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Attachment of polymer chains on plasma-treated surfaces: experiments and modeling

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Abstract. Deposition of linear polymers, such as polyethylene glycol (PEG), on a plasma-treated surface has been studied experimentally and theoretically by means of Monte Carlo (MC) simulations. Acrylic acid is deposited on a silicon wafer in the presence of argon at a pressure of 10 Pa by applying 30 W external power. Active carboxyl sites are obtained having a surface number density of $\sim 2 \text{sites nm}^{-2}$. A homogeneous PEG solution is brought into contact with the treated surface (over 24 h) and a thin film of attached PEG chains is formed. Two different PEGs having molecular weights of 3000 and 5000 g mol\(^{-1}\), respectively, are considered. The corresponding thin film widths, $W$, are measured, yielding $W(3000) = 4.3 \pm 3.1 \text{nm}$ and $W(5000) = 8.8 \pm 1.8 \text{nm}$. For the MC simulations, the linear polymers are modeled as an ensemble of self-avoiding walks of length $N$ (number of monomers) on a simple cubic lattice, executing worm-like or reptation dynamics, which can become attached at an active carboxyl site on the surface. The numerical results for the film widths are in good agreement with the experimental findings. We find that less than 20\% of active sites are effectively occupied by attached chains, corresponding to less than 5\% of the total available surface sites. Scaling arguments predict universal power-law dependences of the film density, $\rho(N)$, as a function of polymer length, i.e. $\rho(N) \sim c/N^v$, with $c \simeq 5 \text{g cm}^{-3}$ and $v \simeq 0.6$. The model also predicts a dependence of the prefactor $c$ on the density of carboxyl active sites.

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1. Introduction

Understanding the deposition of polymers on a surface is a challenging problem from both a theoretical (see e.g. [1]–[3]) and a practical point of view [4]. As a prominent example, polyethylene glycol (PEG) in solution deposited on a suitably treated surface is commonly used in many biomedical applications as a biocompatible thin film displaying large reluctance to protein adsorption and cell adhesion [4]. Recently, plasma has been used to create active sites on the surface where PEG can become attached, containing the carboxyl (COOH) group, a process known as pre-functionalization of the surface [5].

Although many experiments have demonstrated the ability of plasma pre-functionalized surfaces to improve PEG deposition [6], they have neither provided a clear understanding of the mechanism of deposition nor attempted to clarify the polymer dynamics near the attaching surface. For instance, it is believed that the number of COOH active sites is crucial and, as a result, research interest has focused on increasing their surface concentration rather than investigating the interplay between the number of active sites and polymer chains attachment. Furthermore, the role of PEG length in the morphology of the deposited thin films has not been considered so far. Thus, further information is required to improve the efficiency of the plasma pre-functionalization process, aiming at controlling and optimizing the deposition process to obtain a given type of PEG thin film with predetermined and specific characteristics.

In this work, we report on experimental and theoretical work on PEG deposition onto plasma-treated surfaces to elucidate the main characteristics determining the morphology of deposited thin films. Numerical simulations of linear polymers, modeled by self-avoiding random walks on a lattice, allow us to draw conclusions about the width and attained density of the films as a function of polymer length. Predictions are also made about the dependence of film density on the plasma treatment employed. These results suggest that a multidisciplinary approach, such as the present one, which combines experimental results and numerical simulations supported by scaling arguments, is required for better control of the PEG deposition processes.

This paper is organized as follows. In section 2, we describe the experimental setup and illustrate the type of treated (silicon wafer) surface with polymerized acrylic acid using plasma techniques. The characteristics of PEG in solution, the method of grafting and the one used for determining the deposited film widths are discussed. In section 3, we describe the model and the simulation rules. The results are presented in section 4 and the conclusions are summarized in section 5.
2. Experimental setup and procedure

Plasma deposition experiments were performed in a plasma reactor composed of a cylindrical stainless steel vacuum chamber of 30 cm diameter, using a parallel plate configuration. Two horizontal plates of 15 cm diameter are placed 4 cm apart. The upper one acts as the electrode, while the lower one, which is grounded, is used as a sample holder (see [7] for more details). The plasma treatment consisted of six main steps, as follows.

