

A molecular dynamics study of the effects of the inclusion of dopants on ablation in polymethyl methacrylate

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Molecular dynamics simulations are used to elucidate mechanisms of ablation in dopant-polymer systems. In one set of simulations, a uniform distribution of thermal absorbers are added to a polymethyl methacrylate substrate and are excited. Chemical decomposition occurs in the regions near the absorbers. Ejection of large pieces of substrate then follows the thermo-chemical breakdown of material. In another set of simulations, an absorbing cluster is embedded in the polymethyl methacrylate substrate at a depth of 50 or 250 Å. Only the particles comprising the cluster are excited during the laser pulse. Ejection of material is initiated upon the fracture of the cluster and the cleavage of the surrounding polymer bonds with little chemical damage during the process. These two mechanisms of ejection suggest different pathways of ablation in doped polymer materials.

1. Introduction

Some polymers have low absorption coefficients at particular wavelengths, and in order to achieve ablation in these materials, researchers incorporate dopant particles to more effectively utilize the photon energy.^{1–4} The dopant particles vary from uniformly distributed, small organic dyes to large carbon or metal nanoparticles.^{1,5–7} Additionally, polymers have been synthesized to include specific absorbing chromophores in the backbone which assist in initiating ablation.^{8,9} The contribution of each of these dopant types to the ejection mechanism is complicated by the multitude of interactions that occur, including the chemical and physical characteristics of both the dopant and polymer particles. Understanding the fundamental, microscopic processes initiating ablation for each case serves to bolster current research.

For over twenty years, scientists have performed experiments seeking to augment ablation in polymers using various physical and chemical techniques. The earliest work was performed on poly(methyl methacrylate), or PMMA, by Srinivasan.¹ A dopant of acridine was included in the PMMA matrix and the etch depth (ablation yield) was studied as a function of fluence after excitation by a ultraviolet (UV) laser. The dopant molecules absorb multiple photons during the irradiation time period and readily decompose. This process was observed to lower the ablation threshold when compared to the excitation of the pristine polymer. Similar results were observed by Masuhara irradiating PMMA doped with pyrene and benzophenone.¹⁰ Further studies show that using an aromatic dopant molecule, 2-(2'-hydroxy-phenyl) benzotriazole, photochemically induced reactions can initiate ablation in a PMMA substrate.¹¹ The organic dopant absorbs multiple UV photons, is excited to a higher electronic state, and then photochemically decomposes causing ablation in the

substrate. Ihlemann and co-workers also studied the effects of the decomposition of dopant molecules in a PMMA matrix.⁵ Upon UV excitation, the dopants, 1,3-diphenyltriazene or 9,10-dihydroanthracene-9,10-dicarboxylic anhydride, readily decompose into nitrogen or carbon monoxide and carbon dioxide, respectively, forming 'bubbles' beneath the substrate surface. A complex mechanism was proposed in which both an elevation in temperature from thermalization of the photon energies and the production of the gaseous molecules give rise to ablation. Researchers then developed designer polymers which include the highly absorbing triazene functional group found in the previous dopant.⁸ The distinct advantage of using the triazene functional group within the polymer is that photochemical activities could dominate following laser irradiation at a specific wavelength.^{2,12} These novel triazene polymers have shown to be effective in producing high quality structures using laser ablation.¹²

Many of the previously mentioned studies use UV lasers in their investigations of ablation. While the use of dopants and functional groups which are UV active is prevalent, ablation research has also been performed using infrared (IR) lasers and IR active dopants. Thermal mechanisms dominate the ejection process using IR wavelengths.¹³ An IR active dye (IR-165) was added to a PMMA substrate which can absorb up to several hundred photons during a 100 ps laser pulse.^{14,15} At the threshold, the calculated fraction of thermally decomposed polymer was observed to increase with increasing laser energy. The proposed mechanism for ablation is dopant (thermal) induced cleavage of the polymer chain followed by continued unzipping and depolymerization in the plume. Work by Pinto and Lloyd shows a similar mechanism occurs in a IR-165 doped ethyl methacrylate/2-hydroxyethyl methacrylate copolymer substrate.¹⁶ In another study, different sized dopants (IR-165, approximately 1 nm in radius and graphite nanoparticles, approximately 110 nm in radius) were separately included in ethylcellulose polymer films.⁶ Using a long laser pulse (150 ns), both dopant-polymer film systems were observed to ablate at

