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Laser microfabrication of long thin holes on biodegradable polymer in vacuum for preventing clogginess and its application to blood collection

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Abstract

The present paper investigates the excimer laser microfabrication of long thin holes on biodegradable polymer material (polylactic acid, referred to herein as PLA). The fabrication was carried out on several kinds of polymers in the atmosphere. In the case of PLA, a phenomenon was observed after fabrication whereby the inside of the hole is clogged at several points by ablated material and residual gas. Analysis of chemical components of the ablated products was performed using a gas chromatography–mass spectrometer (GC/MS). They are proved to be intermediate products of ester compound and lactide, and their oxides, which indicates that the clogging phenomenon is partially caused by the hydrolysis reaction based on the biodegradable characteristics of PLA. The fabrication was carried out in vacuum and nitrogen gas. The clogging tendency was eliminated in vacuum, whereas it was not eliminated in nitrogen gas, which indicates that the ablated residues are evaporated by lowering the ambient pressure below their vapor pressure, proving the effectiveness of the fabrication in vacuum for preventing the clogginess. The effect of existence of oxygen in the ambient atmosphere on the laser fabrication rate was also investigated, proving that auto-oxidation reactions urge the decomposition of polymer. The fabricated long thin hole on PLA was applied to blood collection. © 2008 Elsevier B.V. All rights reserved.

Keywords: Excimer laser microfabrication; Biodegradable polymer; Polylactic acid (PLA); Effect of ambient pressure; Effect of oxygen; Blood collection

1. Introduction

In recent years, significant research has been conducted in the field of polymer MEMS. A UV excimer laser beam is effective for fabricating polymer materials. This fabrication method has the advantage of readily coping with changes in design for a fabricated object, compared with a conventional batch process using photomasks followed by dry or wet chemical etching. As polymer materials for the excimer laser fabrication, common industrial materials, such as PMMA [\[1\],](#page--1-0) polyimide, SU-8 (epoxy based photoresist) [\[2\],](#page--1-0) Parylene [\[3\],](#page--1-0) and polycarbonate [\[4\],](#page--1-0) are used, and their fabrication results have been reported. By contrast, biodegradable polymers have come to be used for medical purposes. However, there appear to be few reports on the excimer laser fabrication on them. The author has reported the basic performance of laser fabrication of trench [\[5\]](#page--1-0) and hole [\[6\]](#page--1-0) on a microneedle made of biodegradable polymer material (polylactic acid, referred to herein as PLA). In this report, the characteristics of laser microfabrication on PLA material are further investigated compared to other polymer materials. Especially, the clogging phenomenon of a long thin hole, which is specific to PLA material, is reported and its preventing method is proposed [\[7\].](#page--1-0)

The remainder of this paper is organized as follows. In the next section the fabrication results on several kinds of polymers in the atmosphere are reported, thereby the effect of existence of benzene rings in the chemical formula on the high fabrication rate is investigated. In Section [3, t](#page--1-0)he clogginess inside the hole of PLA material after the fabrication is reported. Analysis of chemical components of the ablated products is performed using a gas chromatography-mass spectrometer (GC/MS). In Section [4](#page--1-0) the fabrication results in vacuum and nitrogen gas are reported, showing the effectiveness of lowering the ambient pressure for preventing the clogginess. Finally the blood collection using the fabricated long thin hole on PLA is demonstrated.

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Fig. 1. Optical images of holes in polymer sheets machined by excimer laser beam in the atmosphere.

Fig. 2. Relationship between pulse shot number and fabrication depth on polymer sheets.

2. Laser microfabrication of polymer materials in atmosphere

2.1. Laser machining tool

A laser machine tool (MARUBUN Corp., OPTEL PRO) that emits a KrF laser beam having a wavelength of 248 nm is employed. The pulse length is 10 ns, and a computer program can be used to set the repetition rate up to 500 Hz, in 1-Hz intervals. The energy per pulse can be set up to 20 mJ, in 0.1-mJ intervals. The object sample is placed on a stage, which can travel up to 100 mm with resolution of 1 μ m in both the *x* and *y* directions. This stage is moved by a stepping motor, which is controlled synchronously for laser firing by a computer program.

2.2. Hole fabrication in polymer materials

PLA, polymethylmethacrylate (PMMA), nylon, polydimethylsiloxane (PDMS), Parylene, polystyrene (PS), polycarbonate (PC), and epoxy are adopted as polymer sample materials. Thin holes, $10 \mu m$ in diameter, were fabricated by a pulsed excimer laser beam on sheets of these materials at atmospheric pressure, i.e., in air. The conditions of laser machining are set as follows: the laser beam diameter is $10 \mu m$, the repetition rate is 5 Hz, the energy per pulse is 10 mJ, and the total pulse shot number is 500. To facilitate the observation of the

Fig. 3. Energy absorption of benzene ring for UV wave.

shape of cross-section, the experimental method is as follows: a hole is laser machined from the side surface of a transparent polymer sheet and is observed using an optical microscope from the top surface of the sheet. The fabrication results are shown in Fig. 1. The chemical formulae are also shown in insets of this figure.

Looking at this result, it is proven that the fabrication rate for the polymers having benzene rings in the chemical formulae is larger than those for the polymers not having them. The relationship between pulse shot number and fabrication depth is investigated. The results are shown in Fig. 2. From this figure, the trends of resultant curves are classified into two groups according to their possession of benzene rings in the chemical formulae. These facts are explained by benzene ring's characteristic of efficiently absorbing energy of UV waves. It is well-known that the absorption peak of benzene ring lies in a wavelength of 254 nm, which is close to the wavelength of KrF laser beam used in this research, i.e., 248 nm. Benzene ring resonates at the frequency of the applied UV wave, and it easily absorbs the energy and transmits the energy, as schematically shown in Fig. 3. The energy is transmitted to a chemical bond having comparatively low bond energy, where the break of bond occurs.

In the case of the polymer with benzene rings, most of the energy is consumed in photochemically breaking the chemical bonds of the material in the laser spot before the energy is conducted and consumed in thermally breaking bonds outside the laser spot (see [Fig. 4\(a](#page--1-0))), because the energy is absorbed with high efficiency. Whereas in the case of the polymer without benzene ring, the energy is conducted and consumed in thermally breaking bonds outside the laser spot (see [Fig. 4\(b](#page--1-0))).

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