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Surface modification of bisphenol A polycarbonate using an ultraviolet laser with high-speed, direct-writing technology

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ABSTRACT

The direct-writing surface modification of black bisphenol A polycarbonate (BAPC) was achieved at high laser scanning speeds of 600–1000 $mm\cdot s^{-1}$ using a 355 nm-wavelength, all-solid state, Q-switched, high-average power, nanosecond-pulse width laser. Compared with the widely reported surface modification technologies (e.g., femtosecond laser irradiation and excimer laser irradiation), this modification was low-cost, efficient, flexible, and with great industrialization potential. During the modification, it was found that laser fluence and pulse width were able to significantly affect the water contact angle, wetting behavior, microstructure, roughness, and chemical composition of the surface. When the applied laser fluences were low (i.e., less than the critical fluence of the ultraviolet laser direct-writing surface modification on the BAPC material), the water contact angle tended to decrease, the hydrophilicity was slightly improved, the relative content of the oxygen-containing groups (e.g., C–O and COO^-) increased, the microstructure and roughness only showed a slight change, and the wetting behavior was consistent with Wenzel's law. On the other hand, when the applied laser fluences were high, the water contact angle increased, the hydrophilicity decreased, and the relative content of the oxygen-containing groups also increased. Here, a porous microstructure with periodical V-type grooves was generated and the roughness obviously increased. In this case, the wetting behavior could be explained by the Cassie–Baxter model, i.e., the microstructure and roughness change played a deciding role. It was possible that different laser parameters resulted in different material deformations and removal processes, thereby resulting in different surface chemical compositions, microstructures, roughnesses, and wetting properties.

1. Introduction

The surface properties of a material are important features [1–3]. These properties play a critical role in the practical applications of the material and are primarily affected by the surface microstructure, surface roughness, surface chemical composition, ambient temperature, and so on [4–6].

The thermoplastic polymer bisphenol A polycarbonate (BAPC, chemical formula: $[OC_6H_4C(CH_3)_2C_6H_4OCO]_n$) has been used as an important engineering plastic because of its low cost, good thermostability, excellent optical transparence, excellent mechanical properties, and high electrical insulation. However, because of its low surface energy and high chemical stability, it has a poor surface adsorbability and poor adhesion to other films and coatings. Therefore, integration and fabrication of region-selective metallic patterns onto BAPC surfaces become difficult [7–9], which severely limits its direct applications in advanced fields such as microelectronics, micro/nano fluidic system, microelectromechanical systems (MEMS), and lab on a chip [10–12]. Therefore, to overcome these disadvantages, it is necessary to modify the BAPC surface and improve its surface properties [13].

Compared with other surface modification technologies, laser direct-writing/irradiation modification is more promising [14]. Many researchers have used femtosecond pulse infrared (IR)/visible lasers, nano/microsecond pulse Nd:YAG lasers (1064 nm wavelength), or ultraviolet (UV) (157–351 nm) excimer lasers as the modification light source [1,4,5,15–21]. Because femtosecond laser pulses can have extraordinarily high peak powers in extremely short pulse durations [21], excimer lasers can yield higher single photon energies (than that of IR/visible wavelength laser) [1], or nano/microsecond pulse Nd:YAG lasers can result in the photo-pyrolysis effect, it reveals that the laser modifications can alter the wettability, adsorbability, chemical composition, and microstructure of some polymer material surfaces. However, so far, this technology has primarily been used for static laser pulse irradiation. In addition, femtosecond lasers are expensive and require expensive maintenance; excimer lasers need toxic halogen gas and nano/microsecond pulse Nd:YAG laser modifications produce a larger and inevitable thermal-affected zone.

Over the last 10 years, with the rapid development of laser technology, high-powered diode-pumped solid state (DPSS) UV lasers have become reliable. This technology adopts Q-switched technology and

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has an output wavelength of 355 nm (i.e., the third harmonic of a Nd:YVO_4 laser), pulse widths ranging from 10 ns to several tens of nanoseconds, a high electro-optical conversion efficiency, low cost, convenient maintenance, small volume, good beam quality, and stable output power. Therefore, DPSS lasers have been widely used in the fields of cutting, drilling, electronic packaging, and so on [22,23]. If nanosecond pulse UV lasers with higher single photon energies are used to modify the surface of polymer materials, the process will be low cost and efficient. Therefore, this surface modification technology has a significant industrialization potential. Nevertheless, so far, the research on this topic has remained limited.

In this paper, we reported that the direct-writing surface modifications of BAPC were achieved at high scanning speeds of 600–1000 $mm \cdot s^{-1}$ and using a low-cost, high-efficiency, 355-nm wavelength, all-solid state, Q-switched, nanosecond-pulse width Nd:YVO_4 laser. We investigated the microstructure on the BAPC surface after the modification and measured the water contact angles. The chemical composition of the BAPC surface before and after the laser modification was analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform IR (FT-IR) spectroscopy, respectively. We explored the mechanism of the effect of the UV laser modification on the BAPC surface wetting behavior.

2. Materials and methods

2.1. BAPC sample preparation

We purchased black BAPC boards of 1 mm thick from Jiangsu Dimai Plastic Co., Ltd. (Suzhou, Jiangsu, China) and cut them into appropriate sizes. Next, the boards were ultrasonically washed in distilled water and in ethanol for 10 min at room temperature, respectively. Finally, the boards were dried for use.

2.2. UV laser direct-writing surface modification equipment and process

In this research, a UV laser direct-writing surface modification equipment was applied. It was purchased from Wuhan New R&D laser Co., Ltd. (Wuhan, Hubei, China) and included the following main units: (1) a controlling and monitoring system, (2) a nanosecond pulse UV laser (Nd:YVO_4 laser, 355 nm wavelength, TEM_{00} mode, and Gaussian beam), (3) an optical system, (4) a vacuum unit, and (5) a three-dimensional (3D) workstation (460 mm (x) × 310 mm (y) × 100 mm (z)).

The pulse frequency (i.e., pulse repetition frequency) of the laser was adjustable from 20 kHz to 100 kHz and the corresponding pulse width ranged from 10 ns to 60 ns; these quantities had an approximately linear relationship. At a pulse frequency of 30 kHz, the maximum average laser power was measured to be 9.5 W. The maximal pulse energy was about 320 μJ when the laser was operated at a pulse frequency of 30 kHz. The depth of focus (DOF) was 114 μm and the spot size of the focused beam was 10 μm in diameter.

During the UV laser direct-writing modification, the laser beam was directed perpendicularly to a BAPC sample in the range of the DOF. A surface area of 40 × 40 mm^2 was horizontally raster scanned through the digital galvanometer scanner (0–3000 $mm \cdot s^{-1}$ scanning speed) at a shifting pitch of 35 μm and at a scanning speed of 800 $mm \cdot s^{-1}$, unless specified otherwise. Thus, a larger-area modification (i.e., larger than 40 × 40 mm^2) could be achieved by mosaicking many 40 × 40 mm^2 areas and using the displacement of the x and y axes of the workstation. We performed the modification at room temperature and in air.

After the laser direct-writing surface modification, the samples were ultrasonically cleaned for 10 min with a SCQ-K001 air ultrasonic cleaning machine (Shanghai Shengyan Chaoshengbo Instrument Co., Ltd., Shanghai, China), thereby removing the laser ablation debris from the sample surface.

2.3. Measurements and characterization

To quantify the surface wettability, the static water contact angles of sessile drops on the surface of the BAPC samples were measured at room temperature and in air