Toward the Accurate Modeling of Amorphous Nonlinear Materials—Polymer Stress Relaxation (I)

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We expand our analytical modeling strategy for polymer non-linear stress relaxation (A) to specify the remaining steps to accurately deal with the nonaffine nature of the materials' local strains and stresses relative to their average overall values, and (B) to make it consistent with a new cooperative theory of amorphous materials dynamics, providing a model of tunable fragility that sheds light to most aspects of the behavior, including the glass transition. The stress relaxation models (1) describe a nonlinear (strain-dependent) behavior that becomes linear at very low strains, (2) quantify the effect of temperature, (3) may quantify the effects of changes in free volume, and (4) ensure very fast computations of the materials' response irrespective of the experimental time scale. The models are sensitive to the influence of different initial states of the material, as may result from varying degrees of molecular orientation and aging levels, and are able to predict from experimental stress relaxation moduli (for a poly (methylmethacrylate)—PMMA and a bis-phenol-A polycarbonate—PC) the values of the crossover frequency, v_c, crossover temperature, T_c, and the minimum activation energy, in addition to the initial and long-time plateau moduli, in agreement with independently measured values. POLYM. ENG. SCI., 00:000–000, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

In a stress relaxation experiment, a sudden strain, ε_0, is imposed on the material and then kept constant, while the measured resulting stress, $\sigma(t)$, gradually decreases. As generally recognized, this is a process more difficult to describe and model than creep (gradual strain increase under constant applied stress), which justifies that research has been more significant and advanced in the latter [1–6] than in the former [2, 7–12]. In both cases, only a limited number of workers consider physically sound, molecular-based, descriptions of the behavior but, even when the models rightly adopt a microscopic view, they tend to oversimplify the role of the participating molecular motions by considering that they are completely uncorrelated.

Other theoretical [13–15] and simulation [16–19] works, among many others, have also been published, some of which

have already been very recently discussed and compared with our theoretical predictions and experimental data in [12]. Notwithstanding their undisputed interest, limited additional discussion of these (particularly of [16–19]) will be given here, bearing in mind that the present approach distinguishes itself by being fully analytical, applicable to any time scales, computationally very fast irrespective of the time scale, and the results (i) compare well with actual experimental data for real materials, while yielding useful and meaningful predictions of relevant physical parameters (i.e., numerical values with physical units, not dimensionless), and (ii) allow extrapolation of the behavior to different temperatures and strains (well into the nonlinear viscoelastic domain) and greatly extended time scales. There is a wide computational capability and efficiency gap separating these analytical from present day molecular dynamics simulations, and so a useful comparison between the two approaches might be better justified and truly meaningful after both attain a similar stage of development with respect to both (i) and (ii) above.

One of the explicitly intended contributions of this work is to show that, not exclusively molecular dynamics simulations, but also analytical modeling can (arguably even more efficiently) be used to account for a range of local/microscopic stresses and strains in super-cooled polymer materials, while predicting the actual macroscopic experimental behavior and quantifying relevant physical properties.

A REWORKING OF THE BASIC MODEL OF REFERENCE 12

We will provide here a fuller physical discussion, to set the ground for the model's effective upgrade to (A) more accurately deal with the non-affine nature of the materials' local strains and stresses relative to their average overall counterparts, and (B) make it fully compatible with our proposed cooperative theory of materials dynamics (CSTMD) [20]. Objective B of course requires that CSTMD's basic physical and mathematical foundations be separately explained and discussed in Supporting Information in much greater depth than in [12] and [20], to firmly ground its specific application to stress relaxation.

A few features of the physical response of most materials, namely polymers, must be recognized from the outset and then effectively taken into account in any subsequent treatment, namely:

a. local atomic/molecular displacements within the material generally are non-affine relative to the macroscopic deformations, a similar thing happening with the local and overall average stresses;

b. the old concept and assumption of mainly uncorrelated local motions at the molecular scale is now unanimously untenable,