1. *Deposition of acrylic acid* (AAc) (figure 1). A piece of silicon wafer of 1 cm$^2$ area was located at the lower plate. Before treatment, the chamber was filled with argon until a pressure of 10 Pa was reached. During the discharge, the flows of argon and AAc vapors were kept constant, as well as the applied power (30 W) and total pressure. The plasma parameters of the reactor in this configuration are: plasma potential $V_p = 10$ V and electronic temperature of the plasma $T_e = 5$ eV [8]. The sheet potential at the grounded electrode, where the sample was located, equaled, in this case, the plasma potential.

2. *Rinsing*. The samples were rinsed in phosphate buffer solution (PBS) at 37 °C for 12 h.

3. *Counting active sites*. The concentration of carboxyl groups created on the sample surface (figure 1) was evaluated using the techniques described in [4, 9]. In particular, their surface concentration was obtained by extrapolation of the number of active sites within the AAc films measured at different widths (see figure 2). The latter showed the total number of active sites within a volume of AAc-deposited film, per unit surface area (nm$^2$), as a function of film width. The carboxyl groups found on top of the AAc thin film thus had a number density $\rho_{\text{act}} \simeq 2$ sites nm$^{-2}$.

4. *Grafting of PEG*. PEG is a linear polymer with the chemical structure amino-(CH$_2$-O-CH$_2$)$_N$-amino, where the $N$-repeated monomer (in parentheses) has the molecular weight $M_{\text{unit}} = 44$ g mol$^{-1}$, corresponding to a mass $m_0 \simeq 7.4 \times 10^{-23}$ g, while the monomer–monomer distance is $d_{\text{unit}} \simeq 0.36$ nm. PEG can be obtained commercially as a homogeneous solution for a given polymer molecular weight, $M_n$. The treated surfaces (after steps 1 and 2) were put in contact with a PEG solution of 4 mM concentration for 24 h at a controlled temperature of 37 °C. We performed deposition experiments of PEG for two different molecular weights, $M_1 = 3000$ g mol$^{-1}$ and $M_2 = 5000$ g mol$^{-1}$,
Figure 2. Effective surface density of active sites (nm\(^{-2}\)) as a function of the AAc film width (nm). The straight line is a linear interpolation of the total number of carboxyl groups measured within the AAc-deposited film per unit area (nm\(^{-2}\)) (see [10] for more details). The effective surface density of COOH groups is then obtained by extrapolation to vanishing film width, yielding \(\simeq 2\) sites nm\(^{-2}\).

yielding chains of length \(N_1 = M_1 / M_{\text{unit}} = 68\) and \(N_2 = M_2 / M_{\text{unit}} = 114\) monomer units, respectively. The solutions have a mass density depending on the number of monomers \(N\) given by \(\rho_{\text{sol}}(N) \simeq 1.8 \times 10^{-3} N \text{ g cm}^{-3}\).

5. Rinsing. Washing the samples was necessary to remove any unbounded PEG chain.

6. Thin film width. The thickness of the deposited PEG film was measured with a Solver P47-PRO atomic force microscope (AFM) [11]. The AFM was used in semi-contact (tapping) mode on dry samples using high-accuracy, non-contact silicon tips [11] of typical spring constant \((6 \pm 1) \text{ N m}^{-1}\) and resonance frequency \((200 \pm 20) \text{ kHz}\). Square images were collected at a frequency of 1.5 Hz and 256 pixels per line.

3. Model and simulation rules

We consider PEG as a linear polymer in a good solvent, that is, one in which a hardcore repulsion between monomers is the only existing interaction. For simplicity, we study chain conformations in a discrete three-dimensional (3D) space. Under these conditions, we model PEG as a self-avoiding walk (SAW) (see, e.g., [1, 2]) on a simple cubic lattice. We take the lattice constant \(a_0\) to be equal to the monomer–monomer distance in actual PEG, i.e. \(a_0 = a_{\text{unit}}\). According to the mass density \(\rho_{\text{sol}}(N)\) reported above for the PEG solutions, we obtain the corresponding chain number density in solution as \(N_{\text{sol}} = \rho_{\text{sol}}(N)/(N m_{\text{0}}) = 2.43 \times 10^{-3}\) chains nm\(^{-3}\), to be used in our simulations.