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approximately the same threshold fluence. However, when a shorter 23 ps pulse was used, the ablation threshold using the graphite-polymer system was proposed to be three times smaller for the IR-165-polymer system. This shift in the threshold was due to the localized “hot spots” being formed around the larger graphite nanoparticles and increasing the thermal decomposition of the polymer. Another experiment used aluminum nanoparticle dopants to ablate poly(tetrafluoroethylene) in the near IR.⁷ The ablation threshold of the polymer is lower by a factor of ten compared to excimer ablation of the pure polymer and is attributed to polymer decomposition by shock fronts originating at the metal nanoparticles.

The complex dopant–polymer interactions leading to ablation are initiated by thermal, chemical and/or mechanical processes. MD simulations have proven to be invaluable in describing the molecular-level picture of how these photon absorption events lead to ejection of material in pure substrates. Simulations by Zhigilei and Garrison described the set of conditions necessary for ablation of an organic solid.^{17,18} Upon absorption of a photon, the energy was deposited in the internal potential, or breathing mode, of the particle. The transfer of energy from this particle to its surroundings was controlled by allowing the particle to change size and adjusting the rate at which the radius of the particle interacts. This method allowed an effective depiction of the energy transfer and ensuing ablation process. Further insights were gained by incorporating direct laser-chemical effects in the simulations.^{19–21} Following photon absorption, direct bond scissions in a chlorobenzene substrate occurred and chemical reactions transpired. The exothermic photochemical reactions deposited excess energy in the system compared with pure photothermal interactions, and the ablation threshold was significantly lowered.

Further photothermal and photochemical effects were described with simulations of a more complex PMMA polymer system. The mechanism of ablation differed depending on the excitation channel studied. With photothermal processes, the absorption of a photon increased the kinetic energy of the monomer unit. Ablation was realized when sufficient energy was deposited to cause a critical number of bonds to break and bulk ejection of substrate ensued.^{22,23} In contrast, the photochemical absorption of photons was followed by direct cleavage of covalent bonds in the polymer. This excitation channel led to rapid decomposition through chemical reactions and a decrease in the cohesive energy of the polymer substrate.^{23,24} Following these reactions, ablation was observed with the thermal ejection of large chunks of substrate. The energetic requirement for ablation for the photochemical cases was shown to be less than the pure photothermal interaction.²⁵ Photomechanical processes can also induce ablation when the pulse width is short and the rapid deposition of heat and/or formation of small particles causes the onset of a pressure wave.^{22,23}

Here, simulations of laser–polymer interactions are continued with the inclusion of thermally absorbing dopant particles in a PMMA system. As described above, dopant molecules can add new and interesting physics to the ablation process without severely impacting the properties of the polymer. Several simulation techniques are used to describe the dopant polymer interactions and their effects. In one set of simulations, thermal absorbers are distributed throughout the polymer

matrix which are excited by photons. The effects of the transfer of energy to the surrounding substrate and the resulting ablation process are described. In another set of simulations, a cluster of particles absorbs the photon energy. The mechanisms of material ejection are compared with previous simulations where the photons directly interact with the PMMA polymer.

2. Computational details

Molecular dynamics simulation is used to study the absorption of photons by thermal absorbers in a PMMA substrate. The interaction of photons with PMMA was previously described in detail in ref. 26. The computational system consists of 951 PMMA polymer chains with 19 monomer units per chain in a $53 \times 53 \times 1048$ Å computational cell. Periodic boundary conditions are imposed on the lateral sides of the cell simulating the center of the laser pulse, while a pressure absorbing boundary condition is used at the bottom to prevent the reflection of a propagating pressure wave.²⁷ A coarse-grained description of PMMA is used where each of the functional groups C, CH₂, CH₃, CO, and O is represented by united atoms. Coarse-graining is used to decrease the computation time by eliminating the expensive C–H and C=O bonds which are not essential in observing ablation.^{17,28} In this study, thermal absorbers are excited by the photons. The dopant particles are added to the polymer matrix, and two distinct types of systems considered in this study: one in which there is excitation of a uniform distribution of thermal absorbers throughout the entire sample and another where there is excitation of a cluster of absorbers. In each system, chemistry is allowed to occur following the thermally induced bond breaks. The chemical reaction scheme follows the model described in ref. 26.

