Molecular Dynamics Simulation of Argon Atoms Impacting on A Poly (Ether Ether Ketone) Surface

V.V. Sirotkin

Abstract*: *Molecular dynamics simulation of the collision of argon atoms with energies from 20 eV to 100 eV with a poly (ether ether ketone) substrate was carried out. The purpose of the simulation was to test the assumption that single argon atoms that are a part of accelerated neutral atom beams can significantly change the structure of the chemical bonds on the surface of this plastic, thereby affecting its bioactivity. The simulation results demonstrated that the impact of argon atoms even with energies not exceeding 40 eV can cause breaks in a sufficient number of C-O bonds in the ether groups and C-C bonds in the ketone groups of plastic macromolecules. The free radicals that appear on the poly (ether ether ketone) surface as a result of this process can transform into hydroxyl and carboxyl groups when interacting with the appropriate atmosphere. The appearance of a large number of such groups on the poly (ether ether ketone) surface after treatment with accelerated neutral atom beams was observed experimentally.

Index Terms*: *accelerated neutral atom beam, poly(ether ether ketone), bioactivity, broken bonds, molecular dynamics simulation.

I. INTRODUCTION

At present, Poly (Ether Ether Ketone) (PEEK) plastic is becoming more and more widely used in orthopedics [1]. This is facilitated by the unique properties of this plastic. This material is radiolucent, wear-resistant and bio-inert. The modulus of elasticity of PEEK is close to that of human bone. However, the bio-inertness of the PEEK surface makes it difficult to integrate implants made of this material with the surrounding tissues. The efforts of many research groups so far have not led to the creation of technologies that can increase the bioactivity of the PEEK surface to the required level without destroying the near-surface layer of the material to a significant depth [2-4]. For example, the depth of radiation damage to PEEK resulting from treatment with oxygen plasma or hard ultraviolet exceeds 100 nm. It should be emphasized that the presence of a sufficiently thick damaged layer may significantly impair the strength of the bone-implant interface. In [5-7], argon Accelerated Neutral Atom Beams (ANAB) were used to treat PEEK. As a result, the PEEK surface acquired bioactivity, equal or more than that of titanium surface. The thickness of the damaged near-surface layer did not exceed 5 nm. It is important to note that the effect of ANAB on the PEEK surface led to the appearance of a relief with protrusions of approximately 10 nm in height. In addition, the formation of a large number of hydroxyl and carboxyl groups on the PEEK surface was observed. It was the change in both physical and chemical characteristics of the PEEK surface that caused a significant increase in its bioactivity.

ANAB are formed as a result of collisions of accelerated cluster ions with residual gas atoms and the subsequent electrostatic separation of the fragments generated in the process [7]. Molecular dynamic (MD) simulation performed in [8] showed that the beams used in [5-7] consist of sufficiently scattered single argon atoms and a certain amount of electrically neutral fragments of argon cluster ions. At an accelerating voltage of 30 kV (typical for ANAB [7]), the energy of a single argon atom in ANAB can range from several tens to hundred eV. Given the dissociation energies of chemical bonds in PEEK do not exceed 10 eV (see, for example, [9]), the change in the PEEK surface chemical structure may be expected to be primarily due to the effect of single atoms. The aim of this work was to verify this assumption by performing MD simulation of the collision of single argon atoms with energy within the specified range with a PEEK substrate.

II. MATERIALS ANS METHODS

PEEK monomer contains two ether (R-O-R) and one ketone (R-CO-R) group. The R group that binds these functional groups together is a 1,4-substituted aryl group (Figure 1). Figure 1 also shows the designation of atoms in the monomer for a more convenient further presentation. The dissociation energies of chemical bonds in PEEK are given in Table 1. It should be pointed out that the dissociation energies of C1-C1, C1-C2 and C1-C4 bonds in our model were considered equal, therefore, in the table and further, the common designation C~C is used for these bonds.

