Observation of Newtonian Rings on PVA Polymer During HF Laser-induced Physical Modification Using an Optical Fibre

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ABSTRACT

The ablation of polyvinyl alcohol (PVA) with a multi-line 2.6–3.0 μm HF laser showed a strong interaction due to its relatively high absorption coefficient 7×10^5 cm⁻¹, particularly hydrogen bands at 3597 cm⁻¹. By using the expression for heat diffusion limit, surface temperature (Ts) of 340 K and 449 K were calculated for fluences of 0.3 and 1 Jcm⁻², respectively. The Ts values are well consistent with the PVA melting point of 531 K and SEM photographs. With the average activation energy of 188 KJ mol⁻¹ and rate constant of 6×10⁻¹² s⁻¹, a value of <K>=6×10⁻⁶ s⁻¹ for T=(146–230) K is obtained. The thermal degradation effect in short pulse duration was evident by Newtonian rings which basically is an interference pattern created by light, reflects off the boiling ablated material and the underneath solid material.

Key Words: HF laser, PVA polymer, optical fibre, surface modification, Newtonian rings

INTRODUCTION

The potential advantages of mid-IR lasers (2–3 μm) for controlled materials ablation and modification are well known and stem from strong absorption by water and hydroxyl bond in that region [1–3]. Of a variety of lasers available for such applications there has been a recent growth of interest in the HF system, which produces appropriate wavelengths and under transient pulses it minimizes damages by thermal transfer during the interaction [2–7].

It has also been shown that fluoride glass fibres can transmit sufficiently intense pulses to produce ablation of tissue samples [8–12]. Particular applications of this polymer include PVA gel in controlled drug delivery such as penicillin, treatment of animal infections using PVA-iodine, and PVA solution as blood plasma in order to prevent haemorrhage [13, 14]. For these reasons, experiments were carried out to study the interaction mechanism as well as physical modification of PVA thin films using a small core fibre-delivered pulsed HF laser.

EXPERIMENTAL

As it is shown in Figure 1, PVA polymer (–CH₂–CHOH–) has a relatively strong absorption peak
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Figure 1. Absorption spectrum of PVA polymer between 2.5–15 μm.

between 3500–4000 cm\(^{-1}\) corresponding to 2.50–2.85 μm due to the presence of OH group in the repeat unit. The type of fibre used in this experiment was a fluoride glass with a 70 μm core diameter, a 125 μm core plus cladding and an overall diameter of 250 μm. At a wavelength of 2.8 μm this step index fibre has a V=(2π/λ)N=15.7 where r is the core radius and N=0.2 is the numerical aperture. From calculations given in reference 15 it is found that with this V- value the fibre will support to =123 bound modes and is thus strongly multimode for the HF laser. Most tests were carried out using short samples of fibre (200 mm) which were first cleaved, polished and then mounted on a micropositioner to allow accurate location with respect to the laser input beam.

The laser emitted 20 transitions spanning the wavelength range 2.67–2.96 μm in a pulse of 400 ns duration (FWHM). Its output beam was passed through a 6 mm diameter circular aperture to select a region of uniform fluence and this aperture then imaged to produce a highly selective region of uniform fluence and it was then imaged again to produce a highly demagnified spot suitable for coupling laser energy into the fibre. This image was formed by a 20 mm focal length ZnSe lens operating at an aperture ratio of F/6 and producing ≈150 μm diameter spot at the fibre input surface. Energy measurements were made using a sensitive pyroelectric joulemeter (Jentec).

PVA samples in the form of thin platelets were produced by casting from solution and then the capability of the 0.2 m long fibre to produce microcraters by ablation was tested.

RESULTS AND DISCUSSION

In Figure 2 the variation of the transmitted energy with input energy for a 200 mm fibre sample shows that there is an approximately linear dependence corresponding to a transmission of ≈59% for energies up to 0.75 mJ. Given the low distributed attenuation of fluoride glass fibres in this spectral region [16], this loss is principally attributed to coupling loss at the input and output surfaces [9], and as the input beam considerably exceeds the core diameter, a significant fraction of the beam excites unbound cladding modes. The sharp drop in transmission beyond ≈1.4 mJ input in Figure 2 is due to the onset of irreversible damage at the fibre entrance surface. This corresponds to a fluence of 8 J cm\(^{-2}\) and irradiance of 20 MW cm\(^{-2}\) based on an input beam diameter of 150 μm and the assumption that the fluence is uniform at the input plane.

Qualitative evidence for the latter is seen in Figure 3, where the exit beam diameter is plotted as a function of distance from the fibre tip. At nominally zero distance the beam diameter is ≈110 μm, which is considerably larger than the 70 μm core, suggesting a significant contribution from cladding modes. The full beam divergence angle deduced from the asymptote of the data in Figure 3 corresponds to ≈190 mrad which is close to but somewhat larger than the filling angle with the F/6 input lens. Figure 4 indicates the ablation depth per pulse as a function of fluences and
by assuming that the plume density at higher fluences is reduced and becomes transparent (i.e., \( \alpha_p \rightarrow 0 \)), the corresponding value of absorption coefficient for PVA in the linear part (non-logarithmic) using the relation \( x = F - F_0/\alpha F_0 \) is found to be \( 3 \times 10^4 \) cm\(^{-1} \), where \( F_0 \) and \( \alpha \) are the threshold fluence and absorption coefficient, respectively. In order to relate the rate of temperature increase to absorption coefficient and thermal properties of material one could use the solution of Fourier heat conduction equation given below [17, 18]:

\[
\rho C \frac{dT(x)}{dt} = (1-r)I_0 e^{-\alpha x}
\]  

Where \( C, \rho \) and \( r \) are specific heat capacity \( (1.67 \text{ Jg}^{-1} \text{ K}^{-1}) \), density \( (1.3 \text{ gcm}^{-3}) \) and reflectivity, respectively.

