

The Effects of Excimer Laser Irradiation at 248 nm on the Surface Mass Loss and Thermal Properties of PS, ABS, PA6, and PC Polymers

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ABSTRACT: Excimer laser irradiation provides a new and important method for polymer surface treatment. In this work, the weight loss of engineering polymers PC, ABS, PS, and nylon 6 were investigated following irradiation by KrF excimer laser. The experimental results revealed that the polymeric weight loss is nonlinearly related to the laser energy and laser frequency for most of the materials tested. The effects of laser irradiation on the thermal properties (T_g or T_m) of the polymers were investigated using DSC. It was

found that the T_g and T_m of these materials decreased as a result of laser treatment, indicating the degradation effect of the laser irradiation procedure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1024–1037, 2006

Key words: excimer laser; laser ablation; polystyrene, acrylonitrile–butadiene–styrene copolymer; polycarbonate; nylon; mass loss; melt temperature; glass transition temperature

INTRODUCTION

UV excimer lasers became more popular and are now being used to process polymers. Because of their high speed and precise micromachining abilities, excimer lasers find applications in the fields of semiconductor processing, optical communications, and medicine, in which polymers are extensively used. The interaction of UV laser with polymers is quite complicated, and the mechanisms of UV laser ablation of polymers are not well understood.

In this research, the influence of pulsed UV laser parameters on the engineering polymers, ABS, polystyrene (PS), polycarbonate (PC), and nylon 6 (PA6), were studied.

The ablation weight loss was measured using a digital balance. The laser parameters studied include pulse number, frequency, and energy. The thermal properties (T_m or T_g) of polymer before and after laser treatment were studied using differential scanning calorimetry (DSC).

Excimer lasers can deliver high-power output in short pulses at different UV wavelengths.¹ Irradiation in the far-UV range excites the target molecules to high-enough electronic states, causing direct bond breaking. This “cold” UV processing, described by

Garrison and Srinivasan in 1984,² is also referred to as “photoablation.”

By subjecting the polymer surface to UV–laser light in atmospheric environment, some part of its chemical structure in its hydrocarbon group (CH_x) chain can be altered to form intensely polar groups, such as carbonyl ($-\text{C}=\text{O}$) and hydroxyl ($-\text{OH}$). The presence of these polar groups on the surface can enhance adhesion. High laser energy flux can cause instant fragmentation of polymeric chains, without any oxidation.^{3–5} For example, Kueper and Stuke reported production of unsaturated species in irradiated poly(methyl methacrylate) films.⁶ The wetting behavior of the irradiated polymer improves as a result, and the increased surface roughness due to ablation can be an important effect in enhancing adhesion.^{7,8} Enhancement of polymer surface conductivity due to laser irradiation has also been reported.^{9,10} Surface modification by laser irradiation can be carried out in a variety of ways, depending on the purpose of the surface modification (etching, ablation, deposition, evaporation, surface functionalization, *etc.*), the type of the laser used, the ambient conditions, and the materials to be treated.

The selection of an appropriate type of laser for the intended purpose plays an important role in achieving the desired level of surface modification, without affecting the bulk properties of the treated material. The criteria that should be considered include the optical and thermal properties of the material to be treated, wavelength, pulse energy, and pulse frequency. In this process, the photo energies delivered by the laser and

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the strengths of polymeric molecular bonds should be considered simultaneously, for efficient processing.¹¹

Mechanism of thermal oxidation by laser irradiation

For ABS and PS, hydroperoxide and acetophenone groups have been identified on the polymer chain, as a result of thermal oxidation. The volatile products are phenol, benzaldehyde, and acetophenone. The major physical change due to thermal oxidation of PS is chain scission. Sequences of neighboring hydroperoxide groups are formed through intermolecular hydrogen abstraction. The main chain scissions observed on thermal oxidation of PS are generally attributed to the decomposition of tertiary alkoxy radicals.¹²

For polyamides (PA), thermal oxidation proceeds according to a classical chain reaction. In analogy with low molecular weight amides, the main degradation products can be attributed to preferential free-radical attack on the hydrogen atoms of the methylene groups alpha to the nitrogen atoms. It seems that the hydrogen atoms alpha to the carbonyl groups are not particularly liable. In fact, the degradation products observed point rather to attack of all the methylene groups in the chain except for the preferentially attacked methylene groups next to nitrogen atoms.¹³⁻¹⁵

For PC, phenol and bisphenol A are major degradation products of thermal oxidation, whereas biphenyl carbonate and 2-(*p*-hydroxyphenyl)-2-phenylpropane are formed to a much less extent. Carbon monoxide and methane are also present, but in much smaller amounts. The fact that carbon is the major product indicates clearly that the carbonate group is most liable to thermal oxidation, in PC.^{13,16,17}

Mechanism of photooxidation by laser irradiation

Incident light will either be reflected from the surface or scattered or absorbed in the bulk of the polymer. The absorption of light by polymers is related to their structure. For example, saturated hydrocarbons do not absorb light above 250 nm, but the presence of double bonds (chromophores) shifts absorption capacity to longer wavelengths, with carbon atoms (double-) bonded to heteroatoms with carbonyl compounds absorbing readily in the wavelength region above 290 nm.¹³

In semicrystalline polymers, scattering of light by the crystallites may considerably increase its path, in comparison to that in amorphous materials. Thus, even at low concentrations of chromophoric groups, appreciable quantities of energy may be absorbed above 290 nm.

The chromophores are raised to higher energy levels (excited states) subsequent to photo absorption. The excited states are able to lose the excitation energy

TABLE I
Absorption Coefficient and Penetration Depth for PS and PC, with the KrF (248 nm) Laser

	PS ²⁴	PC ²⁴
Absorption coefficient (cm ⁻¹)	6.3 × 10 ³	1.0 × 10 ⁵
Penetration depth (Å)	15,870	10,000

through several processes, such as fluorescence, phosphorescence, and radiation decay. An additional possibility is energy transfer in which the energy of the excited state (singlet, triplet) is transferred to an acceptor molecule, which also becomes chemically active, thus propagating polymer photo degradation.¹³

The ratio of the polymer molecules reacting chemically to the number of photons absorbed is designated as quantum yield. For some plastics, the quantum yields for chain scissions have been reported to be between 10⁻² and 10⁻⁵.¹⁸ This means that among the 100-100,000 molecules that absorb light, only one polymer molecule undergoes scission, as the energy, which is initially absorbed locally, is distributed to nearby domains. Furthermore, recombination of broken chains may also occur in solid polymers.

Free radicals are formed in polymers exposed to light, as a consequence of the excitation of absorbing groups. In the presence of oxygen, a polymer will simultaneously oxidize (photooxidation). Furthermore, consecutive thermal processes (oxidation) may be superimposed to the photooxidation reactions resulting in photo thermal oxidation.

The photooxidation of PS proceeds with the formation of hydroperoxides. The decomposition of the latter produces alcohols, ketones of the acetophenone type, and water. Decomposition of tertiary hydroperoxides is considered the most probable cause for the observed chain scissions.^{19,20}

Bisphenol A PC structure is affected by below 360 nm light but its absorption is intense only below 300 nm. Early studies attributed yellowing to photo-Fries rearrangement,^{21,22} which produces a phenyl, and subsequent rearrangement, 2,2'-dihydroxybenzophenone group. The consequences of photooxidation are the oligomers and bisphenol A structure.^{13,21-23}

The penetration depth of a UV beam into a polymer is dependent on the nature of polymer material, based on its absorption coefficient. The penetration depth is a distance at which 63.2% of the incident energy is absorbed, and it can be defined as the reciprocal absorption coefficient. Table I provides some examples of the penetration depth for PS and PC polymers.

