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Negative pressure model for surface foaming of collagen and other biopolymer films by KrF laser ablation

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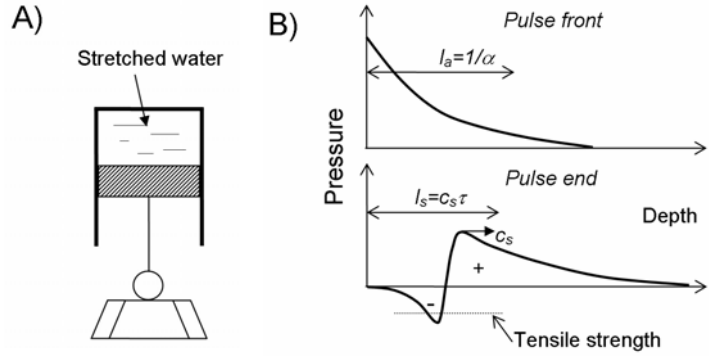
Abstract. A single KrF laser pulse of energy larger than 0.5 J/cm² is enough to create a microfoam layer on the surface of a collagen film and other related biopolymers. This is a new result that can be of interest for many new applications. The target material is excited in the radiation absorption depth of ~17 μm and expands into a foam layer whose new surface is ~5 μm above the original one. The estimated surface transient temperature of ~83°C at threshold fluence does not account satisfactorily for this fast foaming process but consideration of the bipolar pressure variation ~±200 bar, i.e. laser induced acoustic wave suggests that a cold homogeneous boiling is induced by the tensile part of the pressure wave in the laser excited volume. The classical nucleation theory predicts a spontaneous dense and homogeneous bubble formation when the pressure is negative in the inviscid liquid. These results constitute new examples of laser induced fast expulsion of liquid due to the hydrodynamic pressure wave which can also be considered as resulting from the surface acceleration/deceleration sequence.

1. Introduction

A negative pressure, also called tension or stress can break a solid as well as a liquid when its magnitude is larger than a critical value, the tensile strength of the dense media [1]. When the stretched liquid or solid breaks the cavitation phenomenon occurs with the rapid formation of bubbles due to the tendency of the volume to increase and the impossibility of the atoms or molecules to fill completely the new volume. Many techniques can be used to induce a transient or permanent negative pressure in a medium. A simple experiment of liquid stretching is for instance water in a cylinder sealed with a piston on which a large force is exerted so that the liquid volume is forced to increase as seen in Figure 1A. Pulsed laser surface irradiation is capable of generating a strong hydrodynamic pressure [2] with positive and negative waves, Figure 1B, when the material parameters, absorption, thermal expansion, sound speed, fulfil favourable conditions. The tensile part of the laser produced acoustic phenomenon [3], Figure 1B, may have important consequences if the material tensile strength is exceeded [4]. This is the case for instance in front face spallation with expulsion of big fragments of the irradiated solid and in liquid that breaks and leads to bubble formation. The effect is also used in laser cleaning to remove particles from surfaces. Recently we have reported [5] that the irradiation of collagen films with one pulse of the KrF laser produces a microfoam on its surface, as presented below in figures 2 and 3. This is a new result that can be of interest for many new biomedical applications, since by a low temperature laser treatment

a biomimetic interconnected nanoporous foam is created having potentially promising properties for future artificial cellular matrixes. The target material, a dense and dry collagen film or other biocompatible polymer, is excited in the KrF laser radiation absorption depth of $\sim 17 \mu\text{m}$ and expands into a foam layer whose new surface is $\sim 5 \mu\text{m}$ above the original one. In this paper we discuss the mechanism of the foam formation as a function of the properties of the target material and the important perspectives opened up by this new laser process.

Figure 1 **A)** Illustrative experiment of stretching of water in a cylinder sealed with a piston. **B)** Illustration of hydrodynamic pressure waves generated by a short pulse laser irradiation at a surface of a dense media characterised by the absorption length l_a and a sound length l_s (τ is the duration of the laser pulse). Upon increasing absorption pressure is essentially positive and at the end of the pulse a tensile wave starts to develop from the surface and propagates into the bulk at sound speed c_s .



