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Effects of thermal energy deposition on material ejection in poly(methyl methacrylate)

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Abstract

The effects of absorption of 7.9 and 5.0 eV photons by the polymer poly(methyl methacrylate) are studied using molecular dynamics simulations. By rapidly depositing a critical amount of thermal energy in the surface region (greater than 0.03 eV $Å^{-3}$), a pressure wave is formed which causes spallation of the substrate. If there is only one photon absorbed per monomer unit of the polymer, the 7.9 eV photons can supply sufficient energy density to initiate ejection.

Keywords: Ultraviolet absorption; Molecular dynamics; Thermal energy; PMMA

1. Introduction

The removal of polymeric material using laser ablation is a technique that has proven useful in such applications as drilling ink-jet nozzles [1] and developing lab-on-chip devices [2]. Describing the fundamental processes that drive ablation, though, has been challenging due to the complex, heterogeneous conditions caused by the laser pulse. A recent review describes the diverse set of mechanisms which are possible in ablation of polymeric materials [3]. These include photochemical models in which photons excite molecules to a dissociative state and directly cleave bonds [4]; photothermal models in which the molecules excited by photons are rapidly thermalized [5]; photophysical models in which both photochemical and photothermal processes are important [6]. Indeed, much experimental work has been performed on specific polymers, such as poly(methyl methacrylate) or PMMA, that groups the effects of lasers at different wavelengths into these three groups [4,7–10]. However, the microscopic effects of the deposition of pure thermal energy from photon irradiation on polymeric substrates remain vague.

Molecular dynamics (MD) simulations have proven effective in elucidating mechanisms of thermal desorption and ablation of molecular solids. Upon photon absorption, the internal energy of an excited, coarse-grained particle was able to be transferred through an extra degree of freedom which allowed the particle to change size and alter its interaction potential [11,12]. The simulations revealed several distinct regimes after laser excitation. When the fluence of the laser is low, the substrate desorbs small particles and clusters [11,12]. When the laser fluence reaches the critical value, ejection of large clusters or ablation, occurs following surface expansion due to overheating the material [11,12]. If the photon irradiation occurs within a relatively short period of time, the resulting pressure wave can overcome the tensile strength of the material and lead to spallation [13].

In the present work, we simulate the effects of adding thermal energy to PMMA with MD simulations. Using two photon energies and a range of fluences during a short pulse, we assess the amount of ejected material and the conditions that lead to ejection.

2. Computational details

The details of the MD simulation have been previously described [14]. Briefly, an amorphous PMMA sample consisting of 951 polymer chains was constructed in a 51 Å × 51 Å × 953 Å simulation cell with a density of 1.2 g cm^{-3}. In each polymer, 115 coarse-grained particles, or united-atoms, were used to represent the C, CH_2, CH_3, O and CO functional

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groups. Energies of 7.9 eV (equivalent to a 157 nm photon) and 5.0 eV (equivalent to a 248 nm photon) are absorbed per excitation by a PMMA substrate during a pulse width of 5 ps at fluences ranging from 5 to 20 mJ cm^{-2}. The excited particles were chosen randomly, with the probability proportional to the fluence and attenuated with depth by Beer's Law (penetration depth of 100 Å). We assume that only one photon could be absorbed per monomer unit of the polymer, and, with each excitation, the photon energy is equally partitioned to increase the kinetic energy of the six coarse-grained beads of the absorbing monomer. Bonds within the polymer break only due to mechanical stretching and no thermally activated events are included. Periodic boundary conditions were employed on the sides of the simulation cell to simulate the center of a laser, and a pressure absorbing boundary condition was implemented at the bottom of the simulation cell to represent an infinite solid and negate the boundary effects from the laser induced pressure wave [15].

3. Results and discussion

The yield of particles (in MMA equivalents) at 165 ps as a result of thermal excitation is given as a function of fluence for the photon energies in Fig. 1. In addition, the average cluster size of the ejected material at 165 ps is plotted in Fig. 1. In the 7.9 eV/photon curve, there is sudden rise in the number of ejected particles when the fluence is greater than 8 mJ cm^{-2}. Above this threshold fluence, the ejected material is characterized by one to five large clusters, while only monomers, dimers and small clusters eject for the lower fluence simulations. The relatively small ejected particles and the low yields at the lower fluence for the 7.9 eV/photon simulations can be ascribed to a surface vaporization mechanism which is characteristic below the ablation threshold [11,12]. Above the threshold, sufficient energy was added to substrate during the short pulse width to create a large pressure wave (greater than 0.9 GPa for a fluence of 10 mJ cm^{-2}). The resulting tensile wave is greater than the tensile strength of the PMMA sample and leads to cracking and spallation. A similar

