.

Conclusion

The non-linearity of amorphous glassy polymers has been discussed on the basis of experimental and numerical results coming out from our thermo-viscolastic modelling.

It has been shown that the viscoelastic response of glassy polymers is non linear (even for equilibrated glasses), the intrinsic nonlinearity being debited to the non linear character of the underlying structural relaxation phenomena. The most intriguing viscoelastic response of glassy polymers can be reliably replicated with our approach highlighting that mechanical perturbations do interact with the structural relaxation behaviour so that a constitutive link must be established accounting for this interaction.

[1] J. D. Ferry, ''*Viscoelastic Properties of Polymers*'', 3rd ed., Wiley, NY 1980.

[2] L. Grassia, A. D'Amore, The Relative Placement of Linear Viscoelastic Functions in Amorphous Glassy Polymers. *Journal of Rheology* **2009**, *53*, 339–356.

[3] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, Amsterdam 1978.

[4] L. Grassia, A. D'Amore, On the interplay between viscoelasticity and structural relaxation in glassy amorphous polymers. *J. Polym. Science. Part B, Polymer Physics* **2009**, *47*, 724–739.

[5] A. D'Amore, A. Pompo, L. Nicolais, *Comp. Sci. Technol.* **1991**, *41*, 303–325.

[6] D. M. Colucci, P. A. O'Connell, G. B. McKenna, *Polym Eng Sci* **1997**, *37*, 1469–1474.