Taming the Strength of Interfacial Interactions via Nanoconfinement

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Supporting Information

ABSTRACT: The interaction between two immiscible materials is related to the number of contacts per unit area formed by the two materials. For practical reasons, this information is often parametrized by the interfacial free energy, which is commonly derived via rather cumbersome approaches, where properties of the interface are described by combining surface parameters of the single materials. These combining rules, however, neglect any effect that geometry might have on the strength of the interfacial interaction. In this Article, we demonstrate that the number of contacts at the interface between a thin polymer coating and its supporting substrate is altered upon confinement at the nanoscale level. We show that explicitly considering the effect of nanoconfinement on the interfacial potential allows a quantitative prediction of how sample geometry affects the number of contacts formed at the interface between two materials.

The performance of multiphase systems, as nanocomposites and hybrid nanomaterials, depends on the work of adhesion, $\Delta W$, necessary to separate the different phases to an infinite distance in vacuum. This quantity, whose estimation is a major requirement in several engineering applications, is proportional to the number of contacts, $n$, formed at the interface. Because the determination of $n$ requires a microscopic description of the interface, approximate macroscopic methods are adopted in practice. For example, the Good–Girifalco–Fowkes equation, one of the most known among the combining relations present in the literature, describes the interfacial free energy between two immiscible materials A and B, $\gamma_{AB}(\equiv -1/2 \Delta W)$, as a function of dispersive (van der Waals) and polar components; the latter term is further parametrized in terms of the electron-donor and the electron-acceptor contributions. For each phase, three parameters are determined by an experimental procedure in which contact angles of three (or more) reference liquids are measured. These parameters are then used to solve a (overdetermined) system of equations, leading to results too often depending on the chosen triad of liquids. In the case of thin polymer films deposited onto solid substrates, we prove that the number of contacts between polymer and substrate, a quantity directly proportional to the work of adhesion, is actually correlated to sample geometry. A substantial drop in adsorbed amount and in turn in $\Delta W$ is observed upon reduction of the polymer film thickness below 5–10-fold the macromolecular size, $R_g$, that is $\ll 30–300$ nm (see Figure 1), or when the adsorbing coating is capped by another polymer layer (see Figure 2). We explain these effects considering how interfacial interactions are tamed by nanoconfinement.

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In our experiments, we spin-coat ultrathin polymer films of different film thickness $L$ (corresponding to the range $2-30 \, R_g$) onto Si substrates, covered by a native oxide layer ($\approx 2 \, \text{nm}$). Samples are annealed over time under isothermal conditions above the glass transition temperature to favor adsorption of chains onto the supporting substrate; the nonadsorbed material is washed away in a good solvent, following Guiselin’s experiment. The adsorbed layer thickness is an operational parameter directly proportional to the number of chains adsorbed per unit area, $\Gamma$, is measured via ellipsometry and atomic force microscopy (Materials and Methods section in the Supporting Information (SI)). For a
given polymer and a given molecular weight, $\Gamma$ is strictly proportional to the number of directly adsorbed monomers, and thus to the number of contacts between macromolecules and substrate (see eqs S1–S6).

Figure 1F shows the adsorption kinetics for films of polystyrene (PS) of three different spin-coated thicknesses. At short times, the growth of the adsorbed layer proceeds irrespectively of the film thickness, which implies the lack of nanofluctuation effects on the monomer adsorption rate. At later times, a pronounced reduction in $\Gamma^\infty$, the equilibrium adsorbed amount corresponding to the value reached after prolonged annealing, is observed as the film thickness decreases. This quantity is directly related to the depth of the interfacial potential (see the SI for additional details on the kinetics of adsorption). Nanoconfinement, therefore, mitigates the strength of interfacial interactions, without affecting the mechanisms of adsorption (see Figure 1F, and Figures S1, S2, S10, and S12). This observation is in line with our previous work,23,24 showing that adsorption originates from the London potential, and thus to the number of contacts at the PS/SiO$_2$ interface depends on the value of $A_{\text{eff}}$ only and not on the thickness of the single spin-coated layers.

Finally, we have extended our investigation to thin films of monodisperse PS samples of different polymerization degree, $N_i$ covering a broad range of molecular weights ($\approx$50–1500 kg/mol). A linear relation between $\Gamma^\infty$ and $A_{\text{eff}}$ was verified for all samples, regardless of chain length (see Figure S11). We remark that, while the thickness dependence of the Hamaker constant does not depend on the molecular weight, the number of chains necessary to cover a surface of unit area does. Because the number of contacts a polymer chain makes with a flat substrate scales as $N_i^{-1/2}$ ($\sim R_i^{-1}$), all data collapse in a master plot where the normalized adsorbed amount is presented as a function of $L/R_i$, see Figure 1D.

