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Molecular dynamics simulations of entangled polymers: The effect of small molecules on the glass transition temperature

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Abstract

Effect of small molecules, as they penetrate into a polymer system, is investigated via molecular dynamics simulations. It is found that small spherical particles reduce the glass transition temperature and thus introduce a softening of the material. Results are compared to experimental findings for the effect of different types of small molecules such as water, acetone and ethanol on the glass transition temperature of a polyurethane-based shape memory polymer. Despite the simplicity of the simulated model, MD results are found to be in good qualitative agreement with experimental data.

Keywords: molecular dynamics, polymers, glass transition, diffusion

1   Introduction

Polymeric materials are ubiquitous in nature and every day life. Due to their low density relative to the metallic materials, low thermal and electric conductivities, they are often used as protective coatings and insulators [Armstrong & Wright, 1993] but more recently find applications in nanotechnology [Brieger *et al.* , 2006], and even electric circuits and transistors [Noh *et al.* , 2007]. A special focus in research and development of polymers has been to improve the mechanical properties in order to foster the use of polymer-based materials in structural applications. The physical properties of polymers are closely related to several factors. Beside the truly obvious ones like for example the type of polymer itself or the processing parameters, there is strong dependence on the processing history of the polymer. This particularly applies to shape memory polymers, where the actuation and shape recovery depend on all thermal, mechanical, and chemical steps along the materials processing and programming chain [Lendlein & Behl, 2007].

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One of the major issues here regards the effect of environment on thermal and mechanical properties of polymers [Marquardt *et al.*, 2016]. Under usual conditions, polymer materials are in contact with a gas or liquid environment and are thus subject to the penetration of small molecules. The incorporation of small molecules can alter the mechanical properties of polymers strongly. In the case of plasticizers in e.g. PVC, this is desired and necessary. On the other hand, the uncontrolled take-up of low molecular substances by polymers may lead to a degradation of the material and reduce its service life time.

A way to quantify this effect is a survey of the glass transition temperature and its dependence on the concentration of small molecules diffused into the polymer sample. The present work focuses on this issue via molecular dynamics simulations of a generic polymer model [Baschnagel & Varnik, 2005]. Results obtained from simulations are also compared to experimental measurements. Despite the simplicity of the investigated model, qualitative trends observed in the present computer simulations agree well with experimental results.

The paper is organized as follows. In the following section, the model is introduced. Section 3 compiles the results and a discussion thereof. A brief summary and outlook closes the manuscript.

2   Model

A generic model of polymer with finite extensible nonlinear elastic (FENE) potential has been employed during present simulations [Kremer & Grest, 1990], which allows to focus on generic rather than materials specific aspects. Small molecules are introduced as spherical particles. All particle pairs interact via a Lennard-Jones (LJ) potential,

$$U_{\alpha\beta}^{\mathrm{LJ}}(r_{\alpha\beta}) = 4\epsilon_{\alpha\beta}[(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}})^{12} - (\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}})^6], \tag{1}$$

where $\alpha, \beta \in \{\mathrm{p}, \mathrm{s}\}$, and p and s stand for polymer and small molecules, respectively. The LJ potential is truncated and shifted to zero at a cutoff radius of $r_{\mathrm{c}} = 2 \times 2^{1/6}\sigma_{\alpha\beta}$. $\sigma_{\mathrm{pp}} = 1$ is chosen as the unit of length. The diameter of small molecules is chosen to be half of the monomer diameter, $\sigma_{\mathrm{ss}} = 0.5$ and σ_{sp} is obtained as the arithmetic mean, $\sigma_{\mathrm{sp}} = 0.5(\sigma_{\mathrm{pp}} + \sigma_{\mathrm{ss}})$. The energy scale of the Lennard-Jones potential is chosen to be independent of the particle type, i.e. $\epsilon_{\mathrm{pp}} = \epsilon_{\mathrm{ss}} = \epsilon_{\mathrm{sp}} = 1$. The connectivity of covalent bonds along the chain's backbone is ensured by a finite extensible nonlinear elastic (FENE) potential [Kremer & Grest, 1990],

$$U_{\mathrm{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln[1 - (\frac{r}{R_0})^2], \tag{2}$$

where $k = 30\epsilon_{\mathrm{pp}}/\sigma_{\mathrm{pp}}^2$ is the strength factor and $R_0 = 1.5\sigma_{\mathrm{pp}}$ the breaking limit of covalent bonds. The superposition of the FENE and the LJ potentials prevents monomers from overlapping while establishing a steep bonding potential with an equilibrium bond length of $b \approx 0.96\sigma_{\mathrm{pp}}$. It is important to note that this preferred bond length is incompatible with the length scale preferred by the LJ potential for non-bonded interactions, $r_{\mathrm{min,LJ}} \approx 1.12$. This leads to a geometric frustration and facilitates glass formation [Varnik *et al.*, 2002].

The chain length (number of monomers per chain) is set to $N_{\mathrm{p}} = 64$ which is larger than the entanglement length of the model ($N_{\mathrm{e}} \approx 32$ [Baschnagel & Varnik, 2005]). Figure 1 illustrates the model and shows a snapshot of the simulation cell.

The unit of time is given by $\tau_{\mathrm{LJ}} = (m\sigma_{\mathrm{pp}}^2/\epsilon_{\mathrm{pp}})^{1/2}$, where m is the mass of a monomer or a small particle ($m = 1$ for both particle types). Temperature is measured in units of $\epsilon_{\mathrm{pp}}/k_{\mathrm{B}}$