

Simulation of the processes of plasma modification and vacuum metallization of polymer materials by the method of molecular dynamics

Y. A. Timoshina^{1*}, E. F. Voznesensky¹, A. E. Karnoukhov¹, V. S. Zheltukhin¹, and A. I. Teptina¹

¹Kazan National Research Technological University, K. Marksa st., 68, 420015 Kazan, Russia

Abstract. The article presents the results of the development of molecular dynamics models of modifications of polypropylene (PP) material in the plasma of a radio-frequency (RF) discharge and a copper coating deposit by magnetron sputtering on the surface of a polyethylene (PE) material. The model of the RF plasma modification process describes changes in the surface layers of the PP material upon interaction with low-energy plasma ions: the nature of the breaking of covalent bonds in macromolecules, the chemical composition of sputtered particles, and changes in the ordering of the supramolecular structure. The model of the vacuum metallization process describes the processes of the introduction of metal atoms into the polymer structure, the change in the conformation of macromolecules, the formation of macroradicals with uncompensated chemical bonds, and the formation of an interfacial layer between the polymer and the metal coating.

1 Introduction

Currently, polymeric materials are products of the chemical industry and are used for the production of household products. At the same time, with the development of technologies and the growth in the consumption of synthetic polymers, it is promising to modify and functionalize materials based on them in order to impart new properties.

Vacuum-plasma methods are promising methods for modifying and functionalizing the surface of synthetic polymeric materials. RF plasma modification makes it possible to control such surface properties of synthetic polymeric materials as roughness, wettability, and adhesion, while not leading to the destruction of surface layers and deterioration of the physical and mechanical properties of materials [1-6]. The use of the magnetron sputtering method makes it possible to deposit metal and metal-containing coatings of high uniformity on polymer materials of various structures and fibrous composition, and the method is characterized by high productivity and the absence of a destructive effect on the surface of polymer materials [7].

* Corresponding author: ybuki@mail.ru

The mechanisms of material modification in low-pressure RF plasma are considered in detail in [8]. The main ones are low-energy ion bombardment, ion recombination on the sample surface, and thermal flow. During plasma treatment in a low-pressure RF capacitive discharge, a positive charge layer is formed near the sample surface, in which positive plasma ions are accelerated to particle energies up to 100 eV, depending on the type of discharge, input power, pressure, flow rate, and composition of the plasma-forming gas [9].

It is known that when applying metal coatings by magnetron sputtering, the surface of polymeric materials is bombarded by metal atoms with energies up to 20 eV [10]. The specific power of the magnetron has a significant effect on the particle flux density of the sputtered material, determining the deposition rate of the metal coating and the associated thermal load on the substrate material. The pressure in the vacuum chamber is a key factor influencing the change in the energy of metal particles, which directly affects the strength of the adhesive interaction between the metal coating and the polymer substrate [11-13].

When modeling the processes of plasma modification and vacuum metallization of polymeric materials, it is of interest to change the composition and structure of macromolecules of polymeric materials as a result of ion bombardment, as well as to analyze the processes of deposition of metal coatings with the formation of an interfacial boundary. This paper presents the results of modeling by classical molecular dynamics, which makes it possible to study the mechanisms of plasma modification and vacuum metallization of polymeric materials at the atomic-molecular level.

2 Methods and materials

When creating a molecular-dynamic model of the interaction of low-energy ions with PP in RF low-pressure plasma, a crystalline region of isotactic PP was considered, the size of the simulated cell was $6.1 \times 4.0 \times 4.3 \text{ nm}^3$, the number of atoms was 4550, and the boundary conditions were periodic. The bombardment of the polymer surface with an argon ion with an energy of 100 eV was simulated. Taking into account the relaxation time of the polymer, which is $10^{-6} - 10^{-4} \text{ s}$ [14], and the density of the ion flux in low-pressure RF plasma from 2 to 10 $\text{ion}/(\text{nm}^2 \times \text{s})$, the model considers a single act of bombardment with an argon ion. Since the sample in the plasma is negatively charged, positive ions recombine on the surface of the sample, and fast atoms are implanted inside it, the kinetic energy of which is equal to the kinetic energy of the ion.

When creating a molecular-dynamic model of vacuum metallization, the process of deposition of copper atoms on a section of the PE crystalline phase was considered. The size of the simulated cell is $6.1 \times 4.0 \times 8.5 \text{ nm}^3$, the total number of substrate atoms is 9100, copper atoms is 3000. To approximate the results of mathematical modeling to real processes, the PE crystalline phase was subjected to relaxation at a temperature of 300 K. The kinetic energy of copper atoms was 6 eV, the flux density of copper particles was 1400 $\text{atoms}/(\text{nm}^2 \times \text{s})$, and the position of copper particles was set randomly.

The simulation was carried out using the LAMMPS universal software package for classical molecular dynamics simulation [15]. Full-atomic models are considered. As a force field for PP and PE, the multiparticle potential AIREBO-M, developed for hydrocarbons and allowing simulation of systems with pressures up to 14 GPa [16, 17]. The interaction of the argon ion with PP and the interaction of copper atoms with PE was modeled using the Lennard-Jones potential [18, 19].

