Abstract. There are several techniques to probe local mechanical properties of polymer systems. Two frequently used techniques are indentation and scratching, also known as sliding friction. The first is used to determine material parameters such as Young’s modulus and yield strength, the later to resolve issues concerning friction and wear properties. Both techniques are based on contact of a specimen with a well-defined indentation/scratching geometry. If we take a closer look at an indentation experiment, an indenter is pressed into the material and a force, the so called normal force, and penetration into the surface are measured. For the scratching experiment an extra sliding dimension is added and besides the normal force and penetration depth, a lateral force and sliding distance are measured. The first step of a scratching experiment is indentation; this implies that before we can start with investigation of sliding phenomena, all the phenomena governing indentation have to be captured. For polymers this technique should be used with great care, this because of the strong non-linearity and rate dependence of polymer systems. To understand both contact phenomena a combination of experiments and numerical techniques are used. To comprehend macroscopic polymer deformation a polymers’ intrinsic deformation should be captured accurately. This deformation behavior is used as input for our constitutive model and subsequently the model is used for finite element calculations.

Keywords: polymer glasses, solid state rheology, indentation, friction
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INTRODUCTION

Currently there are several constitutive models available that accurately capture the deformation characteristics of glassy polymers [1, 2, 3]. The typical approach to describe the deformation kinetics, which is dominated by a single molecular process, is to use a single-relaxation time, i.e. thermorheological simple, with parallel strain hardening. This type of modeling proved to be successful in capturing experimentally observed phenomena such as necking, crazing and shear banding as well as life time predictions under static load [3, 4, 5]. Despite these successful applications, some problems remain. An important one being the fact that the pre-yield regime is not accurately described, leading to an incapability to capture recovery/unloading phenomena. This typically becomes a problem when looking at contact phenomena like indentation and sliding contact, i.e. friction and wear experiments, where recovery directly influences the real contact area between a single asperity and the polymer. To qualitatively give a verdict on intrinsic friction properties one needs to capture these phenomena accurately.

The cause of this problem is mainly that a single-relaxation time description is, by definition, not capable of capturing the time-dependent mechanical properties of glassy polymers, with relaxation spectra that spread out over many tens of decades. Moreover, in most cases the polymer’s response is determined by several molecular processes, each leading to a spectrum of relaxation times with its own non-linearity and temperature dependence.

An elegant solution to the problems mentioned above is therefore the introduction of a multi-relaxation time model which captures the non-linearity of the pre-yield regime [6] and keeps the framework of the large strain post-yield response in tact [3, 7]. The proposed model, which is based on a multi-mode Maxwell model including time-stress superposition, adequately describes the deformation under monotonic loading. An extension to several molecular processes is rather straightforward.

The strength of this approach will be demonstrated on PC and PMMA. A new characterization method is presented that gives a direct estimate of the required relaxation time spectrum directly from constant rate compression or tension experiments. The spectrum thus obtained can not only accurately describe the loading curves at different strain rates, but is also very successful in describing constant rate load-unload contact problems. Similar to the single relaxation time approach, the influence of thermal history can be included by introduction of an age-dependent state parameter, leading to the definition of a reference state; the un-aged state.
CONSTITUTIVE MODEL

The model presented here is a modification of the Eindhoven Glassy Polymer Model, which is published in its latest form in Klompen [8]. The model is based on an additive decomposition of the total stress tensor into a driving and hardening stress. Physically this can be interpreted as the part describing the inter-molecular interactions, and the latter capturing the network contribution. This is modeled by placing a single Maxwell element parallel to a neo-Hookean spring, according to

\[ \sigma = \sigma_d + \sigma_r = \sigma_d^b + \sigma_d^r \]

\[ = \kappa (J-1) I + G \tilde{B}_e^d + G_r \tilde{B}_e^d. \]

where \( \kappa \) is the bulk modulus, \( J \) the volume change ratio, \( I \) the unity tensor \( G \) the shear modulus \( G_r \) the hardening modulus and \( \tilde{B}^d \) the isochoric deviatoric left Cauchy-Green strain tensor where subscript \( e \) denotes its elastic part.

The plastic deformation rate tensor is coupled to the deviatoric stress via a non-Newtonian flow rule with an Eyring viscosity according to

\[ D_p = \frac{\sigma_d^P}{2\eta}; \quad \eta = \eta_0 \cdot \frac{\bar{\tau}/\tau_0}{\sinh(\bar{\tau}/\tau_0)} \cdot \exp \left[ \frac{\mu p}{\tau_0} \cdot \exp[S_a \cdot R(\tilde{\eta}_p)] \right]. \]

The modification we applied is by replacing the single Maxwell element by a parallel combination of \( n \) Maxwell elements each with their own shear modulus and zero shear viscosity.

\[ \sigma = \kappa (J-1) I + \sum_{i=1}^{n} G_i \tilde{B}_e^d + G_r \tilde{B}_e^d. \]

This with the unique feature where the viscosity of each mode depends on the total driving stress,

\[ \eta_i = \eta_0 \cdot \frac{\bar{\tau}/\tau_0}{\sinh(\bar{\tau}/\tau_0)} \cdot \exp \left[ \frac{\mu p}{\tau_0} \cdot \exp[S_a \cdot R(\tilde{\eta}_p)] \right]. \]

According to the Eyring theory this is allowed, because the stress activation of a single molecular process is governed by the total applied stress.

With a spectrum of relaxation times and corresponding shear moduli obtained at a specific strain rate, we simulate the intrinsic deformation at two other strain rates and an excellent agreement between experimental data and simulations is obtained, see figure 1a. Also the dependence on difference in thermal history is tested. It can be shown that a spectrum obtained at a specific initial age can be shifted to any age with the age-dependent state parameter. Thus a unique spectrum, independent on strain rate and thermal history, can be defined.

APPLICATION

To test the multi mode model, we applied it on flat-tip indentation experiments. We performed indentation experiments on PC and PMMA at different indentation speeds as well as on PC with difference in initial age. In figure 1b one can clearly see that in the case of single mode modeling we do an underestimation of the loading part together with an inadequate approximation of the unloading part, this is due to the underestimation of the initial shearmodulus, see figure 1a. As depicted in figure 1b it is obvious that a multimode description is necessary for an adequate load/unload simulation.

CONCLUSIONS

With our extended constitutive model we show that we get an excellent description of the intrinsic deformation observed in glassy polymers. Together with the good agreement between simulation and experiment of the flat-tip indentation, see figure 1b, gives us confidence that we can apply the same strategy to solve issues concerning intrinsic friction and wear properties of polymer glasses.
FIGURE 1. differences between single mode (...) and multimode simulations (−) as compared to experimental data (markers), where on the left is the strain rate dependence on intrinsic deformation and on the right the load-displacement curve in a flattip indentation experiment.

REFERENCES