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Surface morphological modification of crosslinked hydrophilic co-polymers by nanosecond pulsed laser irradiation

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ABSTRACT

This work reports an investigation of the surface modifications induced by irradiation with nanosecond laser pulses of ultraviolet and visible wavelengths on crosslinked hydrophilic co-polymeric materials, which have been functionalized with 1-vinylimidazole as a co-monomer. A comparison is made between hydrogels differing in the base co-monomer (N,N-dimethylaminoethyl methacrylate and N-[3-(dimethylamino)propyl] methacrylamide) and in hydration state (both swollen and dried states). Formation of craters is the dominant morphological change observed by ablation in the visible at 532 nm, whereas additional, less aggressive surface modifications, chiefly microfoams and roughness, are developed in the ultraviolet at 266 nm. At both irradiation wavelengths, threshold values of the incident laser fluence for the observation of the various surface modifications are determined under single-pulse laser irradiation conditions. It is shown that multiple-pulse irradiation at 266 nm with a limited number of laser shots can be used alternatively for generating a regular microfoam layer at the surface of dried hydrogels based on N,N-dimethylaminoethyl methacrylate. The observations are rationalized on the basis of currently accepted mechanisms for laser-induced polymer surface modification, with a significant contribution of the laser foaming mechanism. Prospective applications of the laser-foamed hydrogel matrices in biomolecule immobilization are suggested.

1. Introduction

The laser-assisted modification of polymeric materials using nanosecond (ns) laser pulses can be currently carried out with high precision and specificity [1,2]. Laser ablation, i.e., the massive removal of polymeric material is the most prevalent result from ns laser-matter interactions at fluences well above the threshold for surface modification. Precise laser processing usually requires the use of ultraviolet (UV) laser wavelengths in order to avoid thermal effects degrading the quality of the modified surface morphologies, as arising from the use of visible (Vis) and infrared (IR) wavelengths [1,3]. Since 2005, a distinct phenomenon, so-called "laser foaming", has been reported to occur in self-standing films of polymers and biopolymers obtained by casting procedures [4,5]. In laser foaming, the absorption of a single UV laser pulse of ns duration produces a layer of foamy material featuring bubbles or pores of micro- to nanometric size at the surface of the films. From a practical point of view, such porous morphologies, having high surface areas, find widespread technological applications such as the fabrication of artificial biocompatible extracellular matrices or scaffolds for culture and growth of biological tissue [6,7]. From a fundamental viewpoint, the foaming process unveils a higher level of specificity in the underlying mechanism whereby the laser energy deposited on the film surface ultimately leads to a morphological modification, as compared to regular laser ablation [5].

In general, the mechanism governing the laser foaming of polymers is determined by the laser wavelength, the physical condition of the substrate and its water content [8]. Modeling of the laser foaming process shows up that it is relevant for moderately absorbing polymers, with absorption coefficients $\alpha < 3000\,cm^{-1}$ [5]. In such cases, photon absorption from a ns laser pulse at the polymer surface may generate a pressure wave, the tensile part of which is, in

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turn, capable of triggering a cavitation and bubbling phenomenon leading to formation of a foam layer. This model proved suitable to account for the foaming characteristics induced by different laser irradiation wavelengths, from UV to IR, on a variety of natural and synthetic polymers from renewable resources [4–6,8–10]. As the matrices of such polymers were prepared by polymer solution casting and further solvent evaporation, without the use of crosslinking agents, they typically had a random association at the molecular level. In the case of collagen, it was demonstrated that UV laser light was capable of inducing conformational changes in the irradiated films, mainly as a result of breaking of the hydrogen bond network and loss of water molecules, which maintain the ordered structure [11]. In few studies on crosslinked gelatin films, the investigations were only limited to dried matrices [8,9]. Significantly so far, there is no research on laser-induced foaming on hydrophilic co-polymeric matrices.

Hydrogels are three-dimensional polymer networks with a unique ability to retain a large amount of water in their swollen state because of the hydrophilic nature of their functional groups [12]. In order to use hydrogels as scaffolds for tissue engineering, their various properties, including porosity and microarchitecture, need to be controlled [13]. In this context, the laser-induced foaming can be used as a post-synthesis technique to increase surface microporosity, and then, diffusion and transport through hydrogels. The present article reports a study of the morphology arising from surface modifications of functionalized hydrogels, as a result of ns pulsed laser irradiation with UV and Vis radiation (266 and 532 nm, respectively). The hydrogels of interest are constituted by N,N-dimethylaminoethyl methacrylate (DMAEMT) and N-[3-(dimethylamino)propyl] methacrylamide (DMAPMD) as monovinyl monomers, 1-vinylimidazole (VI) as a co-monomer, and N,N′-methylenebis(acrylamide) (BIS) as a crosslinking agent. The choice was made on the basis of a recent work in which the synthesis and physicochemical characterization of such crosslinked hydrophilic co-polymers with different proportions of VI was reported [14]. Among them, products containing 20% of VI, designated as MT and MD, were selected because of their largest swelling/resistance ratio in relation to the total materials produced.