The lattice considered has a size of \(S = A \times H_0\), where the attaching surface \(A\) ((\(x, y\))-plane) spans 200 \times 200 sites, and the height \(H_0\) extends along the z-axis over 100 sites. Therefore, the attaching surface (located at \(z = 1\)) has an area of \(A = (72 \times 72) \text{ nm}^2\) and a height of \(H_0 = 36 \text{ nm}\). The latter is chosen to minimize lattice space in order to speed up the simulations, and we have checked that, along the z-axis, 100 sites are sufficient for our present
purposes. This can be verified by considering that, both in solution and attached to a surface at a single chain end, SAWs extend over a linear size $R \sim N^v a_0$, with $v \approx 0.59$ (see, e.g., [3]), yielding for $N = 114$ a linear size $R \approx 7.2 \text{ nm} \ll H_0$.

The active sites on the attaching surface are selected at random, having the density $\rho_{\text{act}}$ determined in the experiments. In our case, their number then becomes $N_{\text{act}} = \rho_{\text{act}} A \approx 10^4$ sites, corresponding to 25% of the whole available area.

The number of chains in solution, $N_{\text{peg}}$, within our lattice is determined from the density of PEG chains in our experiments and is kept constant throughout the simulations. Since the attached chains occupy a finite fraction of the lattice along $z$, of about $H_{\text{att}} \approx N^v \approx 20a_0$ (for $N = 200$), we estimate the effective free space available for chains in solution to be $H_{\text{eff}} = H_0 - H_{\text{att}} = 80a_0$. Then, the effective free volume becomes $V_{\text{eff}} = AH_{\text{eff}} = 1.493 \times 10^4 \text{ nm}^3$, yielding a number of free chains inside it of $N_{\text{peg}} = N_{\text{sol}} V_{\text{eff}} \approx 350$ chains or, equivalently, about 1.2% (for $N_2 = 114$) of the lattice becomes occupied by the chains in solution.

A second issue is the type of polymer dynamics we can take as being both simple and realistic. It is clear that, in the presence of many chains, the motion of a single SAW becomes hindered by the remaining ones. Thus, purely local types of motion cannot be effective in describing the long-time behavior of chains. A suitable solution is provided by worm-like or reptation dynamics [1], which efficiently allow a chain to overcome the previously formed network of attached chains to reach the surface. This is somehow similar to the dynamics of SAWs in random structures (see, e.g., [12]).

Initially, we distribute 350 chains (for a given number of monomers $N$) just having straight line configurations and allow them to move for a sufficiently large number of steps in order that the initial conformations are completely lost [12]. At each simulation (or Monte Carlo (MC)) step, each chain in the solution is taken to be moved by one of its chain ends randomly chosen and a nearest neighbor site to which the chain attempts to reattach. We use the so-called ‘blind ant’ rules for the selected new occupied site (see, e.g., [13, 14]). We use periodic boundary conditions along the $x$ and $y$ axes and blocking conditions at $z = 1$ and 100. During this ‘randomization’ process, attaching chains to the bottom surface is forbidden. After this initialization procedure is completed, the attaching process is ready to begin.

The time evolution of the deposition process is determined by the number of MC steps. The question arises as to how to estimate the order of magnitude of duration of a single MC step, $\tau$. To this end, we can resort to values of the diffusion coefficient of PEG in solution, $D_M$, which can be written $D_M = a_0^2/(2\tau)$, where the lattice spacing represents the length for a single reptation jump and $\tau$ the associated jump time. The diffusion coefficient of PEG has been determined for a wide range of molecular masses $M$ [15, 16]. The measurements have been reported in the form of the empirical equation [15], $D_M = 1.25 \times 10^{-4} [M/(g \text{ mol}^{-1})]^{-0.55} \text{ cm}^2 \text{ s}^{-1}$. For instance, for $M = 5000 \text{ g mol}^{-1}$, $D_M \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Thus we obtain $\tau \approx 1 \text{ ns}$. Our simulations span the order of $10^5$ MC steps, corresponding to about 1 s.