In the first type of system, 1822 dopant particles are uniformly distributed throughout the sample (10% by weight). The dopant particles closely match the properties of the substrate with each dopant particle having the mass of a monomer unit and the interactional potential between the dopant and the polymer being the same as the intermolecular potential between polymers, as described in ref. 26. Additionally, the absorbers contain an internal potential, or breathing mode, to control the transfer of energy from the absorbing particle to the surrounding polymer after excitation. This potential was based on the functional form used by Zhigilei and Garrison to describe the transfer of energy and the subsequent ablation in an organic solid.^{17,18} The internal potential has the functional form

$$U_R = k_1 \Delta R_i^2 + k_2 \Delta R_i^3 + k_3 \Delta R_i^4 \quad (1)$$

where ΔR_i is the change in the size of the radius of the absorber from equilibrium and k_{1-3} are constants which control the rate of energy transfer. To use this potential, the interaction between the absorber and the surrounding polymer is calculated from the edge of the absorber. The equilibrium radius of the absorber is 1.4 Å, and the constants k_{1-3} are chosen so the excitation energy is transferred to the surrounding particles within 5 ps. The absorption of photons by the absorbers is modulated by Beer’s law using a penetration depth of 100 Å, and each absorber can be excited multiple times. As discussed

above, thermal dopants can absorb several hundred photons during a 100 ps laser pulse in experiment.^{14,15} A range of fluences (5–20 mJ cm⁻²) are studied using 1.3 eV photons (equivalent to 1064 nm radiation) and a pulse width of 150 ps. The fluence range was chosen in order to compare with previous simulations of photothermal and photochemical excitation of PMMA.^{22–24} The 150 ps pulse width is within the thermal confinement regime as discussed in ref. 23, and consequently no significant pressure effects are present in the simulations.

In the second type of system, a cluster of particles absorbs the photons during the simulation. Excitation of a cluster of absorbers is used to more effectively compare to experimental systems such as the graphite nanoparticle dopants described in ref. 6. A spherical, face centered cubic (FCC) cluster consists of 140 particles and is 12.5 Å in radius. The particles in the

cluster are based on the carbon interactions in graphite, therefore, each particle is assigned a mass of 12.01 amu, and a Morse-type potential is used for the absorber–absorber interactions with the parameters chosen so that the binding energy is approximately 7 eV and the melting temperature is approximately 4000 K. A Lennard-Jones (LJ) potential is used for the absorber–polymer interactions which is adapted from a carbon nanotube–polymer interaction.²⁹ The breathing mode of eqn (1) is used for the transfer of energy from the absorbers in the cluster to the surrounding particles and the transfer of energy is configured to occur within 5 ps. The cluster is placed at depths of 50 or 250 Å in the PMMA polymer sample, and, since only the cluster particles are absorbing the photons, Beer’s law is not followed. A pulse width of 150 ps is used in the simulations, so no pressure effects are included in this study. Energies of 3–20 keV using 1.3 eV photons are absorbed