Here, the main goal was to find the experimental conditions for the development of surface morphologies, other than regular ablation craters, with emphasis on the generation of a microfoam layer on the surface of the selected hydrogels, in both swollen and dried states. The formation of craters was the dominant morphological change observed by ablation at 532 nm (Vis), whereas additional, less aggressive surface modifications, chiefly microfoams and roughness, were developed at 266 nm (UV). At both irradiation wavelengths, threshold values of the incident laser fluence for the observation of the various surface modifications were determined under single-pulse laser irradiation conditions. The development of surface microfoams on dried MT samples was studied in additional, multiple-pulse experiments at 266 nm with a limited number of laser shots, which allowed a comparison with the foam properties arising from single-pulse irradiation at the foaming threshold fluence.

The observation of ns laser-induced foaming upon UV laser irradiation of functionalized hydrophilic co-polymers is relevant considering the capability of the imidazole group (into VI) to act as a ligand to coordinate a number of transition metal ions eventually dissolved in the swelling water, which in turn can serve as specific sites for the complexation of biomolecules within the hydrogel network [14]. Because such surface-modified morphologies feature micrometric pores or cavities, laser foaming can thus be envisaged as a prospective, post-synthesis strategy to increase the ability of relevant hydrogels for biomolecule immobilization.

2. Materials and methods

2.1. Reagents and hydrogel synthesis

The following chemicals were used as purchased: DMAEMT (Sigma); DMAPMD (Aldrich); VI (Aldrich); BIS (Sigma); ammonium persulphate (APS, Anedra); and N,N,N′,N′-tetramethylethylenediamine (TEMED; Anedra). The hydrogel synthesis procedure, via free-radical crosslinking polymerization, was recently reported [14]. Here, 4.48×10^{-3} mol of monovinyl monomers (DMAEMT or DMAPMD), 1.12×10^{-3} mol of co-monomer (VI) and 1.1×10^{-3} mol of crosslinker (BIS) were used. The polymerization reaction was allowed to occur in 5 cm in diameter plastic Petri plates featuring an air-exposed surface, where the defects arising from mold-release processes were absent. After one-day reaction at room temperature, the disk-shaped hydrogels were cut in squares with a ~1 cm side using a blade. Square samples were thoroughly washed with Milli-Q water and then dried for two days at 28 °C until constant weight. The final products were named *dr* (meaning for dried) MD and *dr* MT hereafter, to reflect both water content and molar co-monomer composition; upon swelling, the resulting matrices were renamed as *sw* (meaning for swollen) MD and *sw* MT.

The water strongly retained on *dr* MD and *dr* MT samples was 2.86 and 9.60 wt%, respectively. For *sw* MD and *sw* MT, the swelling indexes, as defined by the ratio between the mass of water-swollen hydrogel at equilibrium and the dry mass, were 14 and 30, respectively [14].

2.2. Laser irradiation

Laser irradiation of *dr* and *sw* samples of MD and MT was performed in air at room temperature by the second and fourth harmonics (532 and 266 nm, respectively) of a Q-switched Nd:YAG laser (Big Sky Laser-Quantel CFR 400, 6 ns FWHM). In the case of *sw* samples, the water from the surfaces was removed prior to laser irradiation by wiping with tissue paper. Single laser pulses were isolated manually from the output of the laser working at a repetition rate of 2 Hz. The laser output was steered using a quartz prism on the hydrogel samples, which had been placed horizontally on a two-dimensional micrometric translation stage and focused by a plano-convex lens (Thorlabs, quartz, 10 cm focal length) onto the sample surface at normal incidence.

The cross-section of the laser beam at the focal plane *A* was estimated from digital analysis of confocal laser microscope (CLM) images of the burned pattern on photosensitive papers. The CLM used was Olympus LEXT – OLS 4100. The laser output power was controlled in order to keep the incident laser pulse energy E_p at values below 20.0 and 3.5 mJ, at 532 and 266 nm, respectively, as measured by placing a Scientech 756 calorimetric detector right behind the focusing lens. The incident laser fluence ϕ, as applicable to single-pulse irradiation experiments, was estimated by the E_p to *A* ratio [15,16]. For multiple-pulse irradiation experiments on *dr* MT, recording the effect of an accumulative number $N = 2–5$ of laser pulses applied to the same area, ϕ was set to the value of the corresponding single-pulse threshold fluence for laser foaming (see below), to yield effective energy doses of ($N.\phi$).

For the sake of reproducibility, the laser irradiation under both single- and multiple-pulse conditions was carried out on two different samples in any given assay combining type and state of hydrogel and laser wavelength.

2.3. Confocal laser microscopy and scanning electron microscopy

The morphology of the irradiated areas of *dr* samples was characterized using the CLM and a scanning electron microscope (SEM;