2. Laser negative pressure and bubble nucleation

The time average pressure jump developed during the absorption of a laser pulse can be given by [5]:

$$P_{\pm} = \pm \frac{\beta A F}{C_p \alpha \tau^2} (1 - e^{-\alpha z}) \quad (1)$$

where β , A , C_p , α , are respectively thermal expansion coefficient, absorptivity, heat capacity, absorption coefficient of the material and F , τ laser fluence and pulse length. For judging of the importance of the laser pressure effect in a given material a number of characteristic lengths have to be compared to the absorption length. If the thermal length $l_t = \chi \tau$ is lower than l_a the irradiation is called thermally confined and the temperature elevation is confined in the absorption volume. Similarly if sound length $l_s = c_s \tau$ is smaller than l_a the irradiation is stress confined and pressure increase can be high. The condition of stress confinement can introduce some damping of pressure jump given by:

$$D = \frac{(1 - e^{-l_s/l_a})}{l_s/l_a} \quad (2)$$

Examples of laser generated hydrodynamic pressure are given in Table 1 for a laser fluence of 0.5 J/cm^2 for 3 representative materials.

It is noticed that almost no transient pressure is induced silicon since absorption coefficient and thermal diffusion are high. So far no laser foaming has been reported on silicon. PMMA and collagen have more favourable characteristics and display respectively 500 and 200 bar transient pressures, values which are impressively high. Although bubbling occurs on PMMA, it is however suggested that collagen film is more prone to explosive cold boiling because of its water content which can play an important role in decreasing the surface tensile strength and viscosity.

In the previous paper [5] we have considered that the bubble nucleation that explains the foaming effect is much faster in the tensile wave, as in Figure 1B, since the energy barrier is given by:

$$\Delta W(r_c) \approx \frac{16\pi\gamma^3}{3P_-^2} \propto \tau^2 F^{-1} \quad (3)$$

Table 1

Comparison of laser generated hydrodynamical pressure jump induced in 3 representative materials for a KrF laser pulse of 0.5 J/cm² of duration $\tau=25$ ns.

		Silicon	PMMA	Collagen
Absorptivity	$A=I-R$	0.39	0.96	0.96
Absorption coefficient	α (cm ⁻¹)	1.67×10^6	250	600
Thermal diffusion	χ (cm ² s ⁻¹)	0.9	7.5×10^{-4}	7.5×10^{-4}
Sound speed	c_s (m.s ⁻¹)	2200	1600	1600
Absorption length	$l_a=1/\alpha$ (μ m)	0.006	40	17
Thermal propagation length	$l_t=(\chi \cdot \tau)^{1/2}$ (μ m)	1.50	0.04	0.04
Sound propagation length	$l_s=c_s \cdot \tau$ (μ m)	55	40	40
Thermal expansion coefficient	β (°K ⁻¹)	1.00×10^{-6}	2.60×10^{-4}	6.00×10^{-4}
Heat capacity	C_p (J/g)	0.4	1.57	3.9
Density	ρ (g)	3	1.3	1.3
Surface displacement	H (cm)	7.5×10^{-5}	1.15×10^{-4}	1.07×10^{-4}
Surface speed	$v=H/\tau$ (cm/s)	30	4.59×10^3	4.26×10^3
Surface acceleration	$a=H/\tau^2=v/\tau$ (cm ² /s)	1.20×10^9	1.83×10^{11}	1.70×10^{11}
Surface acceleration	a (g)	1.20×10^6	1.83×10^8	1.70×10^8
Pressure transit time	$\tau_s=l_a/c_s$ (s)	2.72×10^{-12}	2.50×10^{-8}	1.04×10^{-8}
Hydrodynamic pressure	P_{\pm} (bar)	5×10^{-3}	509	197
Pressure confinement	$\theta=d/\tau_s=\alpha \cdot c_s \cdot \tau < 1$	9185	1	2.4
Pressure damping	$D=(1-e^{-\theta})/\theta$	0.01	63.21	37.89