Mathematical models for excimer laser surface modification

There are two basic mechanisms in laser-induced surface modification: thermal and photochemical, which

are likely to take place simultaneously. The extent of these processes depends on the laser wavelength, frequency, and the intensity used, as well as the target material properties.^{11,25–27}

When the process is thermally controlled, the absorbed energy increases the density of free electrons and provides them with a substantial amount of kinetic energy, in a very short time. In most cases, the heat energy is sufficient to activate a thin layer of the surface, without melting it. In some cases, however, it may be desired to melt the substrate surface and vaporize some or all species from the surface, thus modifying the surface characteristics of the material. The heated regions are cooled by thermal conduction subsequent to irradiation.

In a photochemical process, however, the process is based on the breaking of chemical bonds with highly energetic photons that activate chemical reactions. The excitation energy obtained by the molecule leads to the breaking of many bonds, particularly the 3.5-eV C—H bond crucial to all polymers, thus creating active sites. These active sites react with the molecular species present in the gas atmosphere medium, and monomers can attach to these active sites.

Details of the ablation mechanisms are still open to debate. Some authors attributed ablation mainly to thermal decomposition, and others attributed it to photochemical contribution. As mentioned earlier, both photothermal and photochemical reactions are likely to contribute, depending on the irradiation conditions and the type of polymer.

For irradiation of solids by laser frequencies corresponding to energies less than chemical bond strengths, it is obvious that a photon is incapable of directly forcing the molecule to undergo an electronic transition for bond breakage, but rather causing vibrations within the molecules. Consequently, material ablation is likely to correspond to evaporation, rather than volume explosion.

According to the model of Garrison and Srinivasan,² ablation can start at less than 1 ps after light absorption occurs. This means that, when the kinetic time scale for light absorption is much shorter than the secondary processes of ablation, such as thermal effects, ablation of the polymer can be attributed to photochemical effect. However, for the 15-ns or longer duration laser pulses, a substantial fraction of the pulse duration is required to heat the material sufficiently, to start significant ablation. If vibrational excitation of the excited state occurs prior to the photolysis process, then this vibrational energy will heat the solid to some degree. Therefore, even at wavelengths as short as 193 nm, quantum process responsible for bond breaking may be accompanied by heat generation.

Nonthermal laser ablation model

The basic principle involved in nonthermal ablation is that the laser photo energy is absorbed by the polymer, and it excites the electronic states that lie above the dissociation energy of the molecules. The dissociation of molecular bonds leads to the splitting of longer polymer chains into small fragments. Numerous bond breaks cause an increase in pressure inside the laser irradiated polymer volume, which causes the molecular fragments to escape. The quantum yield q for molecular bond dissociation is given by²⁸:

$$q = \exp \left[- \left(\frac{h\omega_d}{h\omega_L} \right) \right] \quad (1)$$

where, $h\omega_d$ is the bond dissociation energy and $h\omega_L$ is the energy of a single laser photon. Appreciable quantum yield of bond dissociation can be expected in polymers, at laser wavelengths shorter than 250 nm. Any excess energy $\Delta E = h(h\omega_d - h\omega_L)$ may appear as kinetic energy in the irradiated fragments. The extreme rapidity of the bond-breaking process eliminates heat conduction.²⁸

Assuming that the ablation is a two-step process, in which the laser absorption is followed by material ablation, one can use Beer–Lambert law to establish a relationship between ablation depth/pulse (d_f), the absorption coefficient (α), the incident laser energy fluency (F_0), and the threshold energy fluency (F_T), as follows:

$$d_f = \left(\frac{1}{\alpha} \right) \ln \left(\frac{F_0}{F_T} \right) \quad (2)$$

It is interesting to note that eq. (2) does not contain any time-dependent quantities. If the ablation proceeds layer by layer, the incident laser intensity also varies as a function of spatial coordinates during bond breaking due to “bond shielding effect” and crater wall shadows at different ablation depths.

Another important parameter to be considered for nonthermal ablation is the pulse duration of the laser. The time threshold for thermal damage must be shorter than the thermal relaxation time (t_T) of the polymer, which is given by²⁷

$$t_T = \frac{d^2}{\chi} \quad (3)$$

where, d is the optical penetration depth, and χ is the ratio between the medium’s ability to conduct heat and its storage capacity as given by

$$\chi = \frac{k}{\rho c} \quad (4)$$

TABLE II
Physical Properties of Polystyrene, ABS, Nylon 6, and Polycarbonate

	Polystyrene	ABS	Nylon 6	Polycarbonate
T_g (°C)	110			
T_m (°C)		115	210	150
T_d (°C)	364	329		448
ρ (10 ⁶) (g/m ³)	1.06	1.04	1.13	1.2
K (W/m K)	0.105	0.147	0.23	0.193
C_p (J/mol K)	179	107	142	224
D (m ² /s)	9.29×10^{-8}	9.80×10^{-8}	1.62×10^{-7}	1.82×10^{-7}
R	0.072	0.04	0.05	0.06
ΔH_f (kJ/mol)	10.0	None	26	33.6

T_g , glass transition temperature; T_m , melting temperature; T_d , degradation temperature; ρ , density; K , thermal conductivity; C_p , specific heat; D , thermal diffusivity; R , optical reflectivity; ΔH_f , heat of fusion.

where, k is the thermal conductivity, ρ is the specific gravity, and c is the specific heat per unit mass. The thermal relaxation times for various polymers at different laser wavelengths can be calculated using eqs. (3) and (4). The relaxation time for most bulk polymers is in the microsecond (10^{-6}) range, but relaxation time among various vibrational modes is only a fraction of a nanosecond (10^{-9}).

A process equation has been suggested for laser energy levels above the ablation threshold:

$$d = \frac{Ceft}{s} \quad (5)$$

where, d (cm) is the ablation depth, C (cm⁻³ J) is the coefficient of laser energy absorption, e (J) is the laser energy, f (Hz) is the pulse repetition rate (frequency), t (s) is the irradiation time, and s (cm²) is the beam spot size.²⁹

Thermal laser ablation model

In the thermal model, the incident laser energy is absorbed and then converted into thermal energy,³⁰ which induces decomposition and chemical reactions. Thus, after establishing the temperature profile, the decomposition reactions are assumed to take place. A first-order dissociation is usually assumed, and the temperature dependence of heat capacity is neglected. Thus, we have,

$$N = \exp(-\kappa t) \quad (6)$$

$$\kappa = \frac{kT}{h} \exp\left(\frac{-E_a}{kT}\right) \quad (7)$$

where, N is the fraction of bonds remaining, κ is the rate constant, k is the Boltzmann constant, h is the Planck's constant, and E_a is the activation energy for dissociation, and T is the temperature. The rate law may be assumed to have the same form, with N rep-

resenting the fraction of chromophores that have been chemically altered. Equations (6) and (7) apply only to dissociation of diatomic molecules, but provide a reasonable estimate for polyatomic dissociations.

The relaxation rates ($\cong 10^{11}$ s⁻¹) for change of an electronic state to a thermal vibrational state resulting in polymer heating are markedly higher than the rate of thermal diffusion into the bulk polymer ($\cong 10^5$ - 10^7 s⁻¹). Consequently, energy input due to UV laser irradiation will be restricted to a small volume at the surface, during the time scale of the laser pulse. On the other hand, thermal diffusion is likely to contribute to the ablation process due to the presence of high thermal gradients.

Sancaktar and coworkers^{31,32} defined the threshold intensity for degradation as the laser intensity to create degradation temperature on the substrate surface. To estimate the threshold intensities, it was assumed that phase transition was induced by the laser energy absorbed after the initiation of surface degradation. For a given pulse duration, the threshold intensity, I_d , is given by

$$I_d = \frac{d_f \rho \Delta H_{deg}}{(1-R)t'} \quad (8)$$

where, d_f is the ablation depth (m), ΔH_{deg} is the heat of degradation (J/g), R is the reflectivity, and t' is the ablation time (s), defined as $t' = \tau - t_{d'}$, where τ is the duration of laser pulse (s). The threshold duration for degradation, t_d is

$$t_d = \frac{\pi}{4D} \left[\frac{K(T_d - T_0)^2}{I(1-R)} \right]^2 \quad (9)$$

where, T_d is the degradation temperature of the material (K) and T_0 is the room temperature (K).

