Molecular dynamics simulation of argon clusters impacting on a poly(ether ether ketone) surface

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Abstract. Presented is the molecular dynamics simulation of electrically neutral small argon clusters impact on the surface of Poly(Ether Ether Ketone) (PEEK), a promising orthopedic implant material. The results of the simulation are compared with the data obtained in the experiments on the treatment of the PEEK surface by Accelerated Neutral Atom Beams (ANAB). The comparison results allow the conclusion that the clusters are a part of ANAB. This conclusion is in complete agreement with the results of previous molecular dynamics analysis of the ANAB generation process.

1. Introduction
Poly(ether ether ketone) (PEEK) is a semicrystalline polymer with a molecular backbone containing two ether (R-O-R) and one ketone (R-CO-R) groups. The linking group R between the functional groups consists of a 1,4-substituted aryl group. PEEK is rapidly gaining popularity for trauma and orthopedic applications [1]. The material is biocompatible and radiolucent. The PEEK's modulus of elasticity approximates that of cortical bone. However, it has been shown to be biologically inert and to not integrate well with surrounding tissues.

Efforts of numerous researchers are focusing on increasing the bioactivity of PEEK by modifying the surface to improve the bone-implant union. There exist many surface modification techniques to enhance the bioactivity of PEEK: physical techniques (such as laser, plasma, and extreme ultraviolet), chemical techniques (such as wet chemistry and sulfonation), and coating techniques (such as aerosol deposition, radio frequency magnetron sputtering, etc.) [2-4]. Most of these techniques have met a limited success. For example, plasma and extreme ultraviolet treatment causes deep subsurface damage (>100 nm) which results in weakening the bone-implant interface.

Khoury et al. [5,6] employed the so-called Accelerated Neutral Atom Beams (ANAB) [7] to improve the bioactivity of PEEK. ANAB processing resulted in nanoscale modification of the PEEK surface (<5 nm) and significantly enhanced human osteoblast cell proliferation on it.

The formation of ANAB occurs when a gas cluster ion beam (GCIB) collides with the atoms of the residual gas, which are present along the beam path. An electrostatic deflector is used to separate all charged particles, which remained after fragmentation of cluster ions, from ANAB. Kirkpatrick et al. [7] stated that each destroyed cluster ion turns into an aggregate of electrically neutral atoms still traveling together in close proximity. These aggregates of atoms have a necessary impact on the target surfaces. However, the molecular dynamics (MD) simulation demonstrated that the atoms emitted from the cluster ion as a consequence of collision undergo strong scattering [8]. Thus, the flow of...
individual atoms in ANAB has a rather low density. Therefore, to provide a required effect on the PEEK surface, the beam should contain a significant number of sufficiently massive cluster ion fragments remaining in it after collisions and the subsequent electrostatic separation of charged species. The work is concerned with a verification of this supposition. For this purpose MD simulation of impacting process of cluster ion fragments on the PEEK surface was performed. Parameters of the fragments have been obtained from MD analysis of the ANAB generation process [8]. Results of the simulation were compared with the experimental data from ref. [6].

2. Computational details
The PEEK unit cell has orthorhombic geometry with lattice constants \(a=0.783\) nm, \(b=0.594\) nm and \(c=0.986\) nm [9]. The polymer chains lie in an extended zigzag conformation and are aligned along the \(c\)-axis direction. The sample used for this study consisted of 41 x 81 PEEK chains, each containing 16 monomers. Thus, the sample had dimensions of 23.72 nm \(\times\) 32.22 nm \(\times\) 23.91 nm.

The origin of the coordinate system was chosen at the center of the sample target side. The \(x\)- and \(y\)-axes were established, coinciding with the \(c\)- and \(a\)-axes of the PEEK unit cell, respectively (figure 1). The impact point coincided with the origin.

The accelerating potential for cluster ions was set to 30 kV (typical of ANAB [5-7]).

Fragments of the argon cluster ions were considered. Table 1 presents the sizes of the original cluster ions \((N_c)\) and the fragments formed from them \((n_f)\). The fragment sizes were calculated by MD analysis of the ANAB generation process [8]. The table also lists the probability estimation of charge loss in the fragments \((p = 1 - n_f/N_c)\). Put differently, \(p\) is the probability estimation that some fragment would become part of ANAB. In addition, energies of the fragment impact on the PEEK surface \((E)\) is indicated.

A Lennard-Jones pair potential was used to describe the interaction of argon atoms with each other and with PEEK. A modification of OPLS force field [10,11] was used for the PEEK sample. In the modification, instead of a harmonic potential, a Morse potential was chosen for the bond stretch term. To reduce the computational expense, bonded carbon and hydrogen atoms were grouped to form united pseudoatoms.