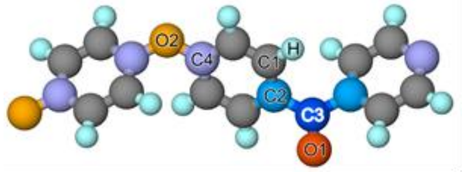

Fig. 1. Designation of atoms in the PEEK monomer.

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Table 1. Dissociation energy of chemical bonds in PEEK [9].

bond type	C3-O1	C~C	C1-H	C2-C3	C4-O2
dissociation energy, eV	7.806	5.368	4.896	4.107	3.443

PEEK is a semi-crystalline polymer (see, for example, [10]). However, in our model, we used substrate, which was a perfect crystal. The unit cell of the PEEK crystal has a orthorhombic geometry with the following lattice constants: a = 0.594 nm, b = 0.783 nm and c = 0.986 nm [10, 11]. At the same time, macromolecules were arranged in a zigzag manner along the diagonal plane b-c.

To reduce computational costs, MD modeling was based on a hybrid approach. At the same time, in the interaction zone, the All Atoms (AA) description of PEEK was used, while for the rest of the substrate, the United Atoms (UA) approximation was used. In this approximation, the bound atoms of carbon and hydrogen are grouped into one pseudoparticle.

The substrate was shaped as a rectangular parallelepiped and was built from 55 macromolecules with an AA description and 560 macromolecules with a UA description. Macromolecules were composed of eight PEEK monomers. The substrate had a size of 11.86 nm × 11.86 nm × 12.03 nm. The total number of atoms in it was 113520.

The coordinate origin was placed in the center of the substrate face, which was hit by argon atoms. Additionally, the x and y coordinate axes were aligned with the c and b directions in the PEEK crystal lattice, respectively.

For the MD simulation, periodic boundary conditions were set on the side faces of the substrate. To stabilize the substrate, the PEEK macromolecules located on its lower face were fixed. In addition, for the absorption of the impact energy, macromolecules located in the lower quarter of the substrate were placed into contact with a thermal reservoir, for which a Langevin thermostat was used. The temperature of the thermostat was 300 K.

A Lennard-Jones pair potential was used to describe the interaction between argon atoms. A modification of OPLS (Optimized Potential for Liquid Simulations) force field [12, 13] was used to model PEEK molecules. The modification was such that we used a Morse potential instead of a harmonic potential to specify the term describing the strain of chemical bonds.

The distances between the atoms of the substrate were periodically estimated to identify the broken chemical bonds in PEEK using the parameters obtained based on the corresponding dissociation energy values.

The simulation of the interaction of incident argon atoms with the substrate was carried out over a 2 ps interval with the time step of 0.1 fs.

The energy of the incident atoms was set in the range from 20 eV to 100 eV. As mentioned above, the presence of single atoms in ANAB is connected with the destruction of accelerated cluster ions. Therefore, the energy of these atoms is defined by the ratio of the initial cluster ions energies to their sizes. Thus, at an accelerating voltage of 30 kV, the selected energy range of single atoms corresponds to a change in the size of the cluster ions producing them in the range from 300 to 1500 atoms.

III. RESULTS

During the study, we analyzed the results obtained when argon atoms hit twelve points on the PEEK surface. The positions of these points were chosen near the coordinate origin. Macromolecules M1 and M2 were hit six times. The macromolecule M1 was located in the uppermost layer of the substrate, the macromolecule M2 lay one layer deeper. Both macromolecules were located in the center of their layers. The coordinates of the points of ten hits corresponded to the midpoints of the distance between the initial positions of the atoms bonded by one of the chemical bonds represented in PEEK. These points are further designated as P# for M1 and P# for M2, where # indicates the bond type, for example, C4-O2 (see Figure 2a). In addition, the centers of aryl groups were hit two times. These points are further designated for M1 and M2 as $P^{\otimes}$ and $P_{\otimes}$, respectively (see Figure 2b).