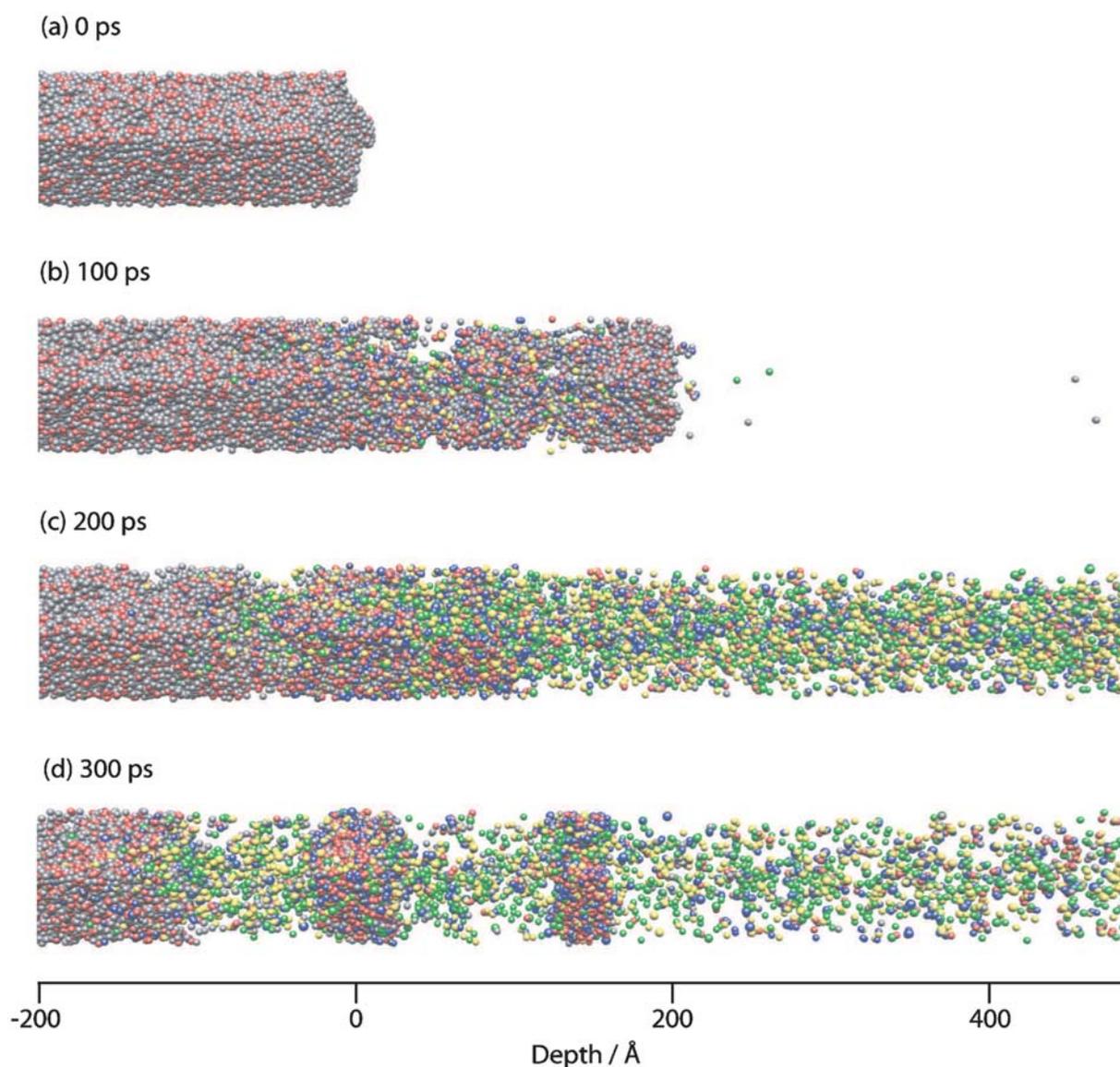


Fig. 1 Snapshots of the thermal absorber simulation using a fluence of 20 mJ cm⁻² at (a) 0 ps, (b) 100 ps, (c) 200 ps, and (d) 300 ps. The particles of the original polymer are colored grey and red, while gaseous particles are colored green, double-bonded carbon is colored blue and radicals are colored yellow.

by the clusters during the simulations to observe ablation in the system. These energies are the equivalent to the amount of energy per particle as observed in ablation experiments using micron-sized carbon black dopants.³⁰

3. Results and discussion

3.1 Uniform distribution of absorbers

Following the excitation of a uniform distribution of thermal absorbers, ejection of material occurs as a result of thermal and chemical damage to the PMMA substrate. Snapshots showing the ejection process are given in Fig. 1 with the excitation of thermal absorbers at a fluence of 20 mJ cm^{-2} . The particles of the original polymer are grey and red, while gaseous particles are green, double-bonded carbons are blue, and radicals are yellow. An indication of ablation is the appearance of clusters in the ablation plume,¹⁸ and in this simulation clusters are about to eject just after 100 ps (Fig. 1b). Several new molecular species are shown below the surface in the region where the substrate fractures. At 200 ps in the simulation (Fig. 1c), many gas molecules have formed and ejected from the remaining substrate. This process weakens the substrate as had been described in simulations of direct photochemical processes, see ref. 23, and allows the further ejection of large pieces of substrate shown in Fig. 1d.