However, in this case, photon penetration depth is smaller than thermal depth i.e., \( d_p < X_T \), thus at the end of laser pulse the polymer surface temperature \( (T_s) \) below ablation threshold is given by:

\[
T_s = T_i + \frac{\alpha F(1-r)}{\rho C(4k\alpha_p)^{1/2}}
\]  

Where \( T_i, F \) and \( k \) are the initial temperature, fluence and thermal diffusivity, and the value of \( r \) by using the Fresnel eqn (3) becomes 0.99.

\[
r = \frac{[(n_m + n_0)^2(an_m)^2]}{[(n_m + n_0)^2 + (\alpha n_m)^2]}
\]  

Where \( n_m \) and \( n_0 \) are refractive indices of medium (polymer) and air, respectively. Hence by substituting \( r=0.99 \) in eqn (2), one can calculate the temperature of polymer surface. For example, at 4, 1 and 0.3 Jcm\(^{-2} \) the temperature becomes 915, 449 and 340 K and therefore it can be seen that near ablation threshold, the final temperature is \( \approx 438 \) K which is very close to polymer melting point i.e., 531 K. In order to obtain more information about the rate of thermal degradation we could use the Arrhenius theory i.e.,

\[
K (s^{-1}) = 6 \times 10^7 e^{-188000/(8.134T)}
\]  

Where \( 6 \times 10^7 \) s\(^{-1} \) is the reaction rate constant, \( <E> \approx 188000 \) Jmol\(^{-1} \) the average activation energy of PVA and \( R=8.134 \) the gas constant, hence for \( T= (146-230) \) K, \( <K> \approx 6 \times 10^{-6} \) s\(^{-1} \).

Figure 5 shows an optical microscope photograph of PVA sample irradiated at low energy using optical fibre. Basically, the photograph consists of three important regions: Region A, where the interaction process exhibits its effect as melting and raising the polymer surface due to heat pressure build up underneath. Region B, which is the most important effect observed during the experiment indicates Newtonian rings which could lead to a better understanding of laser ablation.

In essence, a laser quickly heats a material, creating a microscale explosion of heat and pressure.
Varying reflectivity is at the heart of the Newtonian rings, and basically it is an interference pattern created by light.

In a short-pulse laser ablation process, light reflects off the boiling, ablated material, and the solid material underneath, creating the interference effect. Fluence and material temperature are crucial to the formation of Newtonian rings. Region C, shows the denatured area where the chemical changes result in whitening of the surface and also its diameter indicates the total extension of interaction area of fibre output end at the polymer surface.

Figures 6a and b show the SEM of a PVA sample in air subjected to 60 pulses at an exit energy of 0.1 mJ from the fibre (a) and without fibre (b), respectively. At this energy the exposed region of the surface is raised and small ‘blow-holes’ are evident indicative of the release of gaseous products from the interior of the polymer. Figure 7 shows the result obtained at a higher exit energy of 0.4 mJ where the exposure to 60 pulses produces ≈ 45 μm deep crater of diameter ≈ 65 μm. The appearance of the crater suggests the degradation of polymer has produced volatile products and roll-back due to melting.

Contribution to its formation, a peripheral zone of fibrous material is also evident surrounding the upper portion of crater, which is probably formed by redeposition of the ablated material.

CONCLUSION

The subject of laser polymer interactions is quite vast due to the scale of importance of variables such as the photon wavelength, power density and chemical structure of target materials. It must be assumed a priority that different mechanisms may be operative for different polymers or for irradiation of a particular polymer at different wavelengths. The point to notice
Ablation of PVA polymer using 0.4 mJ of fibre output energy.

is that a particular wavelength contributions from mechanisms including photoablative decomposition (photolysis), photothermal or even multiphoton process may in principle occur, and the question is how to identify the dominant route.

A satisfactory IR ablation of polymers can be achieved provided the physical and optical properties of laser and polymer are well optimized. In order to obtain an acceptable etch quality with IR lasers, it must certainly be tuned to a strong absorption band of polymer. It can be seen from the results and SEM photographs that although PVA has a relatively strong absorption band in the range of (2.6–3.0 μm), the ablation quality however is not very clean. This can be thought in terms of relaxation time (~500 ns) of PVA being approximately the same as the pulse duration (~400 ns). Consequently an adiabatic condition is just met and heat diffusion to adjacent area can take place.

For practical medical applications such as controlled drug release this will not satisfy the quality requirement. However, the problem to some extent can be resolved by a high absorbing laser single mode, which matches with the polymer molecular structure band selected. Finally, to have a more control over the interaction process a better understanding of Newtonian rings and its optimization are needed.

REFERENCES