3 The results and discussion

The results of numerical calculations of the interaction of a low-energy argon ion with the PP surface in a low-pressure RF plasma are shown in Figures 1 and 2. On the images of the simulated area (Figure 1), the arrow marks the position of the argon atom (the recombined ion).

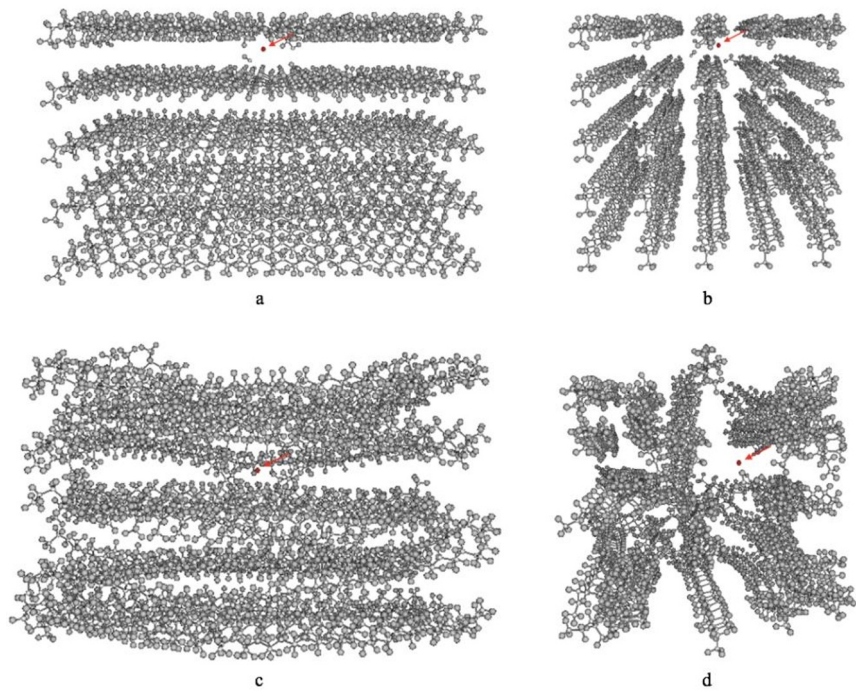


Fig. 1. Image of the simulated PP region (gray) during interaction with an argon ion (red), which has a kinetic energy of 100 eV, in a low-pressure RF plasma at the time $t = 10$ fs (a, b), $t = 1400$ fs (c, d).

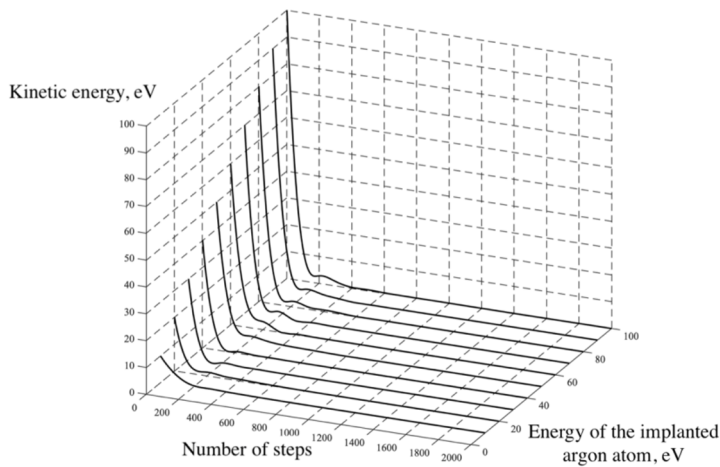


Fig. 2. Change in the kinetic energy of an implanted argon atom upon interaction with PP in low-pressure RF plasma

Visualization of the results of molecular dynamics modeling showed that ion bombardment of PP by argon ions in low-pressure RF plasma leads both to a change in the polymer structure and conformational transformations of macromolecules, and to the

breaking of covalent chemical bonds. During ion bombardment, the main chain of the polymer and C–H bonds are broken; sputtered particles are single atoms and hydrocarbon radicals with the number of carbon atoms from 1 to 3 (CH, CH₂, CH₃, C₂H₂, C₃H₄). Regardless of the initial kinetic energy of the argon ion, the decrease in kinetic energy is exponential. In this case, the kinetic energy of the argon ion decreases to 10 eV in the first 30 fs, and after 150 fs from the beginning of the simulation it is less than 0.1 eV [20].

The results of numerical calculations of the interaction of copper atoms with the PE surface during the deposition of a metal coating by the magnetron sputtering method are shown in Figure 3. Based on the results of numerical calculations, the depth of the interfacial layer was estimated, as well as a quantitative analysis of the depth distribution of copper atoms (Figure 4).

