

Shear and entanglement of polycarbonate blends adsorbed on a nickel surface

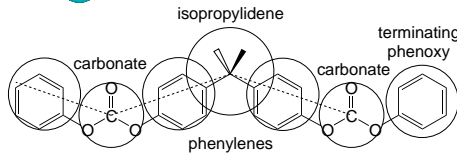
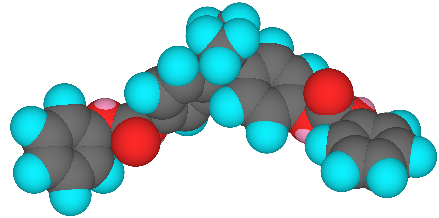
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Motivation

Why polycarbonates?

- High impact strength, ductility, high glass transition and melting temperatures, good mechanical and optical properties
- Ideal material for compact discs, automotive components, and ophthalmic applications [1]
- Attractive test system for the coarse-graining techniques [2]



Chemical structure and coarse-graining scheme of a bisphenol-A-polycarbonate (BPA-PC) molecule. Only one repeat unit is shown.

Simulation details

Studied systems

(1) BPA-PC melts with different chain lengths: $N_1 = 20, 10, 5$ repeat units (2) blends with the major component $N_1 = 20$ and the following additives: $N_2 = 5, 1$ repeat units, diphenyl carbonate (DPC) (all 5% in weight), or phenol (1% – 10% in weight).

Interactions

Ab initio calculations [4, 3] suggest that the internal beads have a weak interaction with the surface but phenylene ends are strongly attracted to it.

A coarse-grained model is used to describe the BPA-PC molecules. Each repeat unit is represented by four beads. The parameters of the interaction are obtained from the *ab initio* calculations and the MC simulation of a single atomistic chain in vacuum [2].

Simulation details

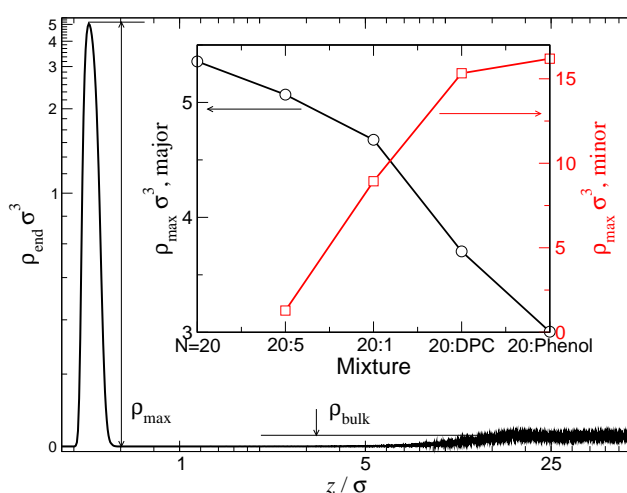
We use *NVT* ensemble with Langevin thermostat which is switched off in the shear direction. The shear rate is

$$s = 2v_w / L_z \tau_r, \quad (1)$$

where τ_r is the Rouse characteristic relaxation time.

