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Effect of Oxygen Chemistry in Sputtering of Polymers

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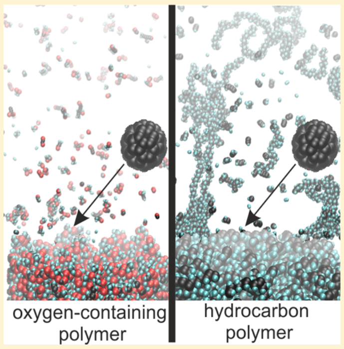
Supporting Information

ABSTRACT: Molecular dynamics computer simulations are used to model kiloelectronvolt cluster bombardment of pure hydrocarbon [polyethylene (PE) and polystyrene (PS)] and oxygen-containing [paraformaldehyde (PFA) and polylactic acid (PLA)] polymers by 20 keV C_{60} projectiles at a 45° impact angle to investigate the chemical effect of oxygen in the substrate material on the sputtering process. The simulations demonstrate that the presence of oxygen enhances the formation of small molecules such as carbon monoxide, carbon dioxide, water, and various molecules containing C═O double bonds. The explanation for the enhanced small molecule formation is the stability of carbon and oxygen multiple bonds relative to multiple bonds with only carbon atoms. This chemistry is reflected in the fraction of the ejected material that has a mass not higher than 104 amu. For PFA and PLA, the fraction is approximately 90% of the total mass, whereas for PE and PS, it is less than half.



Molecular and polymeric solids can be depth profiled with chemical specificity by using energetic (kiloelectronvolt) cluster projectiles as in secondary ion mass spectrometry.[1,2] Although this process can often work well, there are, of course challenging systems. For example, polymers consisting of primarily carbon and hydrogen do not depth profile well, that is, as more and more material is removed the mass spectrum changes and the signal decreases.[3] On the other hand, polymers that contain oxygen exhibit a characteristic mass spectrum regardless of how much material is removed.[3] Obviously, chemistry matters. There have been numerous computer simulations aimed at understanding the physics of the energetic bombardment process, but modeling widespread chemical reactions has been hampered by the lack of available interaction potentials.

Almost all computer studies of kiloelectronvolt projectile-induced chemistry performed to date on organic materials[4] use the reactive empirical bond order (REBO)[5,6] or the adaptive intermolecular reactive empirical bond order (AIREBO) potentials,[7] both of which are restricted to materials composed of hydrogen and carbon atoms. The situation has changed since an optimized version of the Reax-FF potential[8,9] and the charge-optimized many-body (COMB)[10,11] potential have recently become available as a part of the LAMMPS modeling software.[12,13] In this work, molecular dynamics computer simulations and the Reax-FF potential are employed to investigate the effect of oxygen on the energetic cluster bombardment of polymer solids.

The first systems to be investigated with the enhanced set of interactions are two groups of polymers that will allow us to assess the effect of oxygen in the substrate compounds on the sputtering process. The first group consists of polyethylene (PE) and polystyrene (PS), polymers that contain only C and H atoms. PE is a simple linear chain, and PS contains side groups. Both of these polymers are known to be hard to depth profile. The second group, composed of paraformaldehyde (PFA) and polylactic acid (PLA), are polymers that contain oxygen and depth profile well. Analogous to the pure hydrocarbon systems, there is one compound that is a linear chain (PFA) and one polymer has side chains (PLA). In addition, the carbon and oxygen bonding in the two systems is distinct. The PFA has only CO single bonds, and the PLA has an ester group. The repeat units of the investigated polymers are shown schematically in Figure 1. Simulations were performed for C_{60} and Ar_{872} bombardment at different energies and incident angles typical for SIMS experiments. The basic results presented here are common to all the simulations; thus,

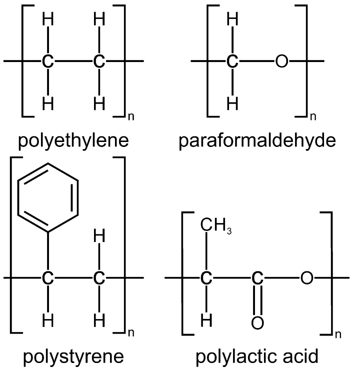


Figure 1. Repeat units of investigated polymers.