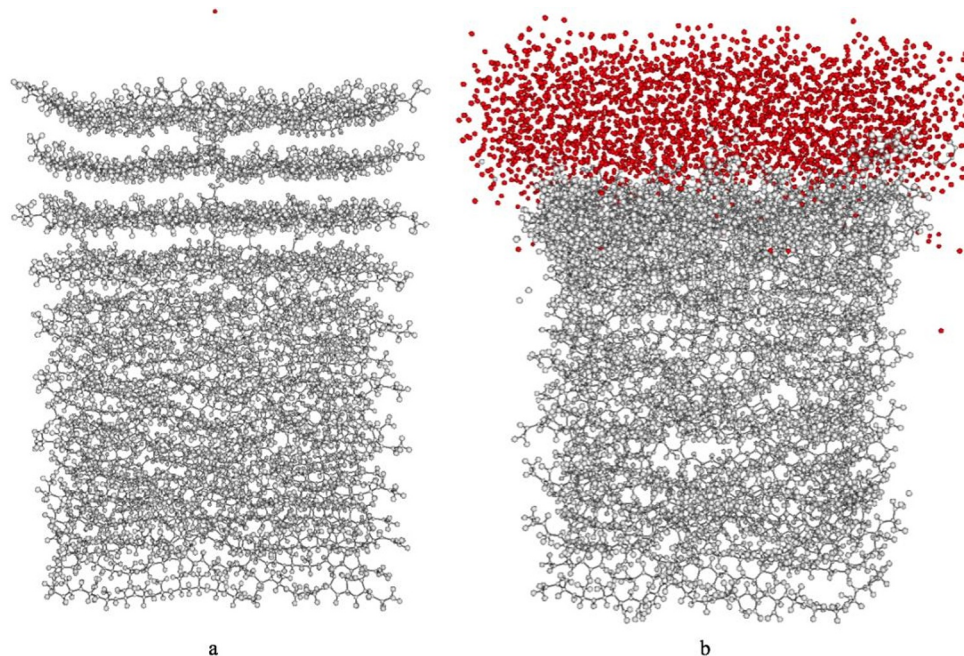


Fig. 3. Image of the simulated PE region (gray) during interaction with copper atoms (red) at the time $t = 0$ ps (a), $t = 8.96 \times 10^{10}$ ps (b)

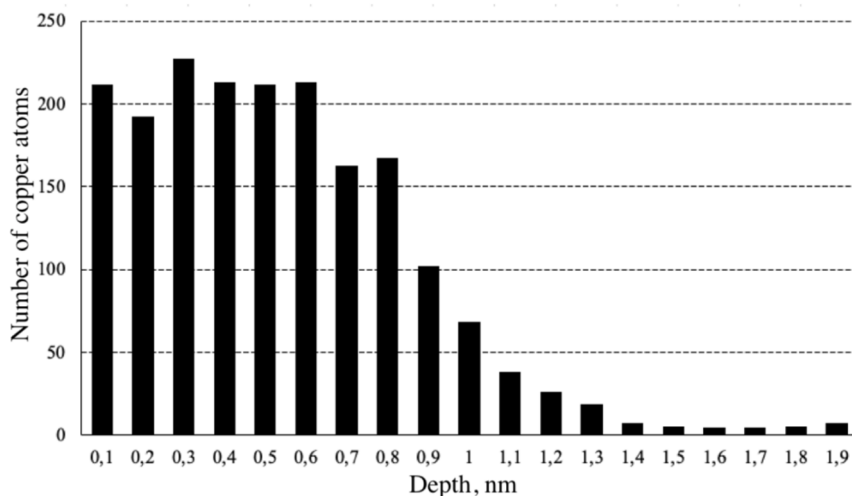


Fig. 4. Quantitative depth distribution of copper atoms in the interfacial layer in the simulated cell

The results of molecular dynamics modeling make it possible to establish that in the process of deposition of a copper coating on the PE surface by the magnetron sputtering method, when metal particles are located on the polymer surface, macromolecules are broken, while the main structural changes occur regularly at a depth of up to three molecular layers on the surface of the polymer material. There is no sputtering of polymer particles, and the resulting macroradicals with uncompensated chemical bonds and altered conformational structure form an interfacial layer. It has been quantitatively established that the depth of the interfacial layer is up to 2 nm. The interfacial layer is characterized by some irregularity in the arrangement of polymer macromolecules with a simultaneous increase in their packing density.

4 Conclusions

The developed model of RF plasma modification describes changes in the surface layers of a PP material upon interaction with low-energy plasma ions, including a change in the ordering of the supramolecular structure of the polymer material and the processes of breaking covalent chemical bonds with sputtering of particles that are single atoms and hydrocarbon radicals with the number of carbon atoms from 1 to 3. The developed model of vacuum metallization of a polymeric material describes the processes of deposition of a metal coating with the formation of an interfacial layer up to 2 nm deep, characterized by a violation of the regularity of the arrangement of polymer macromolecules with a simultaneous increase in their packing density.

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