Once the active sites are switched on, a chain executing reptation moves can touch the attaching plane at $z = 1$. If it does it with either one of its end monomers, it becomes fixed at the plane and its motion just stops (see figure 3), i.e. attached chains remain fixed in space. Eventually, local monomer motions of attached chains can be considered. These local motions are more likely to occur at the beginning of the deposition process where only a few attached chains are present. As time goes on, the higher density of attached chains can hinder the local displacements considerably, making their simulation less relevant for the description of the asymptotic shape of the PEG thin film, which constitutes our main aim. Thus, for simplicity, we do not incorporate them into the present simulations.

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More important for us here is the fact that, as soon as a chain becomes attached at the bottom surface, a new one is incorporated into the lattice from the top of the system, in keeping with the constant number of chains in solution. The newly ‘born’ chain is grown from a randomly selected site at the $z = 100$ plane. The growing algorithm is also based on a reptation type of motion and is very efficient, allowing us to find a successful chain configuration after a number of attempts of $O(N)$.

4. Results

We discuss our results by considering first the dynamical behavior of chains and the attaching process. Then we discuss the morphology of the attained thin films.

4.1. The dynamics of attaching

At the beginning, chains can attach rather rapidly because the bottom surface is easily reachable (figure 3). As the deposition process evolves, chains can reach the attaching sites with increasing difficulty, and the number of attached chains, $N_{\text{att}}$, grows at ever slower rates. The results for $N = 68, 114$ and 200 are reported in figure 4. As one can see, for up to about $10^6$ MC steps, the number of attached chains behaves similarly in the three cases considered. Above $10^6$ MC steps, the different curves of $N_{\text{att}}$ separate from each other. However, their evolutions as a function of MC steps behave similarly when considering the product $NN_{\text{att}}$, which is proportional to the total deposited mass, as illustrated in the inset of figure 4. The data collapse thus obtained suggests that the deposited PEG mass (per unit area) is independent of polymer length. As is apparent from figure 4, the asymptotic value for $NN_{\text{att}}$ has not been reached by our simulations. However, in order to discuss our results from an analytical point of view, we will consider the value obtained at $5 \times 10^8$ MC steps (roughly corresponding to an estimated time of $\approx 0.5$ s) in our simulations, yielding $NN_{\text{att}} \approx 1.56 \times 10^5$. Using this value, we will estimate the density attained by PEG in our films, and derive its scaling properties. We report our final simulation results in table 1 for the three cases studied here.
**Figure 4.** Number of attached chains, $N_{\text{att}}$, as a function of Monte Carlo (MC) steps. Results for chains (from top to bottom) with $N = 68$, 114 and 200 monomers are shown. The inset shows the product $NN_{\text{att}}$ as a function of MC steps. Note the data collapse, suggesting that $NN_{\text{att}}$ becomes independent of $N$ above $10^6$ steps. See table 1 for the final values of $N_{\text{att}}$ obtained here. In the simulations, we have estimated $\tau = 1$ ns as the duration of a single MC step, so that the ‘crossover’ in the inset occurs at about $t \approx 10^{-3}$ s and the maximum time reached here was about 0.5 s.

**Table 1.** Simulation results for the average surface height, $\langle H \rangle/a_0$, in lattice units, the surface standard deviation, $\sigma_H/a_0$, in lattice units, the average surface height, $\langle H \rangle$ (nm), the surface standard deviation, $\sigma_H$(nm), the experimental values for average height, $\langle H \rangle_{\text{exp}}$ (nm), the number of attached chains at $5 \times 10^8$ MC steps, $N_{\text{att}}$, the fraction of active sites occupied by the attached chains, $f_{\text{act}}$ (%), and the fraction of surface sites occupied by the attached chains, $f_{\text{latt}}$ (%), as a function of monomer number $N$. Here, $a_0 = 0.36$ nm.