in which γ is the surface tension of the collagen material. A large tensile wave makes the bubble nucleation activation-less and equation (3) indicates further the dependence on laser parameters (F and τ). The rate of nucleation is given [5] by:

$$J(T) = Zn(r_c) = Zn_0 e^{-\frac{\Delta W(r_c)}{kT}} = N \sqrt{\frac{3\gamma(T)}{\pi n}} e^{-\frac{\Delta W(r_c)}{kT}} \quad (4)$$

in which Z is called Zeldovich factor, $n(r_c)$ is the density number of critical bubbles, n_0 is the maximum concentration of potential bubbles having subcritical radius, N is ~concentration of molecules (each water molecule can be a nucleation centre) and m the mass of these molecules.

3. Laser surface foaming on collagen and other biopolymer films

The collagen material was extracted from rat tail tendon by dissolution in diluted acetic acid in water, 0.3% of collagen, and was casted in film by overnight drying on a Teflon surface. The film surfaces were irradiated with one pulse of the KrF laser as reported in reference [5] in air with increasing fluence. A threshold fluence for collagen foaming is 0.5 J/cm² and SEM pictures of the various polymers are displayed in Figure 2 and 3.

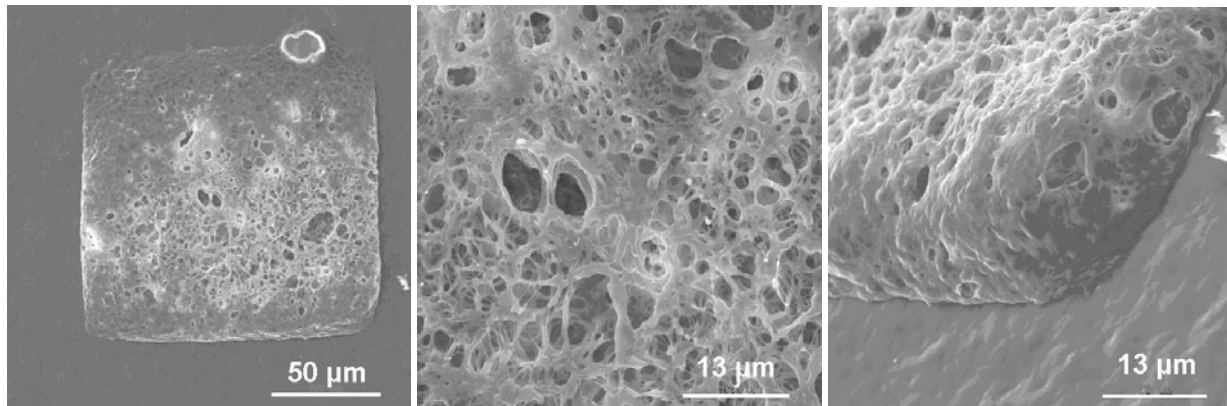


Figure 2 Collagen film surface after ablation with one pulse of the KrF laser ($F=0.7 \text{ J/cm}^2$) showing the foaming phenomenon over the irradiated square spot (size $150 \mu\text{m}$). Left is a large view of the spot. Center is a detail of the spot center. Right is an enlargement of a corner of the spot showing the expanded of the final foam surface well above the starting surface of the original film.