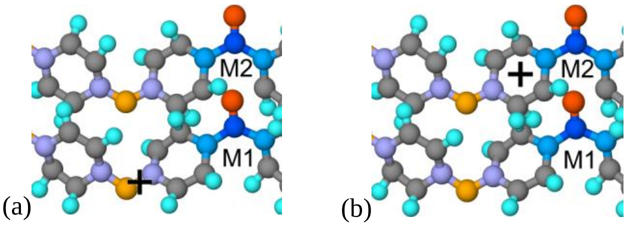


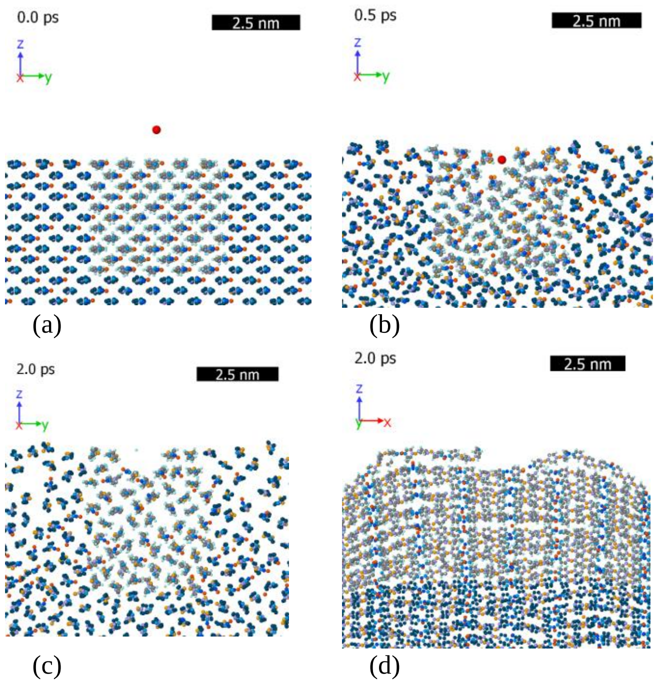
Fig. 2. Impact points $P^{C4\text{-}O2}$ (a) и $P_{\otimes}$ (b) (see explanation in the text).

Naturally, a study of a limited number of “precision” hits on PEEK macromolecules does not reflect the whole variety of possible options for the interaction of single atoms that comprise ANAB with the treated surface. However, the analysis of these limiting cases allows us to identify general patterns of the process under study.

The LAMMPS (Large-scale Atomic/ Molecular Massively Parallel Simulator) software package [14] was used for the MD simulation. The OVITO (The Open Visualization Tool) program [15] was used to display the simulation results.

IV. RESULT ANALYSIS

The simulation results are shown in Figures 3-6. Figure 3 demonstrates the initial state and evolution of the PEEK substrate after the impact of an argon atom with energy of 100 eV at point PC2 C3. The variation of substrate temperature with time as a result of this interaction is shown in Figure 4. It can be seen that the maximum heating of the substrate was observed approximately 0.5 ps after the impact. The further decrease in temperature is associated not only with the effect of the thermostat, but also with a significant expansion of the substrate in the impact zone (see Figures 3b-3d). It can be seen in the figure 5a that in the case under consideration the effect of the impact of an incident atom led to the breaking of two chemical bonds: C2-C3 and C3-O1.



(a) (b)

(c) (d)

Fig. 3. The initial state and evolution of the PEEK substrate after the impact of an argon atom with energy of 100 eV at point $P^{C2\text{-}C3}$. The presented two-dimensional slices of the substrate fragments in the impact zone are 1 nm thick and pass through the origin of coordinates in parallel with: the *yz* plane (a)-(c) and the *xz* plane (d).