The ejection mechanism has a strong chemical component. Localized, high temperature regions near the absorbers are formed in the substrate following excitation and are ripe for chemical damage. For example using a penetration 100 \AA and a fluence of 20 mJ cm^{-2} , 12.8 keV of energy is deposited in the top 100 \AA of the sample in which there are 180 dopant particles and 1726 main chain carbons. When the energy is distributed per absorbing particle, 71 eV is absorbed per dopant *versus* 7.4 eV per monomer. We acknowledge that the energy absorbed per absorber in the simulation is high, and at some point an organic material would decompose thus inhibiting further absorption of photons. Currently, we do not account for this in the simulations. Following photon absorption, thermal decomposition of bonds and chemical reactions occur around these “hot spots” causing degradation of the material and decreasing the cohesive energy of the substrate. The chemical transformation of the PMMA substrate is shown in the contour plot of Fig. 2. The decomposition of the sample is plotted as a function of depth and time for the simulation using a fluence of 20 mJ cm^{-2} . The contour scale indicates the fraction of material in a 10 \AA deep slice that has transformed from the original material (blue) to 100% new species (red). The initial ejection at approximately 120 ps is caused by the thermal and chemical decomposition of the material into 40–50% new species, most MMA monomer. The surface region then rapidly transforms as many gaseous molecules are formed and rapidly eject. This process then leads to additional cluster ejection at 240 ps.

The ejection process and mechanism described above for the excitation of the uniform distribution of thermal absorbers can be compared with previous simulations of direct photochemical excitation of the PMMA substrate. As mentioned in the Introduction, direct photolytic cleavage of the side chain

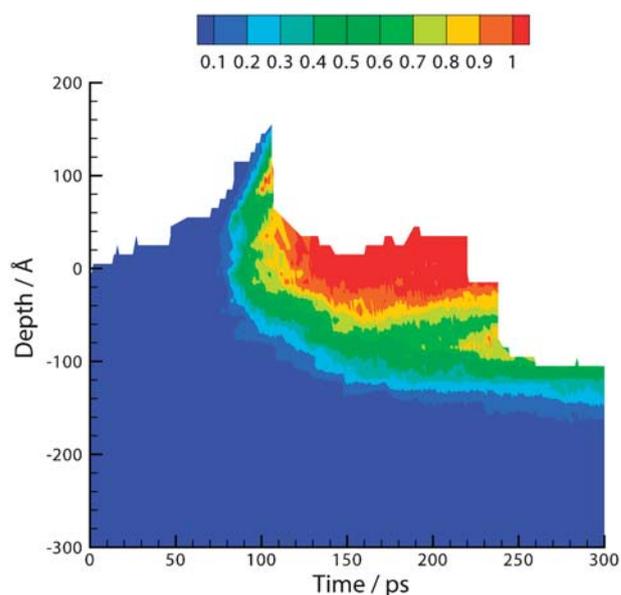


Fig. 2 A contour plot of the transformation of the PMMA substrate with the excitation of the thermal absorbers using a fluence of 20 mJ cm^{-2} . The contour scale ranges from 0 (blue) to 1 (red) indicating the complete chemical transformation in a 10 \AA deep slice.

(Norrish type I) or the main chain (Norrish type II) led to the rapid chemical decomposition of the sample into either many small gaseous molecules or MMA monomer, respectively.^{23,24} Thermal ejection of large clusters of material followed for both cases. The amount of material ejected for the different processes is compared in Fig. 3, where the yield in MMA equivalents is plotted on the left ordinate as a function of fluence. The yields for the Norrish type processes were taken from ref. 23–25. Ablation is observed when the yield increases above approximately 800 MMA equivalents with the appearance of clusters in the plume. The yield for the simulations of the thermal absorbers is similar to the yield for the Norrish type II simulations, as both thermal and chemical

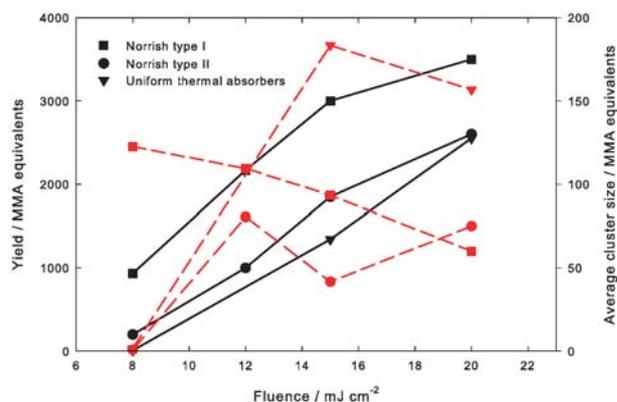


Fig. 3 The yield of particles ejected from the substrate is plotted on the left ordinate (black, solid line) as a function of fluence for the Norrish type I simulations (squares), the Norrish type II simulations (circles), and the thermal absorber simulations (triangles). Additionally, the average cluster size in the ablation plume is plotted on the right ordinate (red, dashed line) as a function of fluence for each simulation.