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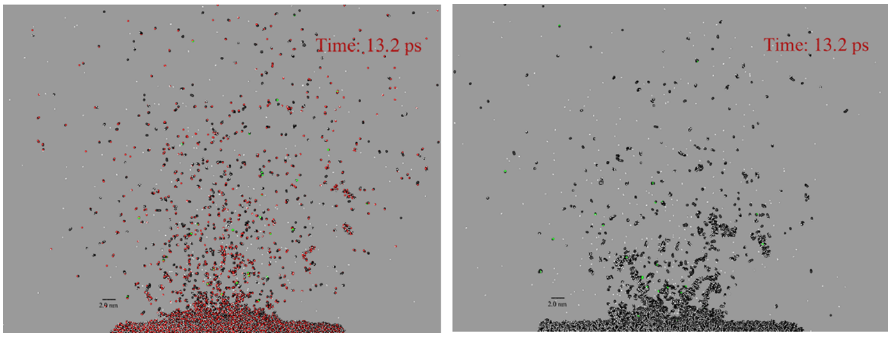

Figure 2. Snapshots of the sputtering stimulated by 20 keV C_{60} impact at 45° at polylactic acid (left panel) and polystyrene (right panel) samples taken 13 ps after projectile impact. Black, red and white dots represent carbon, oxygen, and hydrogen atoms, respectively.

we restrict the discussion to impact by 20 keV C_{60} cluster projectiles at 45° impact angle.

Table 1. Total Sputtering Yield of Polyethylene (PE), Polystyrene (PS), Paraformaldehyde (PFA), and Polylactic Acid (PLA) Induced by 20 keV C_{60} Impact at 45°[a]

system	yield (amu)	yield (nm^3)	% of yield in species of ≤104 amu
PE	5.8×10^4	74	50
PS	4.5×10^4	79	40
PFA	4.0×10^4	69	92
PLA	4.5×10^4	56	87
PLA exptl		64 ± 12	

[a] The yield is expressed in atomic mass units and volume units. The numbers in the last column show contribution of fragments with a mass lower or equal to 104 amu to the total sputtering yield. "PLA exptl" indicates experimentally measured sputtering yield.[14]

The snapshots of the PLA and PS systems bombarded by 20 keV C_{60} at 45° impact angle taken at 13 ps are shown in Figure 2. The sputtering yields for each system are given in Table 1 in both atomic mass units and cubic nanometers. In Table 1 there is also the yield for PLA obtained from a depth profiling experiment performed with 20 keV C_{60} at 45°.[14] The measured value of 64 nm^3 agrees within the experimental error with the calculated value of 56 nm^3. Even though the total yields of hydrocarbon- and oxygen-containing systems are comparable, the nature of the ejected material is quite different, as can be seen in Figure 2 and Table 1. For systems with only C and H atoms, large pieces of the polymer chains are ejected. The choice of the cutoff value for small molecules was determined by examining the mass distributions of particles ejected from all investigated samples. All mass spectra are dominated by lower-mass species, and the last most significant peak from all these spectra was chosen as the cutoff. It is a peak at 104 amu (styrene, C_8H_8) for PS. Thus, we use a mass of 104 amu to categorize the ejected particles as small (≤104 amu) and large (>104 amu) ejected species to make the visual observations more quantitative. For the oxygen-containing polymers, the ejected material comprised predominantly (that is, ~ 90%) small molecules, atoms, and radicals. In contrast, for both hydrocarbon polymers most of the ejected mass in the larger species. There are also long pieces of polymer chains that remain in the sample or extend into the vacuum above the surface. Animations of the PLA and PS bombardment events are given in the Supporting Information.

The large diversity of events that occur during the bombardment event and the large diversity of products make mechanistic analysis challenging. The linear systems of PE and PFA have as the dominant molecular product beside ubiquitous H_2 the unzipping species of ethylene and formaldehyde with eight times as much formaldehyde ejected from PFA than ethylene from PE. The energetics of the unzipping reactions are thus estimated with average bond energies to explain the observed differences. Using average bond energies of 3.6 and 3.7 eV for single bonds of C−C and C−O, 6.3 and 7.7 eV for double bonds of C═C in molecules and C═O in ketones, 8.3 eV for a C═O bond in carbon dioxide,[15] and 11.1 eV for the triple bond in carbon monoxide,[16] one can estimate the reaction energy for ethylene unzipping to be 0.9 eV endothermic, whereas for formaldehyde unzipping it is −0.3 eV exothermic. The stability of the carbon and oxygen multiple bonds make formation of small energetic molecules energetically feasible. To estimate the possible effect on the energy of the system, we examine the 160 carbon monoxide molecules that are sputtered from PLA that form from nonadjacent C and O atoms. If all of these molecules were to end up in the ground state, this would correspond to a release of 1750 eV of energy. This energy can enhance material ejection and also facilitate additional reactions that may lead to further energy release and material fragmentation. While molecules are also created in the PS system, they are formed predominantly by endothermic processes that consume energy.

