Reactive molecular dynamics simulations of the functionalization of polyethylene surfaces using an Ar/O₂ plasma

Johan Minnebo, Erik C. Neyts and Annemie Bogaerts

Research group PLASMANT, University of Antwerp, Belgium

Abstract: In order to study the effects of plasma species on a polymer surface, molecular dynamics simulations of oxygen atoms impacting on an amorphous polyethylene film were carried out. Furthermore, the oxygen atom reactivity after impact was investigated. The results indicate that oxygen atoms with thermal energy react only after impact, and that the breaking of C-C bonds is the initial reaction of the oxidation process.

Keywords: Molecular dynamics, plasma, polyethylene, surface, functionalization

1. Introduction

Plasma treatment of polymer surfaces is known to be a widely used process to improve the surface properties of the material without altering the bulk properties. Polymers typically have a low surface energy, whereas many applications require a higher surface energy. Therefore, plasma surface treatment is commonly used to increase the hydrophilicity and adhesion properties through the introduction of polar functional groups [1], for example for applications in food packaging [2], optical coatings [3] and biomedical materials [4].

Although a significant amount of experimental research has already been carried out in this field, knowledge of the mechanistic details behind plasma-surface interactions is still limited [5], especially when polymers are involved [6]. Polymers have, in contrast to inorganic materials, a complex physical and chemical structure that can be relatively easily modified by various reactive plasma species. In order to gain a better understanding of how the plasma species interact at the plasma-surface interface, a theoretical approach using molecular dynamics (MD) simulations can be employed. Molecular dynamics is an atomistic model that can provide insights in the (reaction) mechanisms involved in plasma-surface interactions.

In the current study, the effect of impinging oxygen atoms with thermal energy as well as with an energy of 1 eV on an amorphous polyethylene (PE) surface was investigated, as well as the reactivity of oxygen atoms after impact. Thermal oxygen atoms are the main reactive species in an argon/oxygen plasma created by a dielectric barrier discharge (DBD) operating at atmospheric pressure [7]. Therefore, the surface modification obtained by the simulations can be related to experimental results.

2. Method

2.1 Molecular dynamics simulations

Molecular dynamics is a simulation technique to follow a set of atoms in time and space, which interact with each other through an interatomic potential. The negative gradient of this potential governs the forces on the atoms, while their motion is calculated by solving the set of coupled equations of motion. The simulations in this work utilize the reactive force field for hydrocarbon oxidation, developed by Chenoweth and coworkers [8]. The oxygen atom impact simulations were carried out using the LAMMPS simulation package [9], while the ReaxFF program [10] was used for the bulk oxidation simulations. Periodic boundary conditions were imposed on the x, y and z directions, and the time step was set to 0.25 fs.

2.2 Model polyethylene structure

The polyethylene structures used in this study were created using a self-written script in the Python programming language. This script generates polyethylene chains through the periodic boundaries in the x and y directions, and allows for branching. The structure size was set to 30Åx30Åx20Å in the x, y and z dimensions, respectively. The minimum chain length was specified to be ten carbon atoms, while the branching parameter was chosen so that a side chain of at least one ethylene unit was placed on approximately one out of every ten carbon atoms of the primary chain. Furthermore, a few ether and alcohol functional groups were added to represent a native oxygen content of 1.2 wt%. The final polyethylene structures had a density varying from 0.91 to 0.93 g/cm³ and contained around 2150 atoms.

3. Results

3.1 Atomic oxygen impact

In order to simulate oxygen atoms impinging on a polyethylene surface, the structure was first allowed to relax for 25 ps, during which an interface layer was formed with polyethylene chains sticking out of the surface (Fig. 1). A distinction can be made between a bulk region, where the change in structure density is minimal, and an interface region, where the structure...
density is significantly lower. The bulk region ranges from 0 to 19 Å, while the interface region ranges from 19 to 25 Å. Before and during the impact simulations, the atoms in the bottom 2Å of the structure were kept at fixed positions to mimic the immobility of the bulk structure. Three different polyethylene surfaces were created, on each of which 200 independent atomic oxygen impacts were simulated at an incident angle normal to the surface. The impinging oxygen atoms were simulated with thermal energy as well as with 1 eV of kinetic energy.

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The impact of an oxygen atom with the model polyethylene surface can have four different outcomes: firstly it can be reflected from the surface without further interaction, secondly it can be stopped at the surface and stay in the interface region, thirdly it can penetrate the surface to reach the bulk region, and lastly it can react with the surface to break existing bonds and/or to create new bonds. These outcomes will be further referred to as “reflection”, “adsorption”, “incorporation” and “reaction”, respectively.