The total ablation depth due to multiple laser pulses is given approximately as:

$$d_{total} = nd_f \quad (10)$$

TABLE III
Injection Molding Conditions for Making Samples

Material	Temperature (°F)				Back pressure (psi)	Hold time (s)
	Barrel 1	Barrel 2	Barrel 3	Nozzle		
ABS	170	180	190	195	750	7
Nylon 6	490	500	525	530	650	8
Polycarbonate	495	505	530	535	750	8
Polystyrene	455	475	505	515	850	6

or

$$d_{total} = \frac{M}{wl\rho} \quad (11)$$

where, n is the number of pulses, M is the ablated mass (g), w is the ablation width (m), and l is the ablation length (m).^{31,32}

The incident laser power intensity I for a laser pulse ($\tau = 25$ ns) is given as:

$$I = \frac{E}{S\tau} \quad (12)$$

where, E is the laser pulse energy (J) and S is the beam area (m²). We note that this equation does not include the plasma shielding effects induced by melting and ablation.

Assuming that all of the absorbed excimer laser radiation is converted immediately into heat, the heat-transfer problem in laser irradiation can be treated by the heat diffusion equation. To simplify the solution, it is assumed that the process is one-dimensional, and the latent heat of melting is neglected. Thus, the variation of temperature with the depth and time is given by,³¹

$$C_p(t)\rho(t) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[K(t) \frac{\partial T}{\partial x} \right] + Q(x,t) \quad (13)$$

The boundary and initial conditions are:

$$\frac{\partial T(x,t)}{\partial x} = 0 \text{ at } x = 0, t > 0 \quad (14)$$

$$T(x,0) = T_0 \text{ for } 0 \leq x < \infty, t = 0$$

where, $C_p(t)$ is the specific heat (J/g K), $\rho(t)$ is the density of the material (g/m³), $K(t)$ is the thermal conductivity (W/m K), and $Q(x,t)$ is the heat generation function (W/m K).

When a laser irradiates a polymer, the heat generation function is largely determined by R , the reflectivity, and α , the absorption coefficient of the polymer, as well as by the power intensity, I , and pulse duration,

τ , of the laser pulse. The energy absorbed at depth x is given by:

$$Q(x,t) = I(1 - R) e^{-\alpha x} \quad (15)$$

where, R is the reflectivity, I is the power intensity (J/s m²), and α is the absorption coefficient (m⁻¹).

According to eq. (15), the intensity of the laser light falls to $1/e$ after it has advanced a distance $1/\alpha$, which is a very small fraction of the wavelength. Thus, the thermal diffusion distance will be much larger than the depth. This means that heat is mostly generated at the surface. Consequently,

$$Q(x,t) = I(1 - R)\delta(x - 0)\eta(\tau - t) \quad (16)$$

where, $\delta(x)$ and $\eta(t)$ are the delta and Heaviside functions, respectively,³¹

An integral transform technique was used to solve eq. (13), yielding the following closed-form solution for the transient temperature during the laser heating process^{27,31}:

$$T(x,t) = \frac{I(1 - R)}{K} \left[\left(\frac{4Dt}{\pi} \right)^{1/2} e^{[-x/(4Dt)]^{1/2}} - x \operatorname{erfc} \frac{x}{(4Dt)^{1/2}} \right] + T_0 \quad (17)$$

where, $D = K/(\rho \times C_p)$ is the thermal diffusivity, K is the thermal conductivity, ρ is the density, C_p is the specific heat for unit mass, and T_0 is the initial temperature. At the surface of the material, $x = 0$, and eq. (17) reduces to^{27,31}:

$$T(0,t) = \frac{I(1 - R)}{K} \left(\frac{4Dt}{\pi} \right)^{1/2} + T_0 \quad (18)$$

Factors affecting laser surface treatment

Different laser conditions provide different treatments on surfaces. High frequency usually increases the thermal effect of laser on the polymer. Therefore, at high frequency, photothermal rather than photochemistry model is used to explain the ablation phenomena.³³⁻³⁵

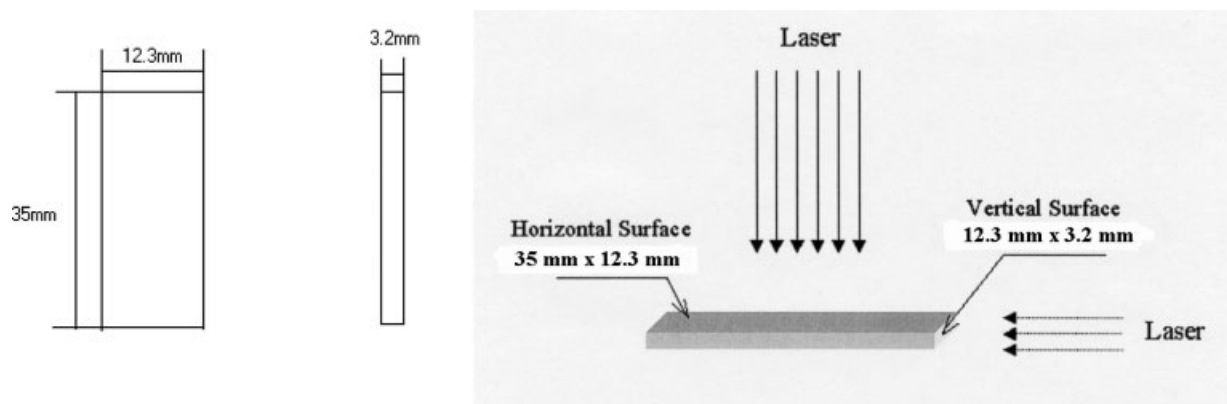


Figure 1 The specimen geometry and irradiation directions.

The pulse number is an important factor in laser surface treatment. With increasing number of laser pulses, the ablation depth increases, and sometimes, the ripple structures formed become larger, and the distance between them increases.^{36–38}

The pulse energy also plays an important role in surface treatment. Under different pulse lengths, the threshold energies of materials are different, because the absorption coefficient (α) for materials under different pulse lengths is different. The relationship between α and F_{th} was discussed by D' Couto et al.,³⁹ who reported that F_{th} usually decreases with increasing α . When the laser energy is under F_{th} level, no obvious ablation occurs, but some structures may form on the polymer surface. When the laser pulse energy is higher than F_{th} , ablation occurs at increasing level with increasing pulse energy.^{40,41}

Since materials absorb different amounts of energy at different wavelengths, laser wavelength is an important criterion that should be considered for surface modification applications.

It is well known that the existence of threshold fluency is a main characteristic of UV laser-induced ablation of polymer surfaces. For a given absorption coefficient, the existence of a fluency threshold indicates that a specific minimum energy density is required for the generation of surface structuring. Repeated irradiation of the polymer makes the structures more pronounced.

An early model by Bahnert and Schollmeyer⁴² recognized the importance of thermal influences, and described a layer, where ablation occurs (fragmented polymer chains), and a layer of molten polymer corresponding to 6×10^7 K/cm, based on Beer's law. The temperature profile within a laser-treated polymer surface depends on its light absorption properties, which create different states of the polymer. On the surface, a critical decomposition value for the polymer is surpassed. Further inside the polymer is a region where the glass transition temperature of the polymer

is surpassed, i.e., where chain mobility exists in the solid phase. Regions further inside the polymer do not contribute to the phenomenon of structuring.

The model of Bahnert and Schollmeyer suggests a synergistic phenomenon between the internal stress field and the high temperature gradient, which creates the surface layer of the polymer, leading to self-organizing material convection and formation of rolls, which solidify when energy input ceases.⁴³

EXPERIMENTAL

Sample preparation

Materials

The polymers used in this research include polystyrene (Styron Dow Chemical), ABS (Magnum Dow Chemical), polycarbonate (Lexan General Electric), and nylon 6 (Nycon). Properties of these materials are shown in Table II.^{3,44,45}

Injection molding

Before injection molding, the particles were dried to ensure that all moisture had been removed. The samples, which were irradiated, were made with Van Dorn 150 ton, and Boy 15 injection molding machines. The injection conditions for different materials are listed in Table III.