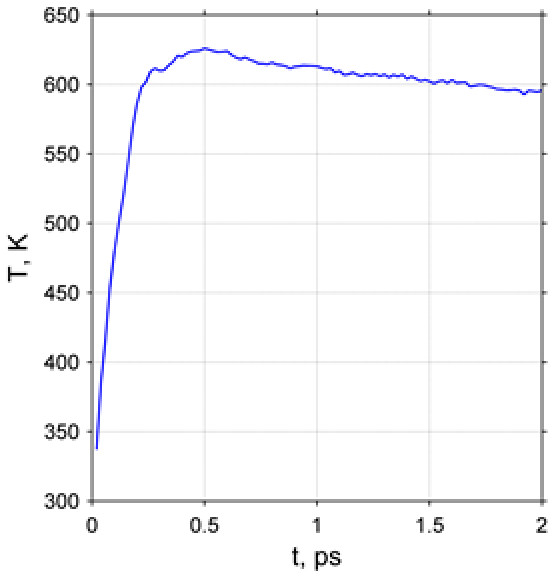
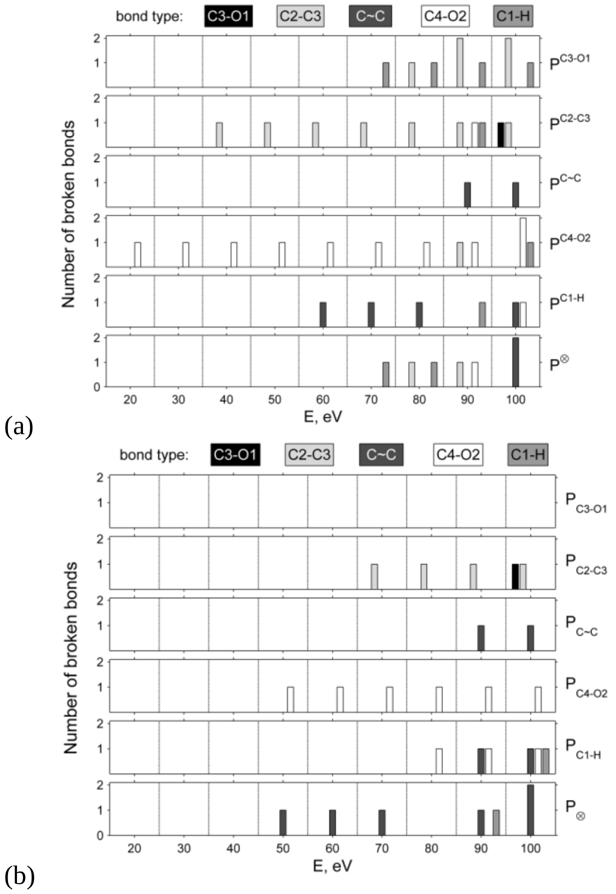


Fig. 4. The time change in temperature of the PEEK substrate after the impact of an argon atom with energy of 100 eV at point $P^{C2\text{-}C3}$.

Analysis of the data presented in Figure 5 generally confirms the "intuitively" expected dependence of the number of broken bonds of a certain type on the value of the corresponding dissociation energy. The largest number of breaks was registered for the weakest C4-O2 bond, which was followed by the C2-C3 bond. The C3-O1 bond, which has the highest dissociation energy, was broken only in two cases. However, the C~C bond was destroyed much more often than the less strong C1-H bond. This is due to the fact that not only the direct (kinetic) effect of the impact of an incident atom, but also the subsequent stretching of PEEK macromolecules (figure 3d) can lead to the breaking of bonds. Therefore, the C~C bond, which, as well as C4-O2 and C2-C3 bonds, is responsible for the integrity of the PEEK macromolecules, are more likely to break than the isolated C1-H bond. The effect of stretching also explains the fact that "untargeted" bonds were often broken as a result of hits. In addition, a strong local overheating that occurred in the impact zone could lead to the breaking of bonds. In many cases, this factor was the reason for the breaking of the C1-H bonds.