In the case of oxygen atoms with thermal energy, Fig. 2 shows that the sticking is still the most likely outcome, but the higher impact velocity leads to a significant decrease in sticking in favor of reflection, while the probability of incorporation increases slightly. More importantly, the oxygen atoms show an increased reactivity towards the carbohydrate chains. Although the single alcohol moiety is still responsible for many reactions (Table 1), approximately 6% of the impinging oxygen atoms react with the carbohydrate chains. The cleavage of a C-C bond is by far the most likely reaction, but hydrogen abstraction, alcohol formation as well as ether formation were also observed. When the impacting oxygen atom binds to a hydrogen atom, but lacks the energy to abstract it, the oxygen is found to remain bonded, as if it was stabilized by a metastable hydrogen bond.

As can be seen in Table 2, the penetration depth of oxygen atoms is rather shallow; the oxygen atoms that can penetrate the surface reach only an average depth of 2,8 Å with thermal energy and 4,3 Å with an energy of 1 eV.
eV. In comparison, experiments have shown that an increase of oxygen can be found up to several nm in the polymer surface [13]. This leads to the conclusion that the impinging oxygen atoms readily diffuse into the surface before reacting.

Table 2: Average penetration depth of the fraction of oxygen atoms that are incorporated in the amorphous polyethylene surface, out of 600 independent impacts, both with thermal energy as well as with an energy of 1 eV.

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<th>Average penetration depth (Å)</th>
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<tbody>
<tr>
<td>Thermal</td>
<td>2.8 ± 1.6</td>
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<tr>
<td>1 eV</td>
<td>4.3 ± 2.4</td>
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In combination with the results from the oxygen atom reactivity on impact, it seems very likely that the oxidation of the polymer surface does not happen directly on impact, but only a certain amount of time after impact. Further simulations have been carried out to investigate the reactivity of oxygen atoms that have diffused to the bulk region of the polymer surface.

3.2 Bulk oxidation

To investigate the oxygen atom reactivity in the bulk of amorphous polyethylene, 200 oxygen atoms were added to the model structure corresponding to approximately 24 wt% of oxygen (Fig. 3). Four independent structures were used to approximate a representative sample of amorphous bulk polyethylene. After a short thermalization of 5 ps, already one third of the oxygen atoms had recombined to form oxygen molecules, leaving on average 127 oxygen atoms free to interact with the polyethylene structure. These oxygen atoms were then followed during a simulation time of 250 ps.

At room temperature, only eight of the free oxygen atoms had reacted with the polyethylene chains to form new functional groups, leading to an average reactivity of 1.5 % after 250 ps. Interestingly, the oxidation process was more likely to begin at the native ether groups than at the carbohydrate chains. While there were only four ether groups present in a polyethylene structure containing more than 700 carbon atoms, two bond breaking reactions involving the ether groups were observed, compared to one reaction involving a carbohydrate chain. Furthermore, the terminal oxygen radicals created during the initiating reaction seem to increase the reactivity of the carbon atom to which they are attached. Of the six terminal oxygen radicals created during the simulations, one was oxidized to an aldehyde by hydrogen abstraction. The aldehyde group was then further oxidized by a free oxygen atom to form a functional group with two oxygen radicals attached to the terminal carbon atom, which was eventually eliminated from the chain by a carbon-carbon bond breaking reaction of another free oxygen atom.

In order to gather more information on the types of reactions that take place during bulk oxidation, the simulations were repeated at a higher temperature of 350K. Because of the increased temperature, 36 of the free oxygen atoms reacted with the polyethylene chains during the simulation, leading to an average reactivity of 7.2 %. Just as at room temperature, the initial oxidation reactions were more likely to involve an ether group than carbohydrate chains: four and three reactions, respectively. After the initial formation of a terminal oxygen radical, several subsequent reactions were observed, confirming the increased reactivity at the site where the chain was broken. The prevalent reaction mechanism, however, was not aldehyde formation but the breaking of the carbon-carbon bond at the terminal site, leading to the formation of formaldehyde and a new terminal oxygen radical. The formaldehyde was quickly oxidized by oxygen attachment, and could be oxidized further to eventually form carbon dioxide.

These results suggest that the main reaction pathway of the oxidation of amorphous polyethylene by oxygen atoms starts with the scission of the carbon backbone of the polymer to form terminal oxygen radicals, followed by the elimination and further oxidation of formaldehyde as shown in Fig. 4.
4. Conclusion

The effects of oxygen atom impact on an amorphous polyethylene surface have been investigated, as well as the oxygen reactivity after impact. With thermal energy, oxygen atoms are most likely to stick to the surface and show no reactivity towards the carbohydrate chains, whereas with an energy of 1 eV, approximately 6% of the impacting atoms is observed to react, leading almost exclusively to the breaking of a carbon-carbon bond.

Free oxygen atoms in the bulk of an amorphous polyethylene structure show a reactivity of 1.5% after a simulation of 250 ps at room temperature, compared to 7.2% at 350K. The main reaction pathway is found to be the scission of the backbone chain, followed by elimination and oxidation of the terminal radical.

5. Acknowledgements

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6. References