Preparation of samples for laser treatment

The injection-molded samples were cut into three separate pieces of ~ 36 mm in length, using a band saw to obtain $1.2 \times 35 \times 0.3$ cm³ rectangular bars (Fig. 1). A special sample holder was designed to hold the samples to ensure that the polished surfaces made a 90° angle with the sample axis.

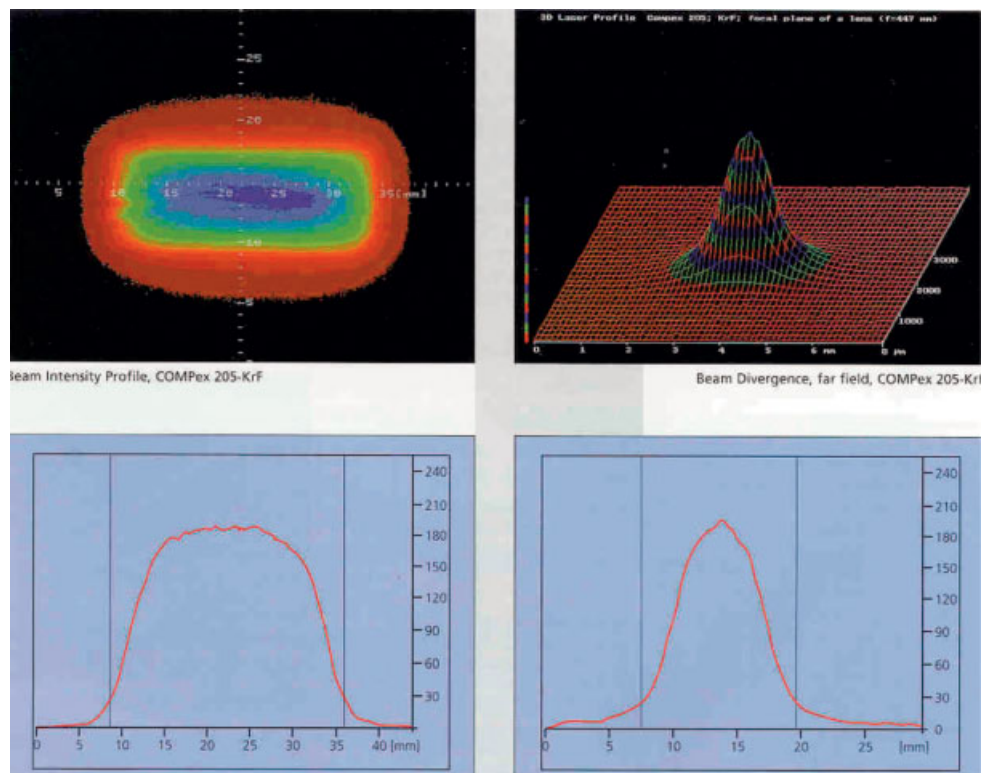


Figure 2 The laser intensity profiles illustrating the variation in power intensity across the laser beam crosssection along its major (left) and minor (right) axes, along with graphical representations (bottom).⁴⁶[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Processing

Excimer laser treatment

A Lambda Physik excimer laser (LPX 240i) was used to treat the specimen surfaces at 248 nm wavelength (KrF). The KrF excimer laser produces laser pulses of about 25 ns duration. The dimensions of the unfocused beam (Fig. 2) are about $19.5 \times 7 \text{ mm}^2$. The variation in power intensity across the laser beam cross section, shown in Figure 2, results in variations in the ablation patterns obtained on specimen surfaces, as shown for PC in Figure 3. Consequently, care was taken to confine the thermal measurement samples to the center of the ablation area. Specimen surfaces were treated under different number of pulses (0–2 K), pulse energy (60–300 mJ), and frequency (1–150 Hz). Sample surfaces were perpendicular to the direction of the laser beam. The ablation effects were observed by investigating the depth of ablation and the weight loss of sample after ablation. The depth of ablation was measured using an extensometer calibrator (Model 3590, Mitutoyo) with $1\text{-}\mu\text{m}$ resolution. The weight loss after ablation was measured with a digital balance (Mettler AE 200) with 0.1 mg resolution.

Characterization

Differential scanning calorimetry

Thermal properties of the model polymers were determined using a Perkin–Elmer DSC7. The samples included original material, laser-treated material, welded-surface material, and weld-sprue material. Prior to measurements for a series of samples, a baseline was determined using two empty reference pans. The samples were 5–10 mg and were tested at a heat-

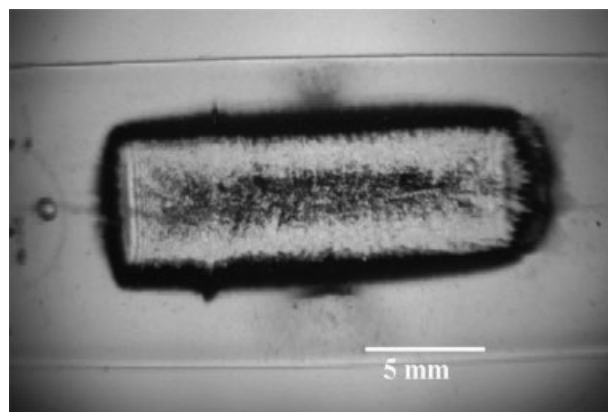


Figure 3 Optical photograph of the irradiated area of PC.

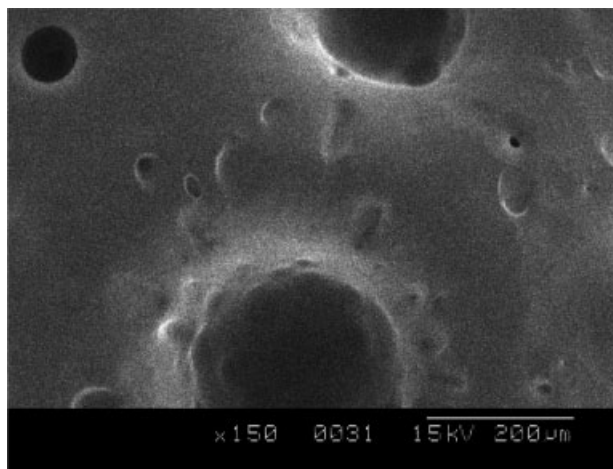


Figure 4 SEM micrograph showing the effect of excimer laser irradiation at high-pulse frequency on the surface morphology of ABS (120 mJ, 300 pulses, 150 Hz).

ing rate of 10°C/min from 50 to 230°C. The glass transition temperature, melting temperatures, and heats of melting were obtained from the DSC thermograms, after subtracting the baseline.

RESULTS AND DISCUSSION

Effects of excimer laser parameters on the depth of ablation and weight loss, for different polymers

Effect of laser parameters on the depth of ablation

The effect of number of laser pulses on the depth of ablation on PC and ABS were measured using a profilometer. The ablation behavior through the irradiation area varies for different polymer samples. Here, we report only on the ablation depth at the center part of the irradiated area. For each material, it is found that the ablation depth increases with increasing number of laser pulses. When the number of laser pulses is larger than 500 at 220 mJ and 10 Hz, the laser irradiation will yield more depth on ABS than on PC. The depth of irradiated ABS samples is created partially due to laser ablation and partially due to the mass movement induced by melting (this will be proven by considering the mass loss, later). For PC samples, mass movement of melt flow is not observed at such low laser frequencies, and the ablation depth increases nearly linearly with increasing number of laser pulses. For ABS, the depth of ablation becomes more sensitive to increases in the number of pulses beyond a specific level; may be because the temperature on the surface of ABS rises to a high enough level after 400 pulses and a larger mass movement is obtained.