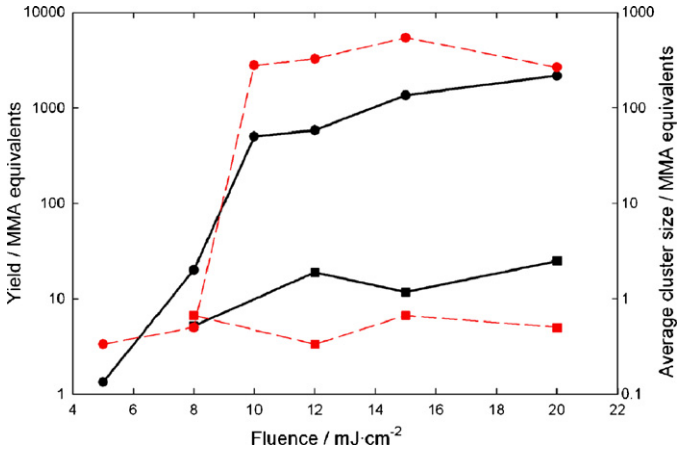

Fig. 1. The yield of particles (solid dark line, left abscissa) and average cluster size (dashed light line, right abscissa) as a function of fluence for 7.9 eV/photon (circles) and 5.0 eV/photon (squares) simulations at 165 ps.

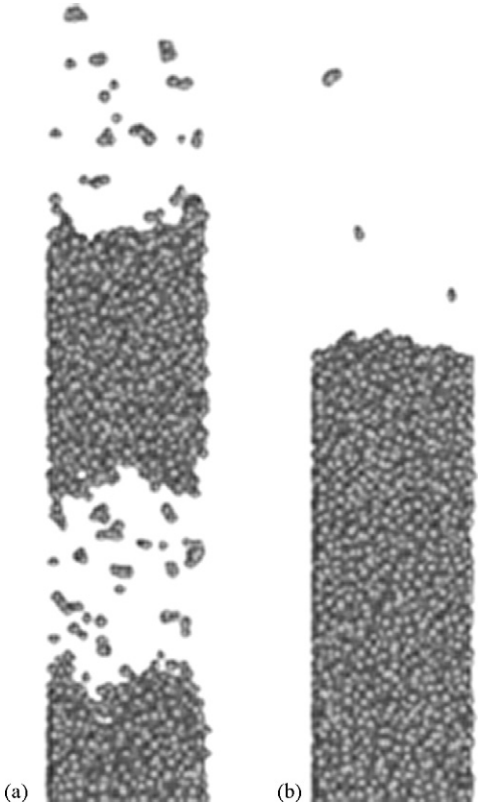

Fig. 2. Snapshots of the surfaces of: (a) a 7.9 eV/photon simulations with a fluence of 12 mJ cm^{-2} showing spallation of the top layer of the substrate at 30 ps and (b) a 5.0 eV/photon simulation with a fluence of 12 mJ cm^{-2} showing surface evaporation at 68 ps.

mechanism occurs in simulations of molecular solids [13,16], in bubble formation of PMMA [17], and experimental ablation of PMMA [18]. Surface evaporation continues after spallation in the high fluence simulations, however, no appreciable change in yield is expected over the timescale of interest.

The amount and type of material ejected for the two photon energies greatly differ at high fluences, as shown in Fig. 1. For 5.0 eV/photon simulations, high fluences as well as low fluences show surface vaporization mechanisms. Snapshots comparing the surfaces of the substrate at a fluence of 12 mJ cm^{-2} irradiated with the two photon energies are shown in Fig. 2. The amount of energy deposited in the substrate is plotted as a function of the initial depth of the absorbing monomer for 7.9 eV/photon simulations with fluences of 8, 10 and 12 mJ cm^{-2} and for a 5.0 eV/photon simulation with a fluence of 12 mJ cm^{-2} in Fig. 3. The energy deposition for the 5.0 eV/photon simulation deviates from exponential absorption because less chromophores were available than necessary due to our assumption that a monomer unit in the polymer can only absorb one photon. For a given amount of energy, more 5.0 eV photons are needed than 7.9 eV photons. At a density of 1.2 g cm^{-3}, there are approximately 1600 monomers per 100 Å depth in the simulation cell, and the simulation is restricted to only one absorption event per monomer unit of the polymer. Therefore, when the maximum amount of photons has been absorbed at a certain depth, more monomers from the lower layer absorb in order to reach a given fluence. Within the top