Table 1 Observed ablation in the substrate following the excitation of the absorbing cluster at depths of either 50 or 250 Å

Energy/keV	Depth/Å	
	50	250
1	No	No
3	No	No
5	No	No
8	No	No
10	Yes	Yes
13	Yes	Yes

processes contribute towards initiating ejection.^{23–25} The average cluster size in the plume is plotted on the right ordinate as a function of fluence in Fig. 3. The average cluster size for the uniform distribution of absorbers is greater than both of the direct photochemical cases. Though small molecules and gases are formed in the simulations of the

thermal absorbers shown in Fig. 1c, chemical transformation takes place after sufficient energy has been transferred from the absorbers to the surrounding polymer matrix to cause pyrolytic bond scissions. In comparison, direct cleavage of the covalent bonds by the photons in the Norrish type I and II simulations allows for a more rapid and efficient decomposition process to occur.

The simulations show the significant effects of the transfer of energy and the chemical breakdown on the ablation process due to the localized energy deposition. The results of such simulations are comparable to those experiments which have improved ablation quality by increasing chemical activity. As discussed above, polymers were designed by Lippert, Dickinson, Wokaun, and Masuhara to include a chromophore which readily decomposed upon excitation with a particular wavelength of radiation.^{2,8,9,31,32} The chemistry that ensued readily decomposed the material and led to ablation. Other