(a)

(b)

Fig. 5. The number of broken bonds of different types in the PEEK substrate after impacts of argon atoms with different energies E into the different points P. The atoms hit the macromolecule M1 (a) and the macromolecule M2 (b) (see explanation in the text).

Figure 5 shows that the C4-O2 and C2-C3 bonds can be destroyed by argon atoms with relatively low energy. The threshold energy was 20 eV for the first bond, and 40 eV for the second bond.

It should also be noted that the bonds in the macromolecule M2, which was exposed to the incident atoms through gaps between the macromolecules on the surface of the substrate, turned out to be less susceptible to impact destruction. This was primarily because the macromolecule M2, surrounded on all sides by other macromolecules, undergoes a smaller deformation after the impact than the macromolecule M1, which is not constrained from above.

The important question is how deeply the PEEK substrate can be damaged if a large number of argon atoms fall on its surface. Hits with impact energy of 90 eV and 100 eV quite often resulted in breaks in more than one chemical bond. Figure 6 demonstrates that, in most cases, changes in the structure of both the subsurface and the surface layers of macromolecules resulting from hits even with these high energy values were not very significant. The formation of gaps in these layers, sizes of which would provide the incident atoms with effective access to deeper layers, is possible only when rather large fragments are knocked out of the macromolecules (see Figure 6a). Therefore, it can be assumed that the use of radiation doses and energies of argon atoms that do not lead to massive destruction of surface macromolecules will limit the depth of radiation damage in PEEK to 3-4 layers, i.e. it will not exceed 2 nm.

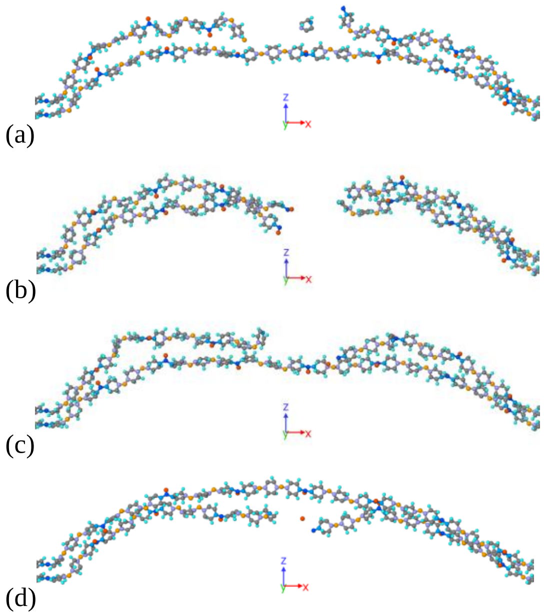


Fig. 6. The state of macromolecules M1 and M2 after 2 ps after the impact of argon atoms with energies of 90 eV (a)-(b) and 100 eV (c)-(d). Impact points: P^{C2-C3} (a) and (c), P^{C3-O1} (b), P_{C2-C3} (d).

V. CONCLUSION

MD simulation of the collision of argon atoms with energy from 20 eV to 100 eV with a PEEK substrate was carried out. The simulation results confirmed the validity of the assumption that single argon atoms that are a part of ANAB can significantly change the structure of chemical bonds on the surface of this plastic, thereby affecting its bioactivity. It has been shown that even the action of argon atoms with energies not exceeding 40 eV can cause breaks in a sufficient number of C-O bonds in the ether groups and C-C bonds in the ketone groups of plastic macromolecules. The free radicals that appear on the surface of PEEK as a result of this process can transform into hydroxyl and carboxyl groups when interacting with the appropriate atmosphere. The appearance of such groups on the surface of PEEK after treatment with ANAB was observed experimentally [6]. Additionally, the simulation confirmed that under the necessary conditions, the use of ANAB does not lead to the appearance of deep radiation defects in PEEK.

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