To illustrate the difference between the ejected material, we delineate the ejected small molecules (i.e., atoms and radicals are ignored) that appear more than 20 times in the simulation and omit the ubiquitous H_2 that contributes relatively low mass amounts. We start with the hydrocarbon species for PE and PS, which have 235 and 141 ejected molecules, respectively, in this category. For PE, in decreasing order of frequency are ethylene, acetylene, C_2, C_3H_3 (2-cyclopropenylium), and C_3H_4 (methyl acetylene) and for PS in descending order of frequency are C_2, C_8H_8 (styrene), acetylene, and C_3H (propynylidyne; observed in cold clouds). In contrast, for PFA and PLA, there are 1357 and 664 small molecules, respectively, in the sputtered material. For PFA there is formaldehyde, followed by carbon monoxide, water, carbon dioxide, CH_2O_2 (formic acid), and C_2H_2O (ketene) with over half of the species being formaldehyde. For PLA there is carbon monoxide, carbon dioxide, water, C_3H_4O (1-propene-1-one), $C_3H_4O_2$ (acrylic acid, malondialdehyde), C_2H_4O (acetaldehyde), C_2H_2O (ketene), and acetylene. For both systems there is also a variety of small radical species including atoms. It is evident that the presence of oxygen in the PLA system increases the variety of product molecules that can be formed. Most of the sputtered small molecules from the

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oxygen-containing polymers have C−O multiple bonds, with water being the notable exception.

The formation of the small molecules occurs by a variety of processes. Some of them are simple fragments of original chains. Many of the product molecules are formed, however, with atoms originally located in different parts of the sample.[17,18] For example, for carbon monoxide molecules found sputtered at the end of the PLA simulation, 26% arise from an original ketone functional group, 16% from the C and O atoms in the main chain, and 58% of them are from atoms in different places in the original sample. Of the carbon dioxide molecules observed, 67% arose from the contiguous atoms in the chain, 12% from recombination of three atoms, and 21% from a mixture of contiguous atoms and recombination. An animation showing the recombination mechanism for CO_2 can be found in the Supporting Information.

The simulations show clearly that the presence of oxygen in the substrate system facilitates the formation of small molecules, especially those with multiple bonds, because the formation process can be exothermic. Not only is the formation reaction energetically downhill facilitating product formation, but the process releases energy for subsequent processes to occur. In the pure hydrocarbon systems of PE and PS, on the other hand, the reaction processes to form small molecules are endothermic. This makes the reactions less frequent and also consumes energy from the system. The consequence is that the nature of the ejected material has a different mass distribution. The ejected material from the oxygen-containing polymers is dominated by small species, molecules, atoms, and radicals, whereas the ejected material from the pure hydrocarbon polymers contains a significant contribution of larger particles.

COMPUTATIONAL METHODS

A detailed description of the molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere.[4] Briefly, the motion of particles is determined by integrating Hamilton's equations of motion. The forces among particles are described by a blend of pairwise additive and many-body potential energy functions. Interactions among H, C, and O atoms are described by a Reax-FF force field[8] splined at short distances with a ZBL potential to properly describe high-energy collisions. The shape and size of the samples are chosen based on visual observations of collision cascades stimulated by impacts of 20 keV C_{60} projectiles. As a result, hemispherical samples with a radius of 18 nm are used. Four systems are investigated. Pure hydrocarbon polymers are represented by methyl-terminated polyethylene, PE, ($C_{202}H_{406}$) molecules, and *n*-butyl terminated polystyrene, PS ($C_{808}H_{818}$). Hydroxyl-terminated paraformaldehyde, PFA ($C_{100}H_{102}O_{101}$), and hydroxyl-terminated polylactic acid, PLA ($C_{300}H_{402}O_{201}$), represent systems containing oxygen atoms. The model systems contain 2433 (1 479 264 atoms), 997 (1 621 122 atoms), 3863 (1 555 580 atoms), and 1177 (1 062 831 atoms) polymer chains for PE, PS, PFA, and PLA samples, respectively. Each polymer chain contains 100 repeat units. The calculated densities of the equilibrated samples are as follows: 0.90, 0.96, 1.39, and 1.36 g/cm^3 for PE, PS, PFA, and PLA, respectively. Rigid and stochastic regions 0.5 and 1.5 nm wide, respectively, are used to simulate the thermal bath that keeps the sample at the required temperature, to prevent reflection of pressure waves from the boundaries of the system, and to maintain the shape of the sample.[4,19] The simulations are run at 0 K target temperature in an *NVE* ensemble and extend to 50 ps, which is long enough to achieve saturation in the sputtering yield versus time dependence. The calculations are performed with a LAMMPS code[13] that was modified for a more efficient modeling of sputtering phenomena. Because it is known that statistical accuracy increases with cluster size,[19] one trajectory was calculated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b00514.

Impact of 20 keV C_{60} at 45° at the polylactic acid sample (MPG)

Impact of 20 keV C_{60} at 45° at the polystyrene sample (MPG)

Recombination mechanism for creation of CO_2 molecule during 20 keV C_{60} bombardment of the polylactic acid sample (AVI)

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Notes

The authors declare no competing financial interest.

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