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Historical perspective

How irreversible adsorption affects interfacial properties of polymers

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ABSTRACT

Growing experimental evidence shows that the behavior of polymer chains confined at the nanoscale level strongly depends on the degree of adsorption correlated to the number density of monomers pinned onto the supporting substrate. In this contribution, after introducing the physics behind the mechanisms of irreversible adsorption, we review recent experimental observations on how adsorption affects properties of polymer melts confined in 1D, focusing on those related to the thermal glass transition, maximum water uptake, viscosity and crystallization. These findings strongly support a new physical framework of confined soft matter, not trivially limited to finite size effects and interfacial interactions, but also enriched by non-equilibrium phenomena.

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1. Introduction

The glassy dynamics of soft materials confined at the nanoscale level has been object of intense investigation since more than 20 years [1,2]. The interest toward the dynamics at the nanoscale originated from the large success of theories predicting a characteristic length scale of the glass transition, ξ , on the order of a few nm [3]. As a consequence, glass-forming materials would show finite size effects when confined into objects having at least one dimension reduced to a few ξ 's; 1D confinement is for example obtained in thin films, while 2D and 3D confinement is instead achieved in nanopores and nanospheres, respectively.

Importantly, regardless of their premises, different theoretical approaches provide the same temperature dependence of ξ , which increases upon cooling, reaches 1–5 nm at the glass transition temperature, T_g , and diverges at a critical temperature $T_c < T_g$. In the model proposed by Adam and Gibbs [4] in 1965, ξ is given by the characteristic dimension of the cooperative rearrangement region (CRR), corresponding to the smallest volume inside which a transition to a different configuration can take place, without perturbing the position of molecules outside the region and on its boundary. According to the Random First Order Transition theory (RFOT) [5], ξ is identified as the dynamics correlation length of the within *entropic droplets*, solid-like regions with aperiodic crystalline structure. ξ here represents also the characteristic length scale of the dynamic heterogeneity, as the entropic droplets are spatially and morphologically independent. In the framework of the two-order-parameter model (TOP) [6–8] a similar scenario

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is proposed. Droplets are replaced by solid-like regions with medium range crystalline order (MRCO) forming inside the isotropic liquid, and the concept of cooperative motion is reinterpreted via orientational correlation among neighboring molecules, stimulated by the presence of directional bonds [9]. Despite the large efforts to verify the correctness of the prediction on $\xi(T)$, it is now evident that the behavior of confined glassformers is affected by more than just these simple finite size effects [10,11]. As a matter of fact, interfacial interactions alter conformations and trajectories of molecules in proximity of interfaces at length scales way larger than ξ . Consequently, the mere effect of finite size effects cannot be promptly deconvoluted from that of interfacial interactions. But, *how do interfaces affect dynamics?* Focusing on the glassy dynamics of nanoconfined polymers [2,12,13], the most widely investigated phenomenon, both the roughness of the supporting interface and the nature of the interaction potential between monomers and substrate should be considered. For a comprehensive introduction to the glass transition of polymers in bulk, confined geometries, and near interfaces the reader may refer to a recent review paper [14], here we will focus on those perturbations in T_g imposed by solid interfaces. Seminal work by Scheidler et al. predicted an increase in structural relaxation time, τ , and hence slower dynamics for Lennard-Jones fluids in proximity of rough substrates [15,16]. In the case of polymers, this hypothesis has not yet been verified. How the interfacial potential affects dynamic is, instead, still argument of debate. Experimental evidence by Fryer et al. indicated a linear proportionality between the shift in thermal T_g – the transition point, between the non-equilibrium glassy state and the equilibrium liquid (rubbery) state, observed while scanning at constant rate the temperature dependence of quantities sensing volume, e.g. via ellipsometry or capacitive dilatometry, enthalpy, e.g. via calorimetry, ... – and the interfacial energy [17]. Further analysis by Napolitano and coworkers [18] and more recently by Floudas and coworkers [19] confute the original trend proposed by Fryer. Moreover, further confusion in these analyses is given by the assumption that a shift in thermal T_g is univocally related to a change in dynamics, that is, an increase in thermal T_g would correspond to slower interfacial dynamics, while a reduction in τ would be related to a drop in thermal T_g . Such a correlation, valid in bulk via the Frenkel-Kobedo-Reiner relation [20] is actually not granted upon confinement –for a review on the breakdown of this fundamental relation the reader may refer to the work of Priestley and coworkers [21] and to the seminal papers of Fukao et al. [22] and Boucher et al. [23]

