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Thermal degradation of Poly(methyl methacrylate) with a 1.064 μm Nd:YAG laser in a buoyant flow

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ABSTRACT

The laser radiative oxidative decomposition of poly(methyl methacrylate) (PMMA) and the evolved decomposition products in the gas-phase are investigated using imaging Fourier transform infrared spectroscopy (IFTS). The spatial and temporal evolution of the gas plume in air was investigated with adequate spatial (0.81 mm^2 per pixel) and spectral resolutions (2 cm^{-1}). Surfaces of black PMMA samples were irradiated from 4 to 22 W/cm^2 with a cw 1.064 μm Nd:YAG laser. Strong spectral emission of methyl methacrylate (MMA) was observed in the infrared. Spatial maps of plume temperature and MMA column density were obtained from modeling the observed spectra by assuming a homogeneous single-plume radiative transfer model (RTM). A spectral model was used to compute the gas emissivity from an experimentally measured, interpolated and extrapolated MMA absorption coefficient database. In addition, the spectral radiance from the irradiated PMMA surface was fitted with Planck's distribution to obtain temporal and spatial surface temperature profiles. The peak signal-to-noise exceeded 50:1, allowing plume temperature and MMA column density determinations with low statistical errors. Laser irradiated PMMA reached a steady surface temperature of 613.9 ± 0.8 K and a peak gas-phase temperature of 700 ± 19 K at 22 W/cm^2. The reported statistical uncertainties for all the results are defined as the half-width of the 95% confidence interval and do not include systematic errors associated with the assumption of a homogeneous plume or the effects of turbulence. As laser intensity increased, gas temperature decreased at the surface-boundary layer. A simplified thermal analysis was developed to understand the wavelength dependent surface heating rates from using both CO_2 and Nd:YAG lasers. An Arrhenius plot of MMA formation at the surface for a single pixel was compared with established kinetics models. At surface temperatures of 450–600 K, an effective activation energy of 30.83 ± 8.29 kJ/mol was obtained, consistent with surface desorption of the monomer.

1. Introduction

Poly(methyl methacrylate) (PMMA) is an inexpensive thermoplastic that decomposes at ~ 493 K [1]. In the presence of oxygen, the main decomposition product is the monomer methyl methacrylate (MMA) [2]. Molecular oxygen exerts a stabilizing effect on PMMA against depolymerization at low temperatures [3–5], thus increasing the initial decomposition temperature when compared to that for thermal degradation in an inert gas. Methyl methacrylate further decomposes to combustible gaseous hydrocarbon species. These hydrocarbon fuels react with oxygen to produce CO, CO_2 and H_2O from combustion. The thermal decomposition of PMMA is a zero or first-order kinetics process and has been reviewed in detail elsewhere [6].

Fourier transform infrared (FTIR) spectroscopy has been used previously to investigate the time dependent thermal degradation of polymers [7]. Recently, imaging Fourier transform spectroscopy (IFTS) demonstrated the ability to monitor the thermal decomposition products from laser irradiated fiberglass reinforced polymers at high spatial resolutions (0.81 mm^2 per pixel) [8]. The use of IFTS at short focal distances allows evaluating temporal and spatial variations of the evolved molecular species in the gas phase. The imagery allows correlating the fluid dynamics to the thermal degradation kinetics of polymers. Since PMMA predominantly

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depropagates to its monomer as a result of thermal degradation, it is important to monitor the infrared emission of MMA with high fidelity. The principal infrared bands of gaseous MMA have been reported previously and are summarized in Table 1 [9].

Radiative transfer models allow accurate quantification of temperature and column densities from the observed plume spectra with low statistical errors [8,10]. For fiberglass reinforced polymers, a simple spectral model describing the apparent plume radiance was recently developed to quantitatively determine evolving spatial maps of the temperature and column densities of the emissive plume molecular species [8]. Radiative modeling requires *a priori* knowledge of the absorption cross section of the emitted products for accurate spectral quantification. Although the HITRAN [11] spectral database contains a comprehensive collection of spectroscopic parameters to compute the absorption cross-section for several molecules, complex hydrocarbon molecular species are not currently included. The oxidative thermal degradation of polymers usually results in complex kinetics with emission from molecular species not readily available in the current spectral databases. Park et al. [9] investigated the infrared radiation properties of MMA from statistical narrow band models to fit the measured FTIR spectra. The monomer column density can also be estimated from total band emissivity calculations from Park et al. [9] as well from radiative transfer models.