| $N$  | $\langle H \rangle/a_0$ | $\sigma_H/a_0$ | $\langle H \rangle$ (nm) | $\sigma_H$ (nm) | $\langle (H)_{\text{exp}} \rangle$ (nm) | $N_{\text{att}}$ | $f_{\text{act}}$ | $f_{\text{latt}}$ |
|------|------------------------|----------------|--------------------------|----------------|--------------------------------|------------------|---------------|---------------|
| 68   | 13.6                   | 5.9            | 4.9                      | 2.1            | (4.3 ± 3.1)                  | 2292             | 23            | 5.7           |
| 114  | 18.4                   | 8.4            | 6.6                      | 3.0            | (8.8 ± 1.8)                  | 1382             | 14            | 3.5           |
| 200  | 25.8                   | 11.7           | 9.3                      | 4.2            | (n.a.)                      | 834              | 8             | 2.1           |

4.2. The morphology of the thin films

In order to better visualize the morphology of the deposited thin PEG film, it is convenient to look at a section of it as a function of one planar coordinate. Results for the thin film height, $Z(x, y)$, are shown in figure 5 as a function of $x$ for $y = 100a_0$, for the three cases considered. In the figure, the mean height values over the whole film are reported.
Figure 5. Sections of simulated PEG thin films for (from top to bottom) \( N = 68, 114 \) and 200. Plotted is the film height, \( Z(x, y) \) (nm), versus \( x \) (nm) for fixed \( y = 100a_0 = 36 \) nm. The horizontal lines are the (total film) mean values: \( \langle H \rangle = 4.9 \) nm \((N = 68)\), \( \langle H \rangle = 6.6 \) nm \((N = 114)\) and \( \langle H \rangle = 9.3 \) nm \((N = 200)\).

In order to compare our results for \( N = 68 \) and 114 with the experimental ones, we have plotted in figure 6 the simulation values for the number density of attached monomer chains, as a function of height \( z \) from the sticking surface. The measured widths are reported on the plot together with the estimated error bars, and they are in very good agreement with our predictions.

A useful quantity predicted by our simulations is the mean density, \( \rho(N) \), of the PEG film as a function of the number of monomers, \( N \), calculated as

\[
\rho(N) = \frac{p N N_{\text{att}} m_0}{A \langle H \rangle}.
\]  

(1)

where \( p \leq 1 \) is the fraction of the total number of monomers that are located within the heights \( 1 \leq z \leq \text{int}(\langle H \rangle/a_0) \). In the following, we present arguments to estimate \( \rho(N) \) and discuss the scaling behavior associated with PEG attachment.

4.3. Theoretical estimates and scaling arguments

According to the inset of figure 4, the product \( NN_{\text{att}} \) becomes independent of \( N \) above \( 10^6 \) MC steps. At \( 5 \times 10^8 \) MC steps, \( NN_{\text{att}} \simeq 1.56 \times 10^5 \), yielding \( \rho = 2.2 p (\langle H \rangle/\text{nm})^{-1} \) (g cm\(^{-3}\)). Next, we empirically find that the fraction \( p \simeq 0.7 \), independently of \( N \). Then, using the fact that the attached SAWs extend in space as \( R \sim N^{\nu}a_0 \) (see, e.g., [3]), we can argue also that \( \langle H \rangle \sim N^{\nu}a_0 \), with \( a_0 = 0.36 \) nm. The present results support this conjecture, yielding numerically
Figure 6. Number density of monomers, $N_\rho(z)$ (nm$^{-2}$), of the simulated polymer films as a function of height, $z$ (nm), for the two polymer lengths, $N = 68$ and 114. The circles represent the experimental (Exp) mean height values, $\langle H \rangle_{\text{exp}} = (4.3 \pm 3.1)$ nm and $(8.8 \pm 1.8)$ nm, respectively, and the squares the present MC results for $\langle H \rangle$. The error bars for the latter are taken from the standard deviations reported in table 1.

$\langle H \rangle \simeq 1.13 N^{0.59} a_0$. Thus, we expect that

$$\rho(N) = \frac{c}{N^v},$$

with $v = 0.59$ and $c \simeq 2 p/(a_0 \text{nm}^{-1})$ (g cm$^{-3}$) $\simeq 3.9$ g cm$^{-3}$. Results for the density $\rho(N)$ are shown in figure 7, which are in very good agreement with our estimates.
Figure 7. Density of deposited PEG films, \( \rho(N) \), as a function of the number of monomers, \( N \), according to equation (1) (circles). The line has the form predicted by equation (2), with the value \( c = 3.9 \, \text{g cm}^{-3} \).