For ABS, the irradiated depth did not increase greatly with frequency at low laser-irradiation frequency (<10 Hz), when the laser pulse energy was 120 mJ and the number of laser pulses used was 400. The

depth increases suddenly when the frequency is above 20 Hz. This may be because ABS begins to melt when the laser frequency is above 10 Hz. This kind of molten mass movement induces larger depth at the center of the irradiated area, since the molten material moves towards its boundaries and form ripples.

The ablation depths for PC and ABS increase nonlinearly with increasing laser energy. This is attributed to the presence of threshold energy for ablation of these materials. Only when the incident laser energy is higher than the threshold energy of the material, can the laser pulses induce ablation depth on the irradiated polymer surfaces. Detailed discussion on threshold energy is provided later.

The afore-mentioned results reveal that the use of ablation depth to describe the ablation behavior of polymers has limitations. The major disadvantage of this method is that it is impossible to separate the mass movement and ablation depth. For example, on ABS, some cavities are produced after laser ablation, as shown in Figure 4. Such cavities affect the accuracy of ablation depth measurements.

Effects of laser parameters on the ablated mass loss

As discussed earlier, the use of ablation depth to describe the ablation of irradiated polymers have some disadvantages. Therefore, mass losses after laser ablation were used to measure the effect of laser irradiation on polymers (Figs. 5–7).

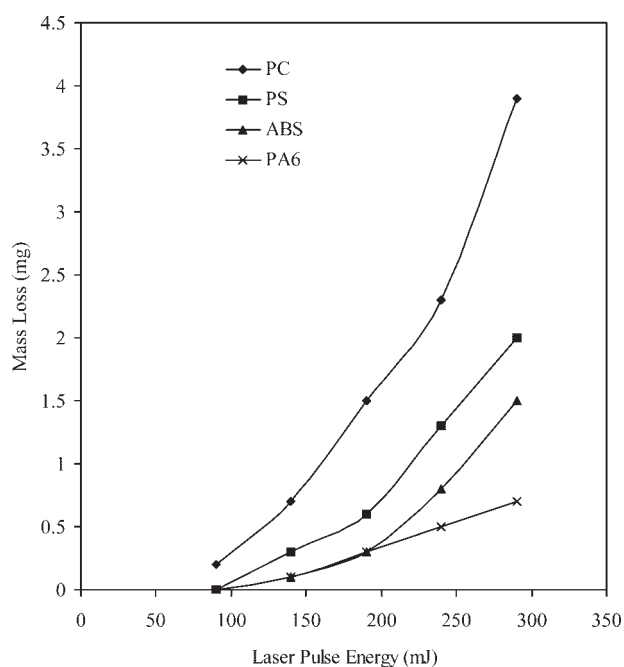


Figure 5 The effect of laser pulse energy on the ablated mass loss, for different thermoplastic materials. Laser frequency is 10 Hz and the number of laser pulses is 400 for ABS, 300 for PC and PS, and 600 for PA6.

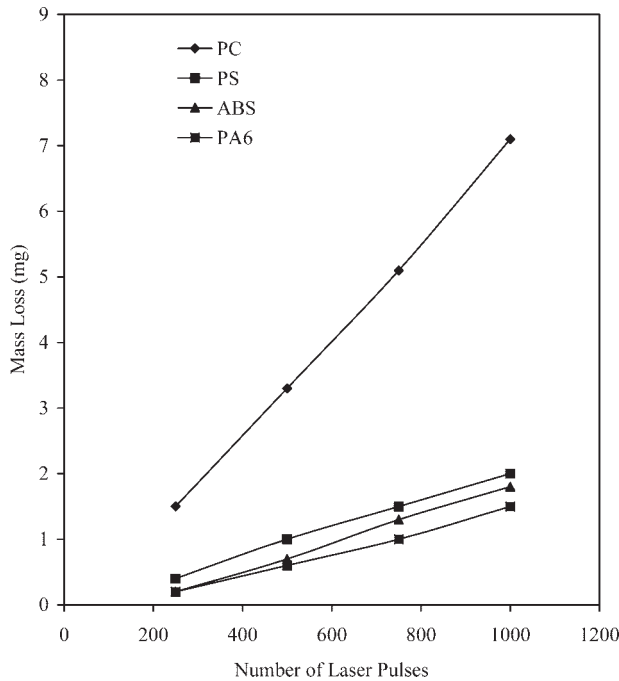


Figure 6 The effect of number of laser pulses on the mass loss, for different thermoplastic materials. The laser pulse energy is 180 mJ and the laser pulse frequency is 20 Hz.

Figure 5 shows the effects of laser pulse energy on the ablated mass loss for ABS, PA6, PC, and PS. The mass loss increases with increasing laser irradiation energy, when the other laser irradiation conditions are kept constant. However, the relationship between the laser irradiation energy and mass loss is not linear. At low energy levels, the rate of mass loss is smaller than that at high energy levels. When the laser energy is lower than a threshold level, the mass loss is zero. The intercepts on the horizontal energy axis represent these threshold levels. Figure 5 reveals that PC has the lowest threshold energy level among the four engineering thermoplastics tested.

The effect of number of laser pulses on the mass loss for ABS, PA6, PC, and PS materials are shown in Figure 6. Increasing the number of laser pulses results in increasing levels of mass loss for ABS, PC, PS, and PA6. For these four thermoplastics, the relationship between the number of laser pulses and mass loss is nearly linear. PC has the largest mass loss. According to the thermal ablation model given by D' Couto,³⁹ the ablation depth (d) can be calculated using the relation,

$$\ln d = \ln k_0 - \frac{E^* \ln(F/F_{th})}{\alpha_{eff} (F - F_{th})} \quad (19)$$

where, k_0 is the Arrhenius preexponential factor, α_{eff} is an effective absorption coefficient, E^* is related to the activation energy E by $E^* = EC_p/R$, where C_p is the

specific heat capacity and R is the gas constant. F is the energy used, and F_{th} is the threshold energy.

We also know that $d = mg/\rho S$, where m is the mass loss, g is the acceleration of gravity, ρ is the density, and S is the irradiated area. Therefore, the mass loss (m) can be calculated using the relation,

$$\ln m = \ln k_0 - \ln \frac{g}{\rho S} - \frac{E^* \ln(F/F_{th})}{\alpha_{eff} (F - F_{th})} \quad (20)$$

Since the differences of density are not large for the polymers under consideration and the irradiated area S is equal to the laser beam cross section, the most important factors that affect the mass loss are α_{eff} , E^* , and F_{th} . When the threshold energy (F_{th}) increases, the mass loss will be reduced. When α_{eff} is large, the mass loss will be large. Considering the effect of laser energy on the ablated mass loss discussed earlier and a previous study by Lazare *et al.*,⁴⁷ we can infer that the F_{th} of PC is lower than that for PS and α_{eff} for PC is larger than that for PS. This is why the mass loss for PC is larger than that for PS. The laser optical properties are not readily available for ABS and PA6. Figure 5 reveals that the F_{th} values for ABS and PA6 are close to that for PS, and it is easy for all of them to be affected by laser irradiation frequency. Therefore, it is reasonable to assume that ABS and PA6 have low absorption coefficients.