Laser lethality experiments with PMMA have been reported with continuous wave (CW) CO_2 lasers at the longer wavelength of 10.6 μm [12–17]. When polymers are irradiated in the longer infrared wavelength, the incident energy is mostly absorbed within a few micrometers from the surface. However, few studies have been conducted at the near-infrared wavelength of 1.06 μm [18–20]. Due to the poor absorption characteristics of organic materials in this region, pigments are commonly added to acrylic thermoplastics. According to Said-Galiev and Nikitin [21], this in-depth absorption follows the Beer–Lambert law:

$$I(z) = I_0 \exp(-\alpha \cdot z) \quad (1)$$

where, $I(z)$ is the irradiance (W/cm^2) at depth z (cm), I_0 is the incident irradiance (W/cm^2), and α is the absorptivity (cm^{-1}) of the material. The absorptivity of clear PMMA varies depending on the type of laser wavelength used, a value of 250 cm^{-1} was obtained with a CO_2 laser (10.6 μm), whereas values of ~25 cm^{-1} were assumed for hydrogen fluoride (HF) and deuterium fluoride (DF) chemical lasers with wavelengths of 2.7 μm and 3.8 μm respectively [22]. When thermoplastic polymers were irradiated with a CO_2 laser, Cozzens and Fox [23] reported that minimal decomposition occurred between 3 and 7 W/cm^2, but at 5–11 W/cm^2 softening was observed. At a higher irradiance of ~22–25 W/cm^2, the material decomposed and vaporized. Since the thermal degradation of PMMA with a cw 1.06 μm Nd:YAG laser has not been thoroughly investigated, this effort aim to explore the spectral emission of the surface-plume boundary layer using IFTS.

The objective of the present work was to investigate the thermal degradation of carbon-black PMMA with a Nd:YAG laser at radiative fluxes between 4 and 22 W/cm^2. The evolved gas phase plume was monitored from FTIR measurements. Following spectral identification of emissive plumes in the infrared, a simplified single layer LBLRTM was developed for quantification of spatial and temporal variations in plume temperature and molecular column densities from IFTS. Also, non-imaging long wave infrared (LWIR) FTIR was employed to investigate the temporal evolution of effluents in the gas phase. The influence of radiative flux was investigated to understand the laser effects on the thermal degradation of PMMA. The effect of plume bending due to buoyancy is correlated between the infrared imagery and spatial maps of temperature and column density as a function of power density. To our knowledge, we present the first two-dimensional spatial maps on the evolved plume temperature and MMA concentration profiles from the surface-boundary layer of laser irradiated PMMA. A kinetics interpretation from established models was made based on the statistical results from the spectral fit of the irradiated surface at 22 W/cm^2.

2. Experimental methods

Black plexiglass®, PMMA with carbon black pigmentation samples, were irradiated by a cw Nd:YAG 1.06 μm laser at 4–22 W/cm^2 in air at atmospheric pressure for 70–420 s. The nearly flat top beam with 2.42 cm diameter nearly filled the 6.45 cm^2 square and 1.27 cm thick samples. Approximate values for various properties of black PMMA are provided in Table 2. At 10.6 μm (CO_2 laser wavelength) the absorptivity of black PMMA is ~100 cm^{-1} [17]. However at 1.06 μm (Nd:YAG laser wavelength) it has been reported between ~ 0.25 and 4.5 cm^{-1}, depending on the amount of carbon-black pigmentation in PMMA from 0.01 to 1 % by weight respectively [18,19].

The evolution of the non-combusting, gas plume was monitored with both an imaging mid-wave imaging Fourier transform spectroscopy (IFTS) and non-imaging high-speed mid- and long-wave Fourier-transform spectrometer (FTS) perpendicular to the laser axis. The majority of the experiments were design to view the gas plume in front of the sample surface with the laser incident normal to the surface, as illustrated in Fig. 1a. A few experiments were conducted with the sample rotated at 30° so that the laser was incident at 60°, so the surface temperature could be observed, as shown in Fig. 1b. For these surface observations, larger samples of 2.54 cm × 5.08 cm were employed to accommodate the projected laser spot size.

The IFTS has been described in some detail previously [24,25]. The 16-tap InSb focal plane array (FPA), with spectral response from 1800 to 6667 cm^{-1}, was narrowed to the central 32 x 32 pixels. With a focal distance of 3.12 m, the spatial resolution is 0.81 mm^2/pixel. A series of 9480 (number of optical path differences samples) modulated images comprise a double-side interferogram on each pixel as the mirror path difference is scanned by 0.3 cm (2 cm^{-1} spectral resolution). The integration time for each image was 10 μs,

Table 1
Principal infrared bands of MMA [9].

Wavenumber (frequency)	Characteristic bands
820 cm^{-1} (12.2 μm)	C–H and C–O–C deformation
950 cm^{-1} (10.5 μm)	=CH (out of plane bending)
1035 cm^{-1} (9.7 μm)	
1170 cm^{-1} (8.5 μm)	C–O stretching
1310 cm^{-1} (7.6 μm)	CH_3- bending
1440 cm^{-1} (6.9 μm)	
1730 cm^{-1} (5.8 μm)	C=O stretching
2940 cm^{-1} (3.4 μm)	CH_3- stretching

Table 2
Thermo-physical properties of black PMMA.

Name	Symbol	Value	Units	Reference
Density	ρ_{PMMA}	1190	kg/m^3	[39]
Surface conductivity	k	0.188	W/(m K)	[39]
Heat capacity	c_p	1465	J/(kg K)	[39]
Absorption coefficient	$\alpha(10.6\ \mu m)$	100	cm^{-1}	[17]
	$\alpha(1.06\ \mu m)$	0.25–4.5	cm^{-1}	[18,19]
Reflectivity	$R(10.6\ \mu m)$	5	%	[17]
	$R(1.06\ \mu m)$	50	%	[18,19]