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Mechanical properties of thin polymer films close to the glass transition: a mesoscale model DIDIER R. LONG, ALAIN DEQUIDT, PAUL SOTTA, CNRS/Rhodia — Polymer dynamics slows down in the vicinity of a solid substrate (when interactions are sufficiently strong), as can be evidenced experimentally by measuring the glass transition temperature Tg in thin films. We extend here the Long and Lequeux model which quantitatively accounts for this effect. We describe the mechanical properties of the polymers on the scale of dynamical heterogeneities (of a few nanometers). We propose a constitutive relation regarding the local relaxation time, the local stress, and the deformation history. The mechanical equations coupled to these constitutive relations are solved, allowing to reach a scale of a few tens of nanometers and macroscopic time scales. In particular, we measure the elastic modulus G' as a function of temperature, for various films thicknesses. This measurement allows for measuring the glass transition temperature of the film as a function of thickness. The results show that the glass transition temperature is shifted as compared to the bulk (corresponding to large film thickness), depending on the strength of the polymer/substrates interaction, with values which are consistent with experimental results.

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