Figure 7 shows the effect of laser pulse frequency on the mass loss for ABS, PA6, PC, and PS. It is found that

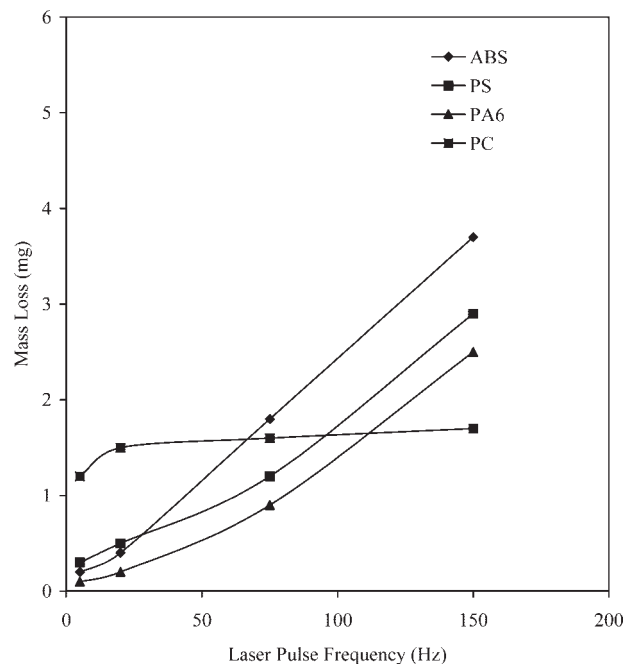


Figure 7 The effect of laser pulse frequency on the ablated mass loss, for different thermoplastic materials. The laser pulse energy is 160 mJ and the number of laser pulses is 400 for ABS, 300 for PC and PS, and 600 for PA6.

the mass loss will increase greatly with increasing laser pulse frequency when ABS, PS, and PA6 are ablated, even if we use the same number of laser pulses and pulse energy. This means that it is easy for ABS, PS, and PA6 to be ablated at higher frequency. However, for PC, it is found that the mass loss increases with laser frequency up to 20 Hz. When the laser frequency is higher than 20 Hz and less than 150 Hz, the mass loss will not change greatly.

The incident laser power intensity, I , for a laser pulse ($\tau = 25$ ns) is given as,

$$I = \frac{E}{S\tau} \quad (12)$$

where, E is the laser pulse energy (J), S is the beam area (m^2), and τ is the laser pulse duration.^{31,32} For example, using the experimental results, $E = 180$ mJ, $A = 1 \times 10^{-4}$ m, and $\tau = 25 \times 10^{-9}$ s, we get $I = 7.2 \times 10^{10}$ W/ m^2 . We note that eq. (12) does not consider any shielding effects induced by melting and ablation.

The total ablation depth due to multiple laser pulses is approximately given by Sancaktar *et al.*^{31,32}:

$$d_{total} = nd_f \quad (10)$$

or

$$d_{total} = \frac{M}{wl\rho} \quad (11)$$

where, n is the number of pulses, M is the ablated mass (g), w is the ablation width (m), l is the ablation length (m), and ρ is the mass density of the material. Our experimental results for the ablated mass of PC, PS, and ABS are 3.3, 1.0, and 0.7 mg, respectively, corresponding to 180 mJ laser pulse energy and 20 Hz laser pulse frequency with 500 laser pulses. Using $w = 5 \times 10^{-3}$ m, $l = 2 \times 10^{-2}$ m and the mass densities of 1.2×10^3 kg/ m^3 , 1.04×10^3 kg/ m^3 , and 1.06×10^3 kg/ m^3 , for PC, PS and ABS, respectively, we can calculate $d_{total} = 2.8 \times 10^{-5}$ m for PC, 9.6×10^{-6} m for PS, and 6.6×10^{-6} m for ABS at 180 mJ, 500 pulses, and 20 Hz. The corresponding experimental results are $d_{total} = 3.2 \times 10^{-5}$ m for PC and 2.8×10^{-5} m for ABS at these conditions. Obviously, eqs. (10) and (11) can predict the ablation of PC quite well, but for ABS, the experimental data is much larger than the theoretical prediction. The reason is the ABS mass flow observed during laser irradiation. The molten materials move from the center to the outside of the irradiation area. Therefore, the depth change of center is much larger in ABS than the laser ablated depth, since the material moves out. This observation proves that using mass loss to calculate the ablation depth is more accurate for describing the ablation behavior of polymers, since the

TABLE IV
The Properties of Irradiated Material^{3,44,45}

	PC	PS	ABS
T_d (K)	721	637	602
K (W/m K)	0.193	0.105	0.147
D (m^2/s)	1.82	9.29	9.8
R	0.06	0.072	0.04

effects of melt flow on the change of depth are eliminated.

By using eqs. (10) and (11), ablation depth per laser pulse can also be calculated. We have $d = 5.5 \times 10^{-8}$ m for PC, 1.92×10^{-8} m for PS, and 1.32×10^{-8} m for ABS, at 180 mJ laser pulse energy and 20 Hz laser frequency.

The threshold time for degradation, t_d , was given by Sancaktar *et al.*^{31,32} with,

$$t_d = \frac{\pi}{4D} \left[\frac{K(T_d - T_0)}{I(1 - R)} \right]^2 \quad (9)$$

where, T_d is the degradation temperature of the material (K), T_0 is the room temperature (K), R is the optical refractivity, K is the thermal conductivity, and D is the thermal diffusivity. In all experiments, laser duration, τ , is 25×10^{-9} s, and $T_0 = 298$ K. With 180 mJ laser energy, we have $I = 7.2 \times 10^{10}$ W/ m^2 . Using the data given in Table IV in connection with eq. (13), we get $t_d = 6.4 \times 10^{-3}$ ns for PC, 2.4×10^{-3} ns for PS, and 3.4×10^{-3} ns for ABS. The ablation time per pulse, t' , is given by^{31,32}:

$$t' = \tau - t_d \quad (21)$$

where, τ is the duration of laser pulse (s). Therefore, for PC, PS, and ABS, the ablation time is approximately, $t' \cong 25$ ns. In other words, the degradation begins almost immediately when the materials are irradiated by KrF laser pulses. Based on the eqs. (9) and (21), the ablation time t' is not affected greatly by laser energy and the laser frequency, and therefore, the ablation time per pulse is nearly the same in all our experiments (*i.e.*, $t \cong 25$ ns).

The threshold intensity for degradation is defined as the minimum laser intensity to create degradation on the substrate surface. For a given pulse duration, the threshold is given by^{31,32}:

$$I_d = \frac{d_f \rho \Delta H_{deg}}{(1 - R)t'} \quad (8)$$

where, d is the ablation depth (m), ΔH_{deg} is the heat of degradation (J/g), t' is the ablation time (s), R is the optical reflectivity, and ρ is the mass density of the material. Based on the thermal oxidation reaction

TABLE V
The Irradiation Condition and Material Properties^{3,44,45}

	PC	PS	ABS
ρ (10^6) (g/m ³)	1.2	1.06	1.04
R	0.06	0.072	0.04
D (10^{-8}) (m)	5.5	1.92	1.32
t' (10^{-9}) (s)	25	25	25

mechanisms for PC, ABS, and PS it is known that the thermal oxidation reaction usually involves breaking the C—H bonds for degradation.¹³ For breaking the C—H bond, ΔH_{deg} is nearly 2.3×10^4 J/g. Therefore, based on the eq. (8) and data given in Table V, the threshold intensity is 6.46×10^{10} W/m² for PC, 2.01×10^{10} W/m² for PS, and 1.32×10^{10} W/m² for ABS.

These threshold energy intensity levels are less than the incident energy ($I = 7.2 \times 10^{10}$ W/m²). The surfaces of PC, ABS, and PS will degrade and produce oxidation products upon irradiation. The laser energy *versus* mass loss curve in Figure 5 shows that the practical threshold energy for PC is smaller than those for PS and ABS. This indicates that most of laser energy irradiated into PS and ABS is not used to degrade these materials. On the other hand, laser irradiation produces heat in ABS and PS samples, and these materials are melted rather than being degraded. Based on the ratios of threshold energy to incident energy, 90% of laser incident energy is used to degrade PC. On the other hand, for ABS and PS samples, only 18% and 28% of laser incident energy is used respectively, to degrade ABS and PS samples. Thermal oxidation usually has several steps,¹³ and it is very difficult to know which ones are accomplished during laser irradiation. Not only the C—H bond but also C—C and C—O bonds may break at different stages of thermal oxidation. Therefore, it is difficult to accurately calculate ΔH_{deg} resulting from laser irradiation. For example, we can use the failure of C—H bonds for illustration, as the breaking energy of C—H bond per mole is usually lower than that of many other bonds (*i.e.*, C—O, C—C),¹¹ and every material we tested has this bond. In addition, the reaction between C—H and O₂ is quite common during laser irradiation of polymers.¹³

Although these arguments are rather simplistic, they are helpful in explaining some of the phenomena in laser irradiation. For example, we know that the mass loss of PC does not increase greatly with increasing laser frequency from 20 to 150 Hz. Based on the above calculations, we know that the laser absorption property of PC is so good that nearly 90% of the irradiated energy had been used to degrade PC even when laser frequency is only 20 Hz. When we increase the laser frequency while keeping the incident energy level the same (180 mJ), there is no more potential to

raise the utilization of laser energy, and the mass loss does not increase greatly. For ABS and PS, however, when laser frequency is 20 Hz, only 23% and 18% of laser energy, respectively, are used to degrade these materials. The rate of energy utilization has much potential to increase for ABS and PS. As a result, when the laser frequency increases, the mass losses of ABS and PS increase greatly, since the energy delivery rate (power) is increased.

