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Technical Paper

A study of laser surface modification of polymers: A comparison in air and water

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ABSTRACT

Laser surface modification is a technique to modify polymer surfaces for various applications. In our earlier work [Physics Procedia, 83:211–217, 2016], we showed that when the laser surface modification process was carried out in water instead of air, the obtained surface characteristics were remarkably different, which led to a significant improvement in the metal deposition characteristics using electroless plating. In this work, we try to explain the underlying fundamental mechanisms that contribute to this improvement in surface characteristics through concurrent experimental and modeling research. The observed images of laser modified surfaces suggest that a hemispherical hump is formed in the case of water at lower laser fluences that breakup with an increase in fluence. Such a behavior was not observed when the process was carried out in air. We explain this phenomenon by simulating the temperature profiles in the polymer during the laser heating process in air and water. The results suggest that subsurface heating effects occur when the process is carried out in water. We further argue that this phenomenon is mainly responsible for the formation of the complex structure that was observed in our previous work.

1. Introduction

Due to the smooth surface characteristics of polymers, surface modification is an important process that enables them for applications in electronic and biomedical industry. Laser surface modification is an efficient technique to modify the surfaces of polymers due to its speed and precision. Moreover, laser surface modification is area selective, which does not involve use of masks as is the case with plasma or chemical etching.

In the literature, several researchers have carried out surface modification of polymers to improve surface adhesion, wettability, hydrophilicity, and surface chemical properties. Hiraoka and Sendova [1] produced periodic structures of sub-micrometer size on polymers using Nd:YAG laser of 266 nm wavelength that improved the polymer's wettability and hydrophilicity. Chan et al. [2] improved surface characteristics by modifying the chemical properties of polymer surfaces using a pulsed UV laser. Applying laser surface modification in order to improve polymer's adhesive properties for subsequent metallization was reported by several researchers using different types of lasers [3–6]. Laser surface modification of polymers has also been widely used in biomedical applications to improve biocompatibility and to enhance cellular growth [7–10].

In our earlier paper [11] on laser surface modification of polymers for subsequent electroless plating, we observed a remarkable improvement in surface characteristics suitable for electroless plating when the process was carried out in water instead of air. The thickness of deposited material was at least 4 times greater for surfaces processed in water as compared to those produced in air. The surface characteristics observed by SEM images were also substantially different. While a crater was generated in the presence of air, laser surface modification in water resulted in the formation of a complex structure with a high degree of porosity. The paper focuses on electroless deposition characteristics for surface modification under the two different media; however, the reason for the generation of distinct surface characteristics has not been explained. In order to generate optimal surfaces for superior metallization characteristics, it is essential to understand the fundamental mechanisms that contribute to different surface characteristics under different media.

In this paper, we attempt to explain the underlying fundamental mechanisms during laser surface modification of polymers that generates distinct surface characteristics in air and water. This is achieved by a synergistic study using experiments and modeling. The paper focuses only on laser wavelengths at which laser–polymer interaction is purely photo-thermal in nature. The

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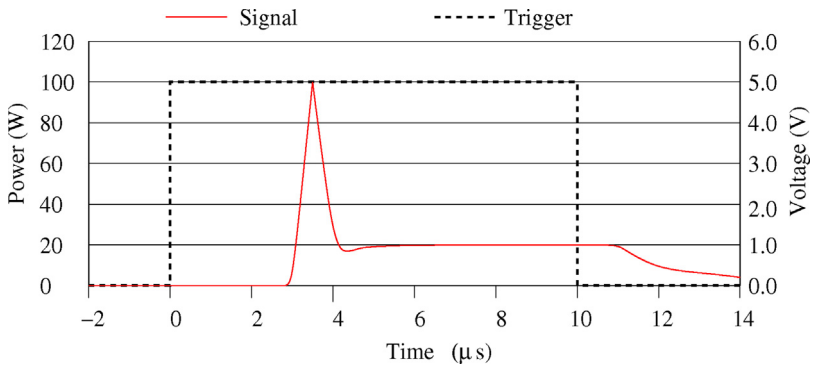

Fig. 1. Pulse characteristics of the laser used in experiments.

photo-chemical interaction that occurs mainly in the UV range has been ignored in this study as it is seen as an unwanted phenomenon in surface modification of polymers for subsequent electroless plating as it causes chemical degradation of the surface. Single-pulse experiments were carried out in air and water over a range of laser fluences and the surface characteristics were observed using a microscope. In addition, a model of laser heating of polymers in air and water for a single pulse was developed in this work using the finite difference method.