Results

Different additives

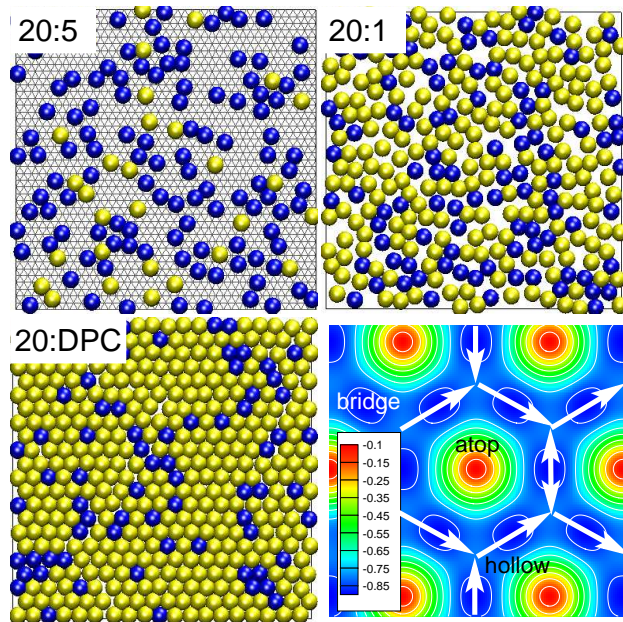


Chain end density profiles for different mixtures. Inset: the maximal density of major and minor component in different mixtures, respectively.

Diphenyl carbonate and phenol provide the most efficient screening of the interaction between the melt and the surface.

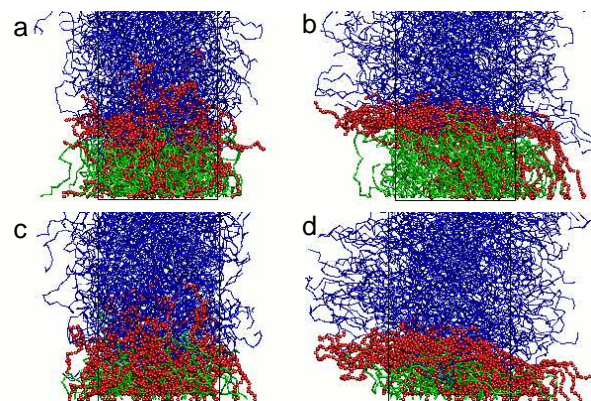
Acknowledgments

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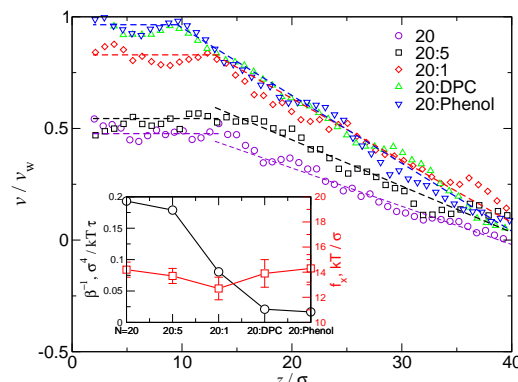
Snapshots of the chain ends adsorbed on the wall. The blue beads are the chain ends of the major component, and the yellow - of the additive.

The adsorbed layer of the 20:5 mixture has a structure of a 2D gas; the packing of the 20:1 mixture is similar to a 2D liquid; for the 20:DPC as well as 20:Phenol mixtures the adsorbed chain ends form a 2D crystal.



Snapshots of the mixtures: 20:5 without (a) and with (b) shear ($s=10$), 20:phenol without (c) and with (d) shear ($s=10$). Green: chains which adsorb both ends; red: only one end (red); blue: no ends

- The decrease in the number of the adsorbed chain ends of the major component results in thinning of the adsorbed layer.
- Under shear the one-end attached chains disentangle from the melt.



Normalized velocity profiles. Inset: the friction force and the friction coefficient.

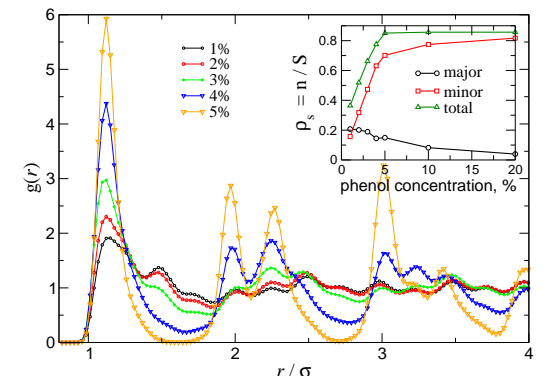
$$f = \beta(v_w - v_s) = \eta \frac{dv}{dz}. \quad (2)$$

The friction coefficient β depends on the density of the attached chain ends.