The bottom quarter of the sample was set to be a thermal bath using the Langevin dynamics method to absorb the excess energy after the impact. The thermal bath was kept at a constant temperature of 300 K.

Several simulations were carried out for each target-projectile combination, and they were computed up to a time of 25 ps. The simulations box had periodic boundary conditions, and the time steps were set to 0.1 fs.

Preliminary equilibration simulations were used to set a target temperature of 300 K.

The MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code developed at Sandia National Laboratories [12].

The Open Visualization Tool (OVITO) [13] was applied to prepare all the figures exemplifying atom arrangements.

| \(N_c\) | \(n_f\) | \(p\) | \(E, \text{keV}\) | \(L_p, \text{nm}\) | \(M_p\) | \(L_I, \text{nm}\) | \(M_{bb}\) | \(M_{sa}\) |
|---|---|---|---|---|---|---|---|---|
| 309 | 34 | 0.890 | 3.30 | 4 | 3.132 | 5 | 1.485 | 89 | 84 |
| 435 | 121 | 0.722 | 8.34 | 5 | 3.915 | 9 | 2.673 | 198 | 222 |
| 561 | 303 | 0.460 | 16.20 | 6 | 4.698 | 13 | 3.861 | 334 | 398 |
| 742 | 508 | 0.315 | 20.54 | 7 | 5.481 | 13 | 3.861 | 357 | 465 |

3. Results and discussion
Some simulation results are presented in figures 1 and 2 as well as in table 1. Figure 2 shows that the impact energy is expended to break bonds in the PEEK chains and to heat the sample. In all considered cases the heating of the sample reaches its maximum approximately at 1.5 ps after the
impact. At this point the argon atoms have transferred bigger part of their energy to the PEEK medium. After the impact and the transfer of the projectile (fragment) energy to the target (sample) atoms, the energy diffuses radially inward to produce an increasing distance between the PEEK chains (figures 1(b)-(c)). The expansion causes a decrease of the sample temperature. The greatest expansion of the sample is observed at 6.5 ps. The expansion is then followed by compression (figure 1(d)).

![Figure 1](image1.png)

**Figure 1.** The time evolution of the PEEK sample after the impact of the cluster ion fragment with \( n_f = 303 \). 2D slices, 1 nm thick, passing through the origin parallel to the \( yz \)-plane (a)-(d), the \( xz \)-plane (e), and the \( xy \)-plane (f).
Figure 2. (a) The time evolution of the sample temperature after the impact of the cluster ion fragments of different sizes. (b) The time evolution of the number of broken bonds in the PEEK sample after the impact of the cluster ion fragment with \( n_f = 303 \).

The impact-induced damage in the sample is of an elongated form (figures 1(d)-(f)). The number of chains that broken by the impact is small enough. At 25 ps, many of these chains are still dangling into the vacuum (figure 1(e)). Damage dimensions depending on the fragment size are listed in table 1. \( M_w \) and \( M_d \) are, respectively, the width and the depth of the damage measured in a number of the broken chains. The damage dimensions in nanometers are determined as \( L_y = a M_w \) and \( L_z = b M_d / 2 \).

It follows from figure 2(b), that the major part of the bonds in the aryl groups (\( M_{C=O} \)) and in the ketone groups (\( M_{C=O} \)) are broken during the projectile energy transfer. The number of the broken bonds between the aryl and ether groups (\( M_{C-O} \)) as well as between the aryl and ketone groups (\( M_{C-C} \)) continues to increase during the expansion.

Table 1 presents the total number of the broken bonds (\( M_{bb} \)) to the end of the simulation per the cluster ion fragments of different sizes. The total number of carbon and oxygen atoms as well as carbon-hydrogen united pseudoatoms sputtered from the sample is also indicated (\( M_{sa} \)). The analysis of these data shows that \( M_{sa} \) increases almost linear with the impact energy \( E \) whereas the dependence of \( M_{bb} \) on \( E \) tends to saturation.

In ref. [6], the ANAB treatment of the PEEK surface was performed at the average energy of argon atoms of 40 eV and the accelerating potential of 30 kV. Therefore the cluster ions with \( N_c \approx 750 \) prevailed in the mass-spectrum of the initial GCIB. Thus, our numerical experiments and the experiments in ref. [6] were carried out under identical conditions. These experiments gave similar results concerning the subsurface damage depth for the PEEK samples (\( L_z < 5 \) nm). Hence the electrically neutral fragments of the cluster ions are really a part of ANAB.

4. Conclusion
Molecular dynamics simulation of the cluster ion fragments impact on the PEEK surface was carried out. The aim of the investigation was to verify the supposition that these electrically neutral fragments are a part of ANAB. This supposition was made in the previously performed molecular dynamics analysis of the ANAB generation process [8]. The comparison of the obtained simulation results with the experimental data for the treatment of the PEEK surface by ANAB supported the validity of the supposition.

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