A description of the laser set-up and characterization techniques used in this work are presented in Section 2. Section 3 presents the model of the laser heating process in air and water. In Section 4, the experimental and simulation results are discussed and the underlying fundamental mechanisms that occur during the process are explained. Section 5 summarizes the conclusions of this work.

2. Experiments

The laser surface modification experiments were carried out on a polycarbonate substrate, which was doped with carbon microparticles to enhance the laser absorptivity. This is a commonly used method to impart colors to polymers or to enhance their optical absorptivity [12]. A high power fiber laser system with a wavelength of 1070 nm, pulse duration of 50 μs, and a beam diameter of 98.6 μm, was used to carry out the experiments. The pulse characteristics for a typical pulse of t_p = 10 μs and peak power of 100 W are shown in Fig. 1. The pulse rises sharply between 3 and 4 μs and falls to 20 % of the peak value at around 4 μs. Subsequently, the power remains almost a constant up to 11 μs, and gradually decays to nearly 4% in the next 2 μs.

The single-pulse experiments were performed in air and water over a range of laser intensities. In the case of water, the height of the water level was about 2–3 mm above the polymer surface. The images of the modified surfaces were captured using Alicona InfiniteFocus, which is a 3D micro coordinate measurement and surface roughness measurement device. Depending on the size of the laser generated spot, different values of magnification were chosen. The magnifications used were 20×, 50×, and 100×, which have a vertical mean resolution of 50 nm, 20 nm, and 10 nm, respectively. In addition, SEM was used to capture the top-view of the laser modified surfaces. The polymer surface was coated with a 20 nm carbon coating to facilitate SEM imaging of polycarbonate.

3. Modeling

The laser–polymer interaction with an infrared laser radiation is predominantly photo-thermal in nature and the photo-chemical decomposition can be ignored. In order to understand the laser heating process of polymers in air and water, a heat transfer model is presented in this study. The laser heating in water is modeled considering two different phases – polymer and water (see Fig. 2), in which the polymer heating occurs due to laser radiation and the water phase heating occurs due to heat transfer between the heated polymer and the ambient water. This is a consequence of water being transparent to light with a wavelength of 1070 nm, and therefore it does not absorb any laser radiation. In the case of air, modeling is carried out considering a single phase system comprising of only the polymer phase with a convective boundary at the top surface (see Fig. 2). Since air is a poor conductor, heat transfer due to conduction can be ignored.

Photothermal heating by laser radiation can be described using the heat conduction equation with the absorbed radiation represented by a volumetric heat source [13]:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + S, \tag{1}$$

where ρ, c_p, k and T represent density, specific heat, thermal conductivity and temperature, respectively. The heat source term is represented by S. In air, the heat source term can be written as:

$$S = (1 - R)\alpha I(x), \tag{2}$$

where α and R represents absorptivity and reflectivity, respectively. The intensity, $I(x)$ varies along the depth according to the Beer-Lambert's law:

$$I(x) = I_0 \exp(-\alpha x), \tag{3}$$

where I_0 is the laser intensity at the surface.

In the case of air, Eq. (1) is solved by imposing the following boundary conditions:

$$-k\frac{\partial T}{\partial x}|_{x=0} = h_a(T_s - T_0), \tag{4a}$$

$$T|_{x=L} = T_0, \tag{4b}$$

where h_a is the heat transfer coefficient of air, T_s is the surface temperature of the polymer, T_0 is the ambient temperature and L is the length of the target simulated. The value of L is chosen such that the boundary condition in Eq. (4b) is satisfied.

In the case of water, coupled heat transfer equations are solved for both polymer and water. The equations are coupled with a common interfacial temperature between the two phases. For the polymer phase, the same equation (Eq. (1)) is used to describe the laser heating with a modification in the heat source term (Eq. (2)) to account for reflection at the water surface (exposed to air), given by:

$$S = (1 - R_w)(1 - R)\alpha I(x), \tag{5}$$

where R_w is the reflectivity at the water surface, which is calculated as 0.04 using Fresnel equations [14]. Simultaneously, the heat