References

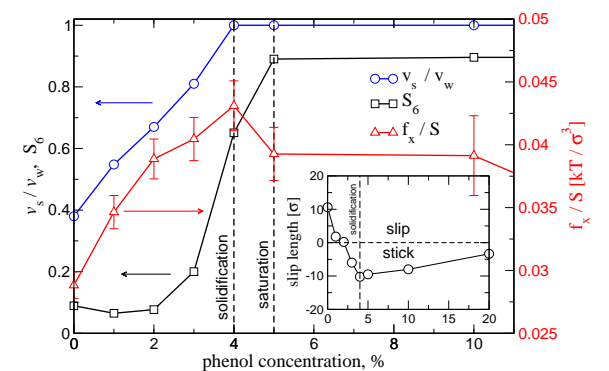
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- [2] C. F. Abrams, and K. Kremer, *Macromolecules* **36**, 260 (2003).
- [3] L. Delle Site, A. Alavi, and C. F. Abrams, *Phys. Rev. B* **67** (2003).
- [4] L. Delle Site, C. F. Abrams, A. Alavi, and K. Kremer, *Phys. Rev. Lett.* **89** (2002).
- [5] X. Zhou, D. Andrienko, L. Delle Site, and K. Kremer, *EuroPhys. Lett.* **70**, 264 (2005).
- [6] X. Zhou, D. Andrienko, L. Delle Site, and K. Kremer, *J. Chem. Phys.* (2005).

Different concentrations



The 2D radius distribution function of attached chain ends in the mixtures of BPA-PC and phenol (1%-5% in weight).

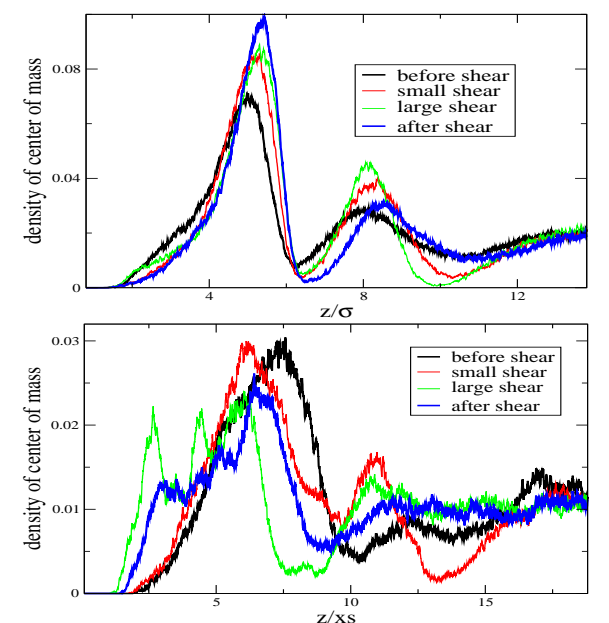
The adsorbed chain ends form 2D crystal in the mixtures with larger phenol concentration.



The normalized slip velocity $1 - v_s/v_w$, the bond orientational order S_6 , and the friction force f_x in the mixtures with different phenol concentration. Inset: the slip length in these systems.

A transition from the slip to the no-slip boundary condition occurs upon increasing the phenol concentration in the mixture.

Different chain lengths



The center of mass density of the BPA-PC melt with two different chain length $N = 10$ (up) and $N = 20$ (down), respectively.

For short polymers, more chain ends adsorb on the surface; the adsorbed ends do not desorb when the shear is removed.

For longer polymers, chain ends can desorb due to the increase of the shear force on a single molecule; some chains re-adsorb after removing the shear.

Summary

- The slip boundary condition changes to the no-slip when the epitaxial ordering of the adsorbed parts of the chains locks the motion of the surface layer.
- At high shear rates, entanglement of the adsorbed chains with the bulk of the melt leads to the chain desorption.