A solution to this problem could come from the recent hypothesis of Simmons and coworkers [24,25], correlating the ratio between the confined and the bulk thermal T_g to its suppression in a freestanding film of equivalent thickness, increased by a factor proportional to the work of adhesion and the softness of confinement. The latter quantity is an exponential term of the ratio of the Debye-Waller factors of the confining medium (substrate) and of confined material, while the former indicates the energy necessary to separate the polymer and the substrate to an infinite distance. The work of adhesion, ΔW , can be parameterized as: [26]

$$\Delta W = N_{dir} (W_{mm} + W_{ss} - 2\sqrt{W_{mm}W_{ss}}) = N_{dir} W_{ms} \quad (1)$$

where m and s respectively indicate monomer and substrate properties, W_{ij} is the energy per unit area to bring in contact the species i and j in vacuum, and N_{dir} is the number of monomers in direct contact with the substrate. The experimental validity of this assumption is ensured by measurements performed before the publication of the model [11, 27]. Here we stress on the evidence that, of all the parameters present in this framework, only N_{dir} can be finely tuned. The others are univocally identified once film thickness and the chemical nature of the polymer and substrate has been fixed.

Routes to create materials with desired interfacial dynamics should then focus on methods allowing a direct control of the number of

monomers in direct contact with the substrate. The most straightforward way to achieve this goal is to control the amount of polymer chains adsorbed onto the substrate. In the following sections, after introducing our recent work on the kinetics of adsorption of polymer melts, we revise current literature on how adsorption affects the properties of polymers confined at the nanoscale level.

2. Kinetics

Previous work, based on limited data set, proposed that the kinetics of adsorption of polymer melts onto solid substrates should follow a saturating exponential law [28] of the type

$$h_{ads}(t) = h_{t=0} + \Delta h [1 - \exp(-t/t_{ads})] \quad (2)$$

where h_{ads} is the thickness of the adsorbed layer, $h_{t=0}$ is its value at $t = 0$, Δh the increase in thickness during the whole kinetics and t_{ads} a characteristic time of the process. The use of thicknesses of the adsorbed layer rather than an adsorbed amount is justified by the extremely small surface roughness of this samples (typically $< 4 \text{ \AA}$) [29,30] and by the direct proportionality between adsorbed amount and thickness, valid in the hypothesis of density of the adsorbed layer comparable to that of bulk samples. The latter hypothesis is verified considering the linear relationship with slope on the order of unity between the absolute values of thickness values obtained via atomic force microscopy and the result of an ellipsometric model using bulk density [31].

Eq. (2) represents a kinetics where the adsorption rate is proportional to the space available at the adsorbing interface. While valid in the case of small molecules, this expression cannot be applied to polymers since it implies that molecules assume always the same conformation within the whole adsorption process, and that the “pinning” of molecules is a reversible process. On the contrary, experimental work by Granick and coworkers [33] showed that the number of contact made by a chain onto the substrate decreases with the adsorption time and, in turn, chain conformations change with the thickening of the adsorbed layer, as confirmed by work by Koga and coworkers [34,35] – to which the reader might refer for a discussion on the structure of adsorbed layers. Moreover, even in the case of an energy gain upon pinning of one monomer is smaller than $k_B T$, the process of adsorption of the whole chain is irreversible: [36,37] desorption of one entire macromolecule would require the coordinated desorption of (almost) all the directly adsorbed monomers, which is an extremely unlikely event.

Based on a large data set [31], see a few examples in Fig. 1, comprising measurements at different temperatures above T_g on monodisperse samples of polystyrene (PS) within a broad molecular weight range, we proposed a new form of the kinetics of irreversible adsorption for polymer melts including a linear growth at short annealing times followed by a logarithmic thickening at longer times: [25]

$$h_{ads}(t) = \begin{cases} h_{t=0} + vt & t \ll t_{cross} \\ h_{cross} + \Pi \log(t/t_0) & t \gg t_{cross} \end{cases} \quad (3)$$

where v and Π are respectively the growth rate in the linear regime and in the logarithmic regime, h_{cross} and t_{cross} are the coordinates (thickness and time) of the crossover point between the linear regression of $h_{ads}(t)$ at short annealing times and the logarithmic trend at longer times, and $t_0 = 1 \text{ s}$.

The linear regime, reconcilable with Eq. (2) for $t/\tau \ll 1$, is related to a first order reaction mechanism where adsorption proceeds based on the availability of monomers and free space at the interface. As the occupied surface approaches saturation, such a simple adsorption mechanism becomes less probable, chains need to stretch at the cost of a larger entropic penalty, before pinning. Such process is self-retarding and induced a reduction of the adsorption rate, in line with a logarithmic growth.

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