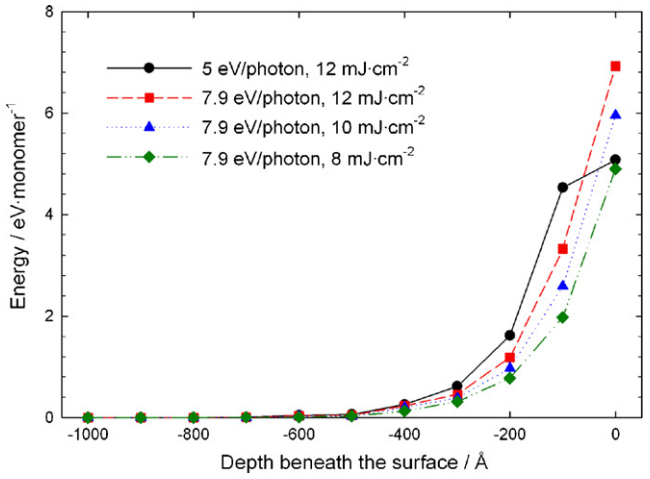

Fig. 3. The energy deposited per monomer in the system as a function of depth. The 7.9 eV/photon simulations with fluences of 10 and 12 mJ cm^{-2} exhibit spallation. The others do not.

100 Å of the polymer sample (defined here as the surface layer where the majority of energy is deposited), two simulations that show spallation, fluences of 10 and 12 mJ cm^{-2} with 7.9 eV/photon, deposit 5.9 and 6.9 eV/monomer. The pressure wave and subsequent tensile wave as a result of the high energy deposited in the surface layer cause cracking and ejection of a large or several large clusters of material. In contrast, the 7.9 eV/photon simulation with a fluence of 8 mJ cm^{-2} and the 5.0 eV/photon simulation with a fluence of 12 mJ cm^{-2} only deposit 5.0 eV of thermal energy per monomer in the surface layer of the sample. Even though the 5.0 eV/photon simulation with a fluence of 12 mJ cm^{-2} deposited an equal amount of thermal energy as the 7.9 eV/photon simulation with a fluence of 12 mJ cm^{-2}, the energy density in the surface layer was not sufficient to generate a concentrated pressure wave necessary for spallation of material. The higher energy simulations with 5.0 eV/photon show a void in the material that forms then collapses as the tensile strength material of the material withstands the wave.

In order to assess the effects of rapid thermal deposition on only the surface of the substrate, simulations were performed where the top 100 Å of the substrate was heated with 5.0, 5.9 and 6.9 eV per monomer in the layer over 5 ps. For the 5.9 and 6.9 eV/monomer simulations, spallation of large clusters occurs with yields of 735 and 750 MMA equivalents, respectively. However, when 5.0 eV/monomer was deposited in the upper 100 Å of the sample, only surface evaporation occurs. The density of thermal energy deposited in the surface layer of the polymer sample within 5 ps, therefore, must be greater than 0.03 eV $Å^{-3}$, or 5 eV/monomer, in order to create a tensile wave which is capable of initiating spallation. In each of the simulations of photon absorption that have large yields, the energy density in the top layer is greater than this critical value. To achieve ejection of material with 5.0 eV photons at high fluences, the critical energy density in surface layer of the sample must be attained. If there are multiple absorption sites on each chromophore through doping [19,20] or multiple photons are absorbed by each chromophore after photochemical changes, such as incubation [9], then a sufficient number of 5.0 eV photons can be absorbed to reach this energy density for a purely thermal process to cause ejection of material. In addition, if a larger penetration depth was used, less energy at a given fluence would be deposited in any given layer near the surface of the substrate. Higher fluences or dopants [19,20] in the surface layer therefore would be required to reach the critical energy density.

4. Conclusions

Rapid deposition of thermal energy causes ejection of material in a PMMA substrate. If the energy density near the surface layer reaches a critical value within 5 ps, a tensile wave is formed that fractures the sample and leads to photomechanical ablation. At high fluences, 7.9 eV photons are able to supply the surface layer with enough thermal energy to cause photomechanical ejection of material. Since the monomer units in the polymer are restricted to absorbing only one photon, 5.0 eV photons are not capable of depositing the critical amount of thermal energy in the surface layer. If photon absorption is purely thermal, spallation is a direct consequence of the amount of energy placed in the surface layer of the sample. However, if a large pressure differential is created by another event or sequence of events within a short period of time, such as the formation of small energetic particles [21], which was not considered in this study, ejection of the surface layer can occur.

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