Such a plot reveals that a size-independent value of $\Gamma^\infty(L)$ is reached at thicknesses $L > L_0 \sim 7R_i$. In our reasoning $L_0$ indicates the thickness at which the number of polymer/substrate contacts reaches a given value, ensuring bulk work of adhesion. Remarkably, the onset of confinement effects on the adsorbed amount ($\sim 7R_i$) is in line with the length scale within which properties of the air/polystyrene surface are affected by the substrate.38 While it seems unrealistic to rationalize such unexpectedly large molecular length scale via mechanisms involving adsorbed chains having at least one monomer in the polymer/surface layer,39 our results indicate that confinement effects are directly ascribable to changes in work of adhesion, in agreement with the outcome of recent in silico experiments.35

In view of the results in Figure 2, we conclude that in thin polymer coatings the equilibrium adsorbed amount deviates from bulk value, following the modification in the strength of the interaction potential induced by confinement in nanoscopic geometries. We remark that the trend observed for the impact of nanoconfinement on the kinetics of adsorption, see Figure 1F, is shared by other nonequilibrium phenomena, e.g., physical aging,36 where the kinetics of equilibration (in our case the monomer adsorption rate) are not affected by a change in thermodynamic driving force (the depth of the interfacial potential).

At a fundamental level, determination and modeling of the interaction of two materials placed in intimate contact should take into account this experimental evidence. On a more applied side, the method described in this Article allows tuning the equilibrium adsorbed amount—a quantity permitting control of glass transition temperature,37,38 crystallization ability,39 viscosity,40 etc.—without modification of the polymer/substrate pair, even without altering the thickness of the
spin-coated film (L), which has never been accomplished before.

**METHODS**

Thin films of polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(4-tert butyl styrene) (PbTS), and poly(4-methylstyrene) (P4MS) were prepared by spin-coating dilute solutions of the polymers in good solvents (benzene for PMMA, toluene otherwise) onto silicon wafer substrates. Details on molecular weight, polydispersity, and source of the polymers used in this study are presented in Table S1; further information on sample preparation is provided in the SI; no unexpected or unusually high safety hazards were encountered. Film thickness, L (from 10 to 500 nm, corresponding to the interval 2Rq < L < 30Rq), was varied by changing the concentration of the polymer solution. Spin-coated films were dried in vacuum and preannealed above the glass transition temperature, to allow structural relaxation without altering the adsorbed amount. The value of the spin-coated thickness was determined after drying, via ellipsometry. For the experiments in Figure 2E, we fabricated a series of multilayers of the type air/PS/SiO2/Si following the procedure described above; then we spin-coated solutions of PMMA in acetic acid directly onto the PS films—as polystyrene is not soluble in acetic acid, the previously spin-coated films of PS are not affected by the deposition of the upper layer. The samples were again dried in vacuum for 20 min and preannealed as described above. For the adsorption experiments, spin-coated films of thickness L were annealed on a hot plate for different times to allow for adsorption of polymer chains onto the substrate. After annealing, nonadsorbed polymer chains are washed off reproducing Guiselin’s experiment; samples were rinsed and soaked for a fixed time in the same good solvent used to prepare the spin-coated solutions, in a one-step protocol for the monolayer samples and a two-step (first in acetic acid, then in toluene) protocol for the bilayer samples. The thickness of the adsorbed layer, hads, a direct measurement of the adsorbed amount, was measured using ellipsometry (MM-16, Horiba), using a bulk optical method, validated by independent measurements via atomic force microscopy.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.8b00240.

Methods for the preparation of single-polymer-layer and polymer-bilayer systems; determination of spin-coated thicknesses and the adsorbed amount via ellipsometry; data handling and fitting to the kinetic model of irreversible adsorption; the effect of nanoconfinement on the kinetics of irreversible adsorption, on the calculation of the effective Hamaker constant, including the role of retardation forces; and figures on the role of finite size effects on the kinetics of adsorption, on the impact of molecular weight on the adsorbed amount and a comparison of adsorption kinetics of single and bilayer systems having the same Hamaker constant (PDF)

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**Notes**

The authors declare no competing financial interest.

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