Effect of heat conduction and sample thickness

Our experimental results reveal that not only laser parameters and absorption coefficient of materials but also the sample shape and the thermal environment will affect the ablation of polymers. Figure 8 shows the effect of heat conductivity on the mass loss from PC due to ablation. When we compare PC samples irradiated in the air with those bonded with a piece of steel and then irradiated, we find that the mass loss from the PC sample in air is larger than that bonded with steel. When the number of pulses increases, this trend becomes more obvious. This behavior proves that laser ablation of PC is not a pure photochemical process.

Obviously, mass loss is related to the heat accumulation induced by laser irradiation on the PC samples. The sample thickness also affects the mass loss from irradiated PC samples, as shown in Figure 9. The mass loss of the thick samples of PC is smaller than that

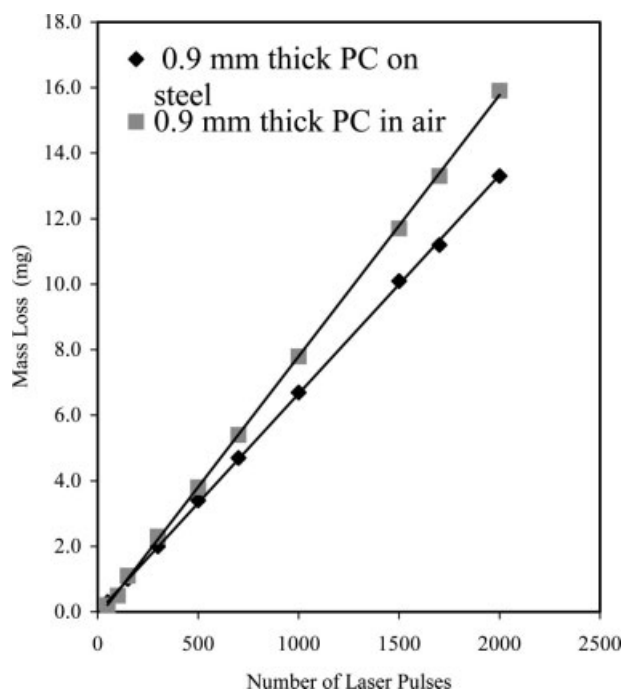


Figure 8 The effect of heat conductivity on the mass loss from PC due to ablation. The laser energy is 220 mJ and the laser pulse frequency is 20 Hz.

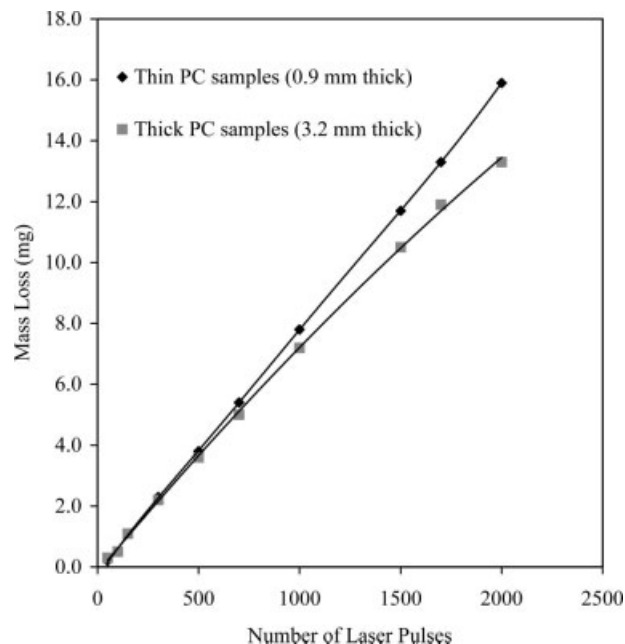


Figure 9 The effect of sample thickness on the mass loss from PC due to ablation. The laser pulse energy is 220 mJ and the laser pulse frequency is 20 Hz.

from the thin samples, under the same laser irradiation conditions used. We attribute this behavior to the fact that in thicker samples the heat energy is dispersed to a larger volume of polymer material, thus reducing its intensity and ability to melt, and assist in ejection of ablated PC.

Effect of laser treatment on the thermal properties (t_g or t_m)

After laser irradiation, we used DSC to evaluate the thermal properties of irradiated polymer surfaces. Figures 10–12 show the effects of laser parameters on the glass transition temperature of ABS, PS, and PC. Figure 10 shows that glass transition temperatures for ABS, PS, and PC decrease with increasing laser pulse energy. We know that the mass loss for irradiated PC at the same energy level is larger than that for PS (see Section 3.1.2). However, the decrease in glass transition temperature for PC surface after ablation is less than that for PS. PC has a higher absorption coefficient in comparison to PS. This means that a laser pulse with the same energy and same frequency can penetrate deeper in PS than in PC. Therefore, the laser energy will be distributed through a larger volume of materials in PS than in PC, and the energy per unit mass of PS will be less than that in PC. The surface material in PC samples is degraded and released to air, while the material just below the surface is not exposed to much laser energy due to high absorption at the surface. In PS, however, since the energy is not

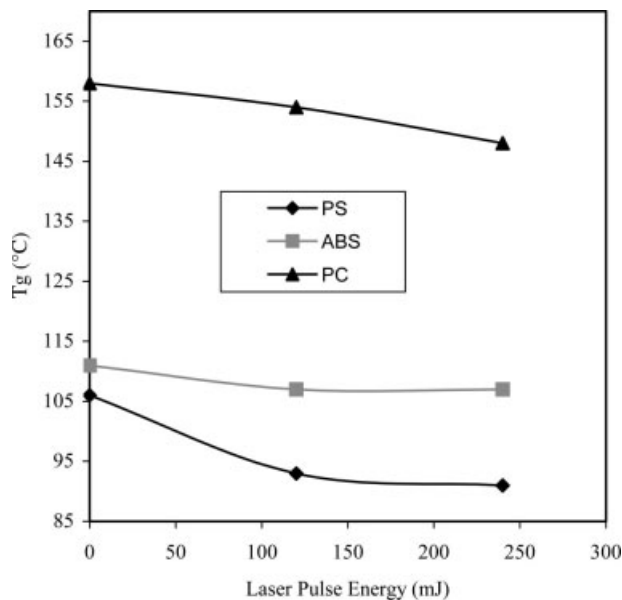


Figure 10 The effect of laser pulse energy on the glass transition temperature of ABS, PS, and PC. The laser parameters are 400 pulses for ABS and PC and 300 pulses for PS, at 20 Hz.

just concentrated on the surface, more materials are affected by laser irradiation. This renders the laser energy density not enough for ablation but enough for degradation. Therefore, DSC tests on PS after ablation show larger decrease for the glass transition of degraded but not largely ablated PS surface after irradiation. The effect of laser energy on the glass transition of PS is also larger than that on the glass transition of ABS.