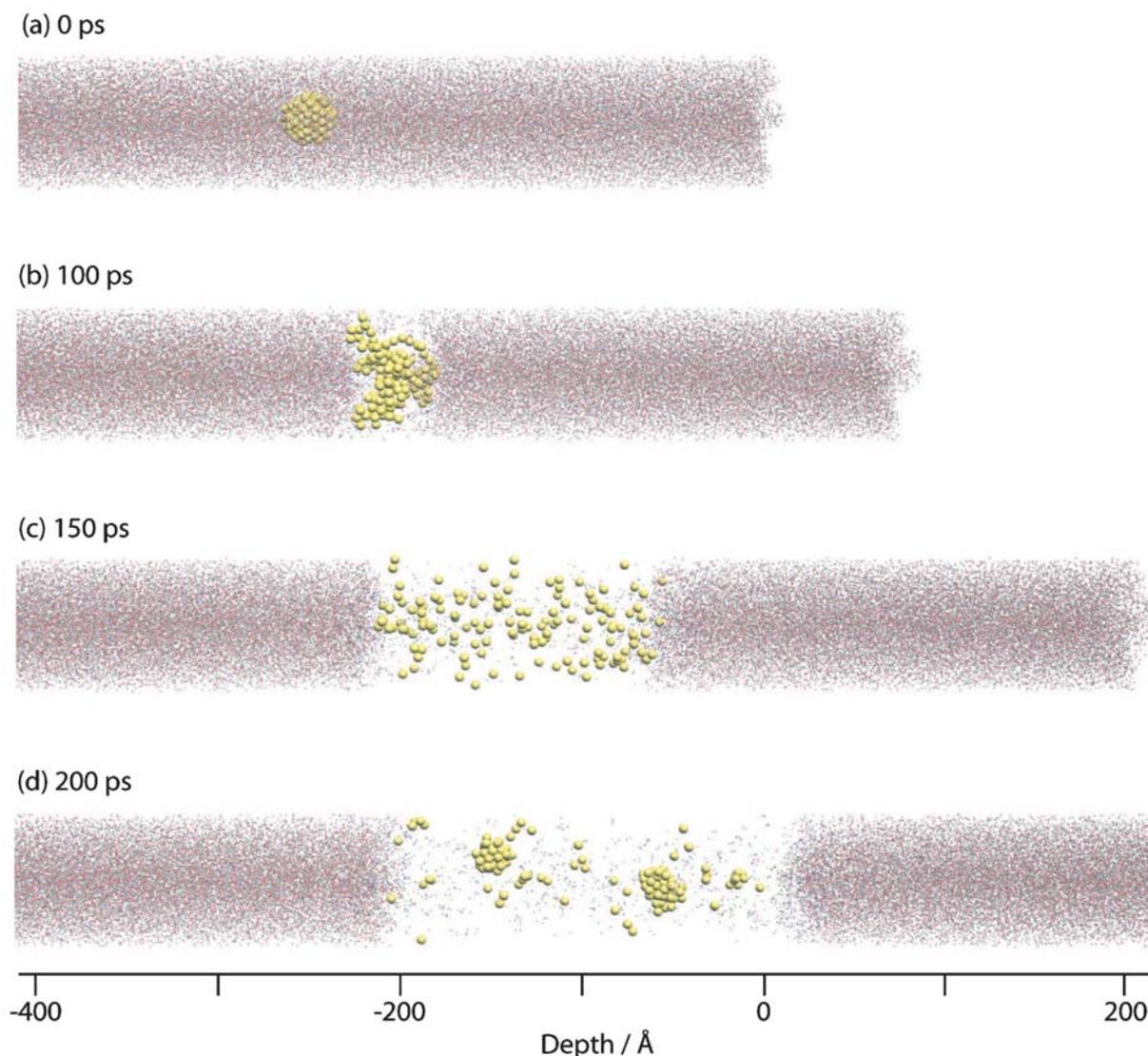


Fig. 4 Snapshots of the cluster absorbing simulation using an energy of 13 keV at (a) 0 ps, (b) 100 ps, (c) 150 ps, and (d) 200 ps. The particles of the original polymer are colored grey and red, while the cluster particles are colored yellow. All particles are of similar size and the polymer particles are depicted smaller for visualization purposes.

dopant–polymer experiments by Dlott show enhanced ablation with an increased fraction of decomposed material near the “hot spots” in the substrate.⁶ The simulations show that areas of high local temperature in the substrate can lead to significant pyrolysis of the material and initiate chemical transformation of the polymer material prior to ablation.

3.2 Cluster of absorbing particles

In this system, a spherical cluster of absorbing particles is embedded within the polymer substrate. Rather than exciting particles uniformly distributed throughout the sample, only the particles in the cluster absorb photons. Following laser excitation of the cluster, ejection of material occurs when the energy deposited in the cluster is above a threshold value. The amount of material ejected is equal to that of the top 50 Å of substrate when the cluster is at a depth of 50 Å, or of the top 250 Å when the cluster is at a depth of 250 Å. Table 1 summarizes whether ejection was observed at a range of input energies for either of the two cluster depths. The threshold for ablation occurs when between 8 and 10 keV of energy is deposited in the absorbing cluster. As mentioned in the Computational details section, the energy deposited in the system is used instead of fluence. Above this energy, the entire substrate above the absorbing cluster is ejected.

The mechanism of ablation for this system is different from the mechanism described for ejection with the uniform distribution of thermal absorbers (section 3.1) or the direct photochemical and photothermal excitation of the polymer in the previously published simulations.^{22–25} Ablation occurs when sufficient energy is absorbed by the cluster to fracture the cluster structure, cleave the surrounding polymer bonds, and propel the ejecta upward. This bond cleavage process is shown in Fig. 4 with snapshots of the simulation of 13 keV deposited in the absorbing cluster. Particles of the polymer are colored grey and red with the cluster particles colored yellow. While chemistry proceeds following bond breaks in the simulation, it is not indicated in this figure. All particles are of similar size, however, the cluster particles are depicted much larger than the polymer for visualization purposes. In Fig. 4a, the spherical cluster is apparent within the substrate at a depth of 250 Å. By 100 ps, Fig. 4b, the cluster is deformed in shape and many of the surrounding polymer bonds are broken. In Fig. 4c, the top 250 Å of substrate is clearly detached from the remaining polymer and is traveling in the outward direction. Additionally, no coherent structure is visible for the particles which comprised the absorbing cluster. By 200 ps (Fig. 4d), the polymer chunk continues to eject, retaining its initial structure and some of the particles of the absorbing cluster are aggregating together.

An examination of the contour plot of the chemical transformation of the polymer further provides evidence of the cluster fracture-bond cleavage mechanism. In Fig. 5, the transformation of the substrate is plotted as a function of depth and time for the simulation using the absorbing cluster at a depth of 250 Å and an energy of 13 keV. The contour scale goes from 0 indicating the pristine polymer to 0.28 where 28% of the polymer has been chemically converted to other species.

