Simulation of low-pressure rf plasma treatment of ultrahigh molecular weight polyethylene

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Abstract. Methods of molecular dynamic simulation of the bombardment of polymeric materials by low-energy (up to 100 eV) ions generated in radio-frequency low-pressure (13.3-133 Pa) plasma are discussed. A model of RF plasma treatment of ultrahigh molecular weight polyethylene (UHMWPE) has been developed. It has been established that the bombardment of UHMWPE by argon ions initiates the fast rotation of the polymer chains, and the rupture of intramolecular bonds.

1. Introduction

Treatment of a material surface by a plasma of a radio-frequency (RF) discharge at low (1.33-133 Pa) pressure is an effective method of modification their nanostructure [1-5]. The main factor of the RF plasma action is the ionic bombardment by plasma ions having kinetic energy from 30 to 100 eV at ion current density from 0.3 to 1.5 A·m⁻² [1].

It was found that the surface of ultrahigh molecular weight polyethylene (UHMWPE) becomes hydrophilic after argon rf plasma treatment [2–5]. Adhesion properties of UHMWPE are significantly improved at the same time. The reason for the abrupt change in surface properties is the formation of polyethylene free radicals as a result of the breaking of molecular bonds caused by the low-energy ionic bombardment. The radicals react with atmospheric oxygen to form hydrophilic functional groups after the plasma treatment is finished. The described mechanism of plasma modification of UHMWPE is confirmed by the results of the study of free radicals by the electron paramagnetic resonance [2–5]. At the same time, the composition of the volatile and nonvolatile radicals formed during the plasma treatment, as well as the role of molecular conformations, the depth of modification, the sputtering ratio, and other issues remain unclear. Experimental observation of plasma exposure over time during processing is not possible. The mechanism of plasma modification of the polymeric surface can examine in depth by the molecular dynamic method [6, 7], during the plasma action among others.

The goal of this work is to develop a molecular dynamic model for modifying UHMWPE in argon RF plasma at low pressure of a plasma-forming gas.
2. Model of plasma treatment of UHMWPE

Polyethylene [-CH2-]n is a product of polymerization of ethylene [8]. The geometrical structure of a polyethylene macromolecule is a flat zigzag with carbon atoms in the vertices. The distance between adjacent carbon atoms is 0.154 nm, C–C carbon bonds form an angle of 109°28’. Hydrogen atoms are located on both sides of the zigzag plane at 0.109 nm from a carbon atom, at an angle of 120° relative to the C–C bond. The distance between two adjacent macromolecules is usually taken equal to the length of a single bond (C–C) [8].

Polyethylene refers to crystal-amorphous polymers, alternating amorphous and crystalline regions (crystallites), with the proportion of crystalline regions in UHMWPE reaching 95–97% [9]. The packaging of macromolecules in crystallite is orthorhombic. Therefore, a crystal section of UHMWPE with the zigzag plane oriented parallel to the surface is considered in the model.

The simulation was carried out for a unit cell of a polymer of 4.7x5.5x5.3 nm³. The united atom model (UAM) is used, in which the monomer unit -CH2- is considered as one particle [10-15]. This approximation is justified by the fact that the energy of the C–C covalent bond is 3.57 eV, while the energy of the C–H bond is 4.37 eV. Therefore, the C–C bonds as well as weaker intermolecular bonds are more likely to break by an Ar⁺ ion action to the UHMWPE macromolecule rather than the C–H covalent bond.

The model is described by the system of Cauchy problem for coordinates and speeds of each interacting particles

\[
\frac{d\mathbf{v}_k}{dt} = \frac{1}{m_k} \sum_{l \neq k} \mathbf{F}_{kl}, \quad k = 1, \ldots, N + 1,
\]

\[
\mathbf{v}_k(0) = \begin{cases} 0, & k = 1, \ldots, N, \\ \frac{(2W_i/m_i)^{1/2}}{2}, & k = N + 1, \end{cases}
\]

(1)

Here \(\mathbf{v}_k\) is the velocity vector of the particle indexed \(k\), \(\mathbf{r}_k\) is a radius vector, \(\mathbf{r}_{k0}\) denotes the coordinates of the initial position of the particles, \(\mathbf{F}_{kl}\) is the force field vector acting between particles indexed \(k\) and \(l\), \(m_k\) is the mass of the particle \(k\), where \(k = 1, \ldots, N, m_{N+1} \equiv m_{ion}\) is the mass of the bombarding ion, \(W_{ion}\) is ion kinetic energy, \(t\) is time, \(N\) is the number PE particles in the model cell, the particle numbered \(N + 1\) corresponds to the incident ion. The force field \(\mathbf{F}_{kl} = -\nabla U_{kl}\), where potential \(U_{kl}\) is calculated as the sum of the potentials of valence and non-valent interactions [10].

The force field of particles in polyethylene was modeled using the potential of Dreyding [11–15]. The interaction of an argon atom with macromolecules of polyethylene was modeled using the Lennard-Jones potential [15–17].

The Verlet algorithm [10] was used to solve equations (1), (2). The model was implemented using the LAMMPS package [18]. Visualization was carried out using VMD package [19, 20].

3. Results of numerical calculations

Due to the small size of the interacting objects (~10^{-10} m) and high speed of an Ar⁺ ion (~7·10⁵ m·s⁻¹), the numerical integration of the system of equations (1)-(2) was carried out at a timestep \(\delta t = 0.1\) fs.

The simulation results showed that the bombardment of UHMWPE by argon ions initiates the rapid rotation of the polymer chains, propagating in the material, and the rupture of intramolecular bonds (figure 1). The spray ratio is from 1 to 5 particles, depending on the energy of the incident particle. The sprayed particles are short-chained radicals [-CH2-]n, where \(n = 2 \div 6\).

4. Conclusion

The simulation shows that due to the rupture of intermolecular and interatomic bonds and low-energy ion implantation, uncompensated carbon bonds with a long lifetime, capable of forming functional groups after plasma treatment, appear in the surface nanoscale. In the case of inter-molecular penetration of implanted ions, stress states arise in the surface layer, resulting in an increase in surface energy. The cumulative effect of these factors contributes to surface activation and an increase in the adhesion of the UHMWPE fibers to the matrices.
Figure 1. Snap-shots of the argon-polyethylene system for ion energy of 100 eV at \( t=0 \) (a), \( t=27 \) fs (b), and \( t = 48 \) fs (c).

Conflicts of interest
The authors declare no conflict of interest relating to the material presented in this paper.

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