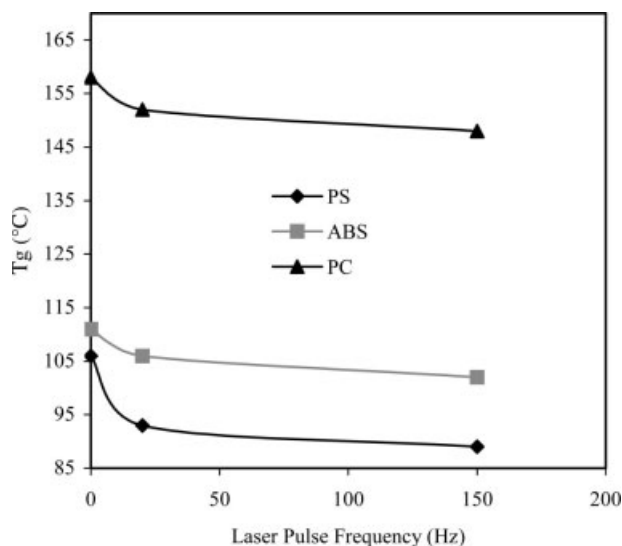


Figure 11 The effect of laser pulse frequency on the glass transition temperature of ABS, PS and PC. The laser parameters are 400 pulses for ABS and PC and 300 pulses for PS, with all of them treated at 160 mJ.

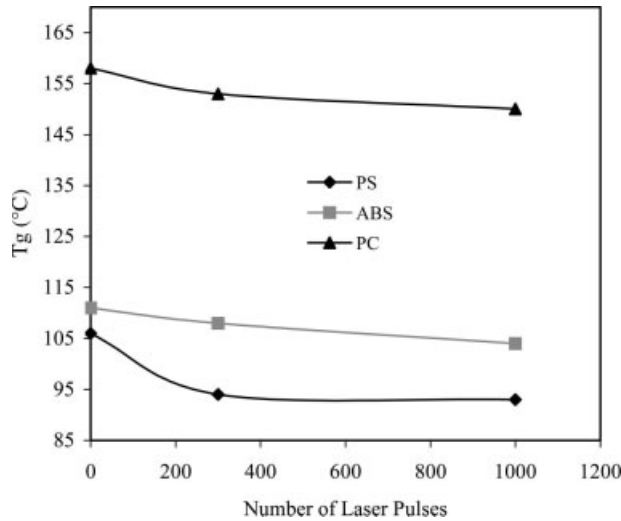


Figure 12 The effect of laser pulse number on the glass transition temperature of ABS, PS, and PC. The laser parameters are 180 mJ at 10 Hz.

The effects of laser frequency on the glass transition temperature of ABS, PS, and PC are shown in Figure 11. The glass transition temperatures of ABS, PS, and PC all decrease with increasing laser frequency, but at a decreasing rate. For example, the glass transition temperature of the untreated PS is 106°C. After laser irradiation at 20 Hz, the glass transition temperature of PS reduced to 93°C. When the laser frequency is increased to 150 Hz, the glass transition temperature of irradiated PS is 89°C. This means that bulk of degradation occurs at low frequency (20 Hz). We also know that the mass loss of ABS and PS is large only at high frequency. This is because when the laser irradiation frequency is high, heat from laser energy will not conduct fast, since the conductivity of these polymers is not good. Consequently, at high laser frequency, the surface temperature on PS and ABS samples become high, and surface materials are ablated easily, resulting in large mass loss at high laser frequency. On the other hand, since heat did not efficiently conduct below the surface of these materials, the degradation of the remaining material did not increase greatly.

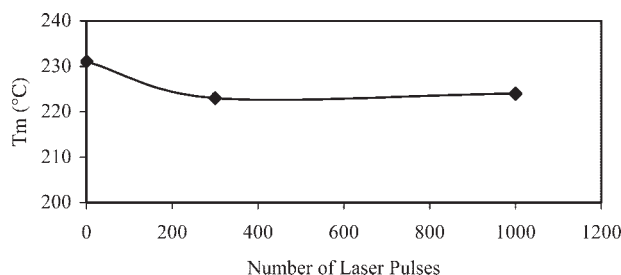


Figure 13 The effect of laser pulse number on the melting temperature of PA6. The laser parameters are 180 mJ at 10 Hz.

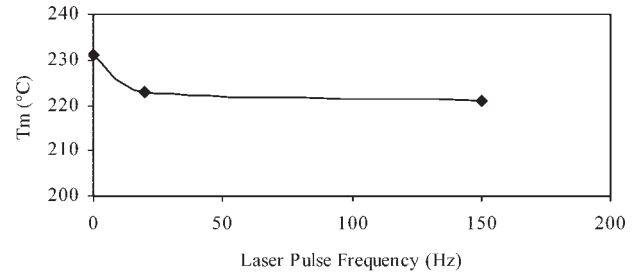


Figure 14 The effect of laser pulse frequency on the melting temperature of PA6. The laser parameters are 600 pulses at 160 mJ.

Figure 12 shows that the glass transition temperature decreases nonlinearly with increasing number of laser pulses. It drops fast at lower number of laser pulses and then decreases slowly. The rate of degradation is controlled by the material's temperature, which in turn, is controlled by the unbalance between the incident energy and the energy that is dispersed to the environment. If a balance is formed, the temperature will not increase. At the beginning of irradiation, the material temperature increases greatly with increasing number of pulses. However, after several pulses, the rate of dispersion of energy increases with increasing temperature and the rate of increase of temperature decreases. Consequently, the increasing rate of degradation that is affected by the increasing rate of temperature is also reduced. This may be the reason why the glass transition temperature does not decrease linearly with increasing number of laser pulses (Fig. 12).

As for PA6, Figures 13–15 reveal that, compared with the untreated samples, laser-irradiated PA6 samples have lower melt temperature.

SUMMARY AND CONCLUSIONS

In this research, the ablation rate and thermal properties of various engineering polymers such as PC, ABS, PS, and PA6 were investigated subsequent to irradiation by KrF excimer laser. The mass loss for ABS, PS,

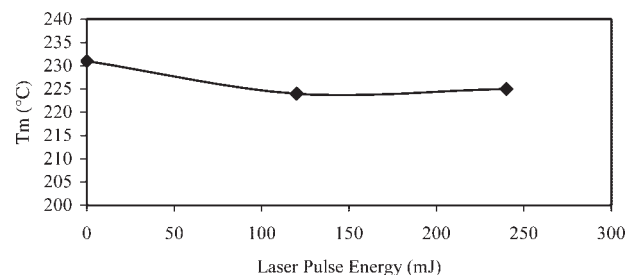


Figure 15 The effect of laser pulse energy on the melting temperature of PA6. The laser parameters are 600 pulses at 20 Hz.

and PC increases with increasing laser pulse energy. The variation of ablated mass loss is nonlinear for ABS, PS, and PC at the low energy levels due to the presence of thresholds. The mass loss for ABS and PS increases with increasing laser pulse frequency. The mass loss for PC increases with laser frequency only up to 20 Hz. Theoretical calculations revealed that the threshold intensities for degradation, I_{dt} , in ABS, PS, and PC were smaller than the incident laser power intensity, I , when the laser conditions were 500 pulses with 180 mJ at 20 Hz. Consequently, laser irradiation led to the degradation of ABS, PS, and PC.

The material with the higher absorption coefficient (PC) interacts with the incoming laser wave over a shorter depth, thus dissipating larger energy per unit volume through its near surface region. This results in larger mass loss for the PC, even at lower laser energy levels. For the material with lower absorption coefficient (ABS), however, the impinging laser wave penetrates the material at larger depths and causes it to melt in a larger scale, with a lower energy density. This is why the weight loss for ABS is less than that for PC. The resulting melt flow, cavitations, and resolidification in ABS produce surfaces more identifiable with melting, with the presence of larger cavities, especially at higher laser pulse frequencies, which produce larger thermal loads.

The effects of laser treatment on the thermal properties (T_g or T_m) of different polymers were also investigated using DSC. It was found that the T_g and/or T_m for PC, ABS, PS, and PA6 all decreased as a result of laser treatment, indicating the degradation effect of the laser ablation procedure.

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