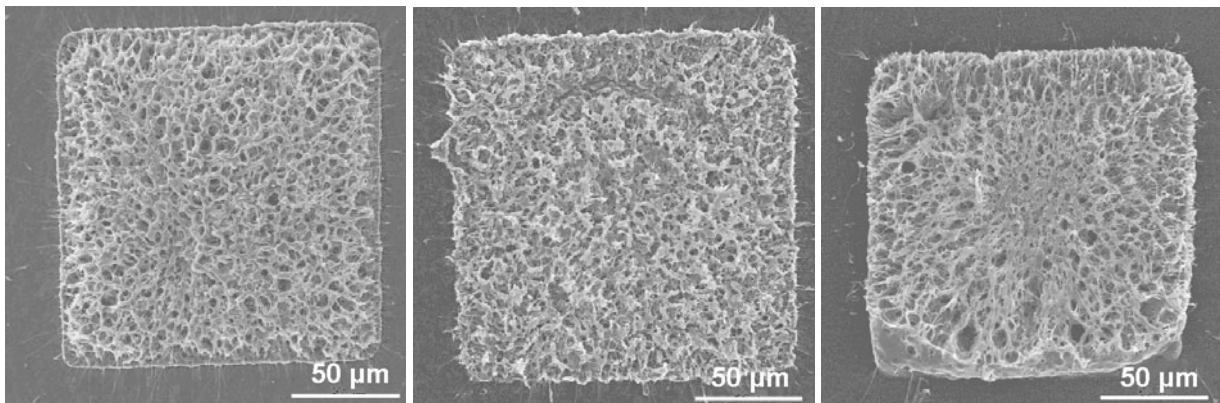


Figure 3 Foaming with one pulse at higher fluence (5 J/cm^2) on various biopolymer films: from left to right 1) collagen film surface 2) Blend of collagen/poly(vinyl pyrrolidone) (50 %). 3) Chitosan

4. Discussion

The estimated surface maximum transient temperature, as given by equation (5):

$$T = T_0 + \alpha F / \rho C \quad (5),$$

with T_0 being the ambient temperature, is $\sim 83^\circ\text{C}$ at $F=0.5 \text{ J/cm}^2$ [5] and does not account satisfactorily for the observed sudden dense nucleation of bubbles, since phase explosive type ablation requires the temperature be close to a critical temperature, like 374°C at normal pressure for water, a 15% constituent of the film. Interestingly however the laser foaming can be compared to the well known process of regular polymer foaming which necessitates a foaming agent whose purpose is to develop high pressure dissolved gas upon heating. In some case by introducing a sudden pressure drop, for instance during polymer extrusion [6], triggers the nucleation and growth of the wanted bubbles and the foam forms then stabilises by rapid quenching. Similarly in the laser foaming the bubble nucleation and growth is triggered by the pressure drop, also called rarefaction wave [7], from the high compressive phase to the tensile phase of the laser induced acoustic wave. The main difference is that the new pressure wave is negative and therefore bubble nucleation can develop spontaneously as voids, without the necessity of a high gas pressure in it, if the material tensile strength is exceeded, as suggested in Figure 1B. This tensile limit is obtained in collagen probably because it contains some percentage of

water, 15% as we measured [5]. These water molecules, bonded to collagen, are necessary for the cohesion and functioning of the proteinic materials, at normal thermodynamic conditions, and can not be eliminated easily by room temperature drying during film preparation. However during the laser experiment and because of the large negative pressure they are labile enough to facilitate the formation of voids and bubbles and can be vaporized. It is interesting to note the dynamics of foam expansion which must take place in a timescale of the order of the pressure transit time ~ 10 ns in the absorption volume as listed in Table. This short period of foam expansion gives a stress rate as high as 10^7 s⁻¹, which may confer new original properties to the foam material.

5. Conclusions and perspectives

KrF laser irradiation of dry collagen films, with only 15% residual water, induces a foaming of the surface. Other biopolymers behave similarly. The mechanism of foaming requires bubble nucleation and growth which are made possible by a pressure drop down to a tensile state which exceeds the strength of the material. This is attributed to the bipolar pressure waves of the acoustic effect of the laser excitation. Microscopic examination of the foam reveals the interconnection of the cells, a property of interest for potential applications in biosystems. For instance collagen is a natural abundant proteinic material which is easily recognized and colonized by cells. Such microfoam can be a key technology to improve cell attachment, manipulation and implantation for tissue repair for instance. In some other application the microfoam could be filled with other material and could be used as drug carrier.

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