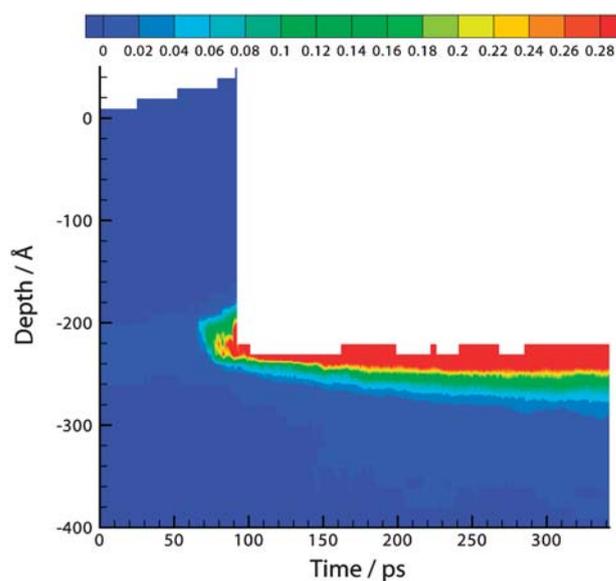


Fig. 5 A contour plot of the transformation of the PMMA substrate with the excitation of the absorbing cluster using an energy of 13 keV. The contour scale ranges from 0 (blue) to 0.28 (red) indicating the amount of chemical transformation in a 10 Å deep slice.

During the irradiation event (≤ 150 ps), few chemical species are being formed around the absorbing cluster. Immediately preceding ejection, some new chemical species are formed, however, the fraction is much less than the 40–50% shown for the uniform thermal absorbers, Fig. 2. Simulations of the excitation of the absorbing cluster are also performed without chemical reactions (not shown). No difference in the initial ejection is observed, eliminating the role of chemical damage in this process. Though after the initial ejection of the upper 250 Å, continued chemical reactions on the remaining surface of the polymer substrate are prevalent as shown in Fig. 5. The residual chemical damage following the ejection of the top layer along with the remaining temperature gradient allows further chemistry and surface ejection to occur for longer timescales than examined in this study.

In relating this ejection mechanism to experimental systems with large dopant clusters, both the size of the cluster in the simulation as well as the simulation conditions must be considered. The absorbing cluster is 12.5 Å in radius or 25 Å in diameter, approximately half the width of the sample as shown in Fig. 5a. With this relative size difference, the absorbing cluster only has to fracture and the remaining polymer bonds to cleave for ejection of material. Because of the periodic boundary conditions imposed on the lateral sides of the computational cell, the simulation corresponds to an array of dopants that effectively sever the material in a plane. Dopants in experimental systems are added up in the range of approximately 1–15% by weight.^{1,6,11,14,16,33} For sufficiently high dopant densities, this thermo-mechanical bond cleavage mechanism can undoubtedly play a role in the ejection process. The generalization of this mechanism to a range of cluster and energy densities is currently under investigation.

4. Conclusions

Ejection mechanisms are discussed using dopants in two simulation systems. For the uniform distribution of thermal absorbers, localized high temperature regions are created in the substrate and mixed thermal-chemical decomposition of material follows similar to direct photochemical excitation of the polymer. The transformation weakens the substrate and ablation of material follows. Subsequent ejection follows from the residual chemical damage. A separate mechanism for ablation is apparent in the set of simulations using an absorbing cluster. For those simulations, ablation is initiated after the cluster fractures and the surrounding polymer bonds are cleaved. Minimal residual chemical damage is observed and no secondary ejection is seen on the nanosecond timescale employed in the simulations.

The two sets of simulations give a glimpse into the diverse set of mechanisms that are possible to set off ablation using micro-scale dopants within a polymer system. Small dopants can cause chemical effects similar to those discussed in experimental investigations where chromophores serve to break down the material in a controlled manner at specific wavelengths. In contrast, cleavage of polymer bonds with highly concentrated, “explosive” clusters can also cause ejection of material. Future studies will examine the details of these interactions using larger systems with variant rates of energy transfer and attempt to maximize the photon efficiency in initiating polymer ablation.

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