Figure 8. 3D image of the simulated PEG deposition surface. Here, \( N = 200 \) with 834 attached chains. The coordinate axes are in lattice units \( a_0 = 0.36 \, \text{nm} \). The color scale is proportional to monomer \( z \) height. (Artwork by F Marini.)

It is interesting to estimate the constant \( c \) heuristically. Since the concentration of active (sticking) sites is, in lattice units, \( p_a = 0.25 \), this means that there is one active site every four lattice positions. We then associate a number (area) of \( A_s = p_a^{-1} \) sites to each sticking place, known as a sticking area. We wish to determine the mean number of monomers per unit lattice size, \( \langle N_{\text{mon}} \rangle \), which are located on top of a single sticking area (for heights smaller than \( \langle H \rangle \)), forming what we call a sticking column. We argue that an attached SAW starting at the sticking site will get out of the single sticking column after \( N_{\text{out}} \) steps. Then we suggest that, to a first approximation, \( N_{\text{out}} \sim \langle N_{\text{mon}} \rangle \). We can estimate \( N_{\text{out}} \) using the scaling relation \( A_s^{1/2} \sim N_{\text{out}}^\nu \), from which we obtain \( N_{\text{out}} \sim 3.24 \). Numerical results for \( \langle N_{\text{mon}} \rangle \) yield values (3.0, 2.8, 2.8) for \( N = (200, 114, 68) \), respectively, which is in good agreement with our estimate.
The number $\langle N_{\text{mon}} \rangle$ (i.e. $N_{\text{out}}$) can be interpreted as the effective factor $\langle N_{\text{mon}} \rangle \simeq pN N_{\text{att}}/L^2$ (see equation (1)), where $L = (A/a_0^2)^{1/2}$, and here $L = 200$ lattice sites. The quantity $N_{\text{out}}$ is related to $c \simeq N_{\text{out}} m_0/a_0^3$, and the value $N_{\text{out}} \simeq 3.24$ yields $c \simeq 5.14 \text{ g cm}^{-3}$, which is in good agreement with the numerical results, equation (2). Furthermore, from this value of $C$, we obtain an estimate of the asymptotic one for $N N_{\text{att}} \simeq 2.1 \times 10^5$, consistent with the time dependence displayed in figure 4.

It should be noted that $N_{\text{out}}$, and thus also the constant $c$, depend on the concentration of active sites $p_a = \rho_{\text{act}} a_0^2$, yielding $c \propto N_{\text{out}} \sim \rho_{\text{act}}^{-x}$, with $x = 1/(2\nu) \simeq 0.85$, providing further tests to the scaling arguments presented here. These issues will be discussed elsewhere. Finally, in figure 8 we show a 3D plot of the simulated PEG surface obtained for $N = 200$ monomers.

5. Conclusions

In conclusion, PEG deposition on plasma pre-functionalized surfaces is a rather complex and challenging problem. In this work, we have applied chemical and physical techniques to analyze the deposited films, combined with numerical simulations of the polymer deposition to obtain a more complete picture of the process. We can thus optimize the latter by employing a new multidisciplinary approach that we believe can be of validity and usefulness in more general circumstances. Specifically, it is found that typically less than about 5% of surface sites are involved in attaching PEG chains. This shows that the number of COOH sites required for efficient PEG attachment is only a small fraction of the available surface area. The results for the obtained film widths agree remarkably well with the experimental measurements. Predictions for the attained film density as a function of the number of PEG units have been discussed and are useful in estimating the PEG molecular mass required to attain a given film density. An accurate prediction of the latter is of crucial importance in many biomedical applications. Future experimental work is required to deal with the measurement of the deposited PEG film mass and its density, and with the dynamics of attaching, in particular to verify the predictions of the model regarding the time scales involved in the PEG deposition process. Also, the possibility of varying the density of active sites experimentally needs to be considered in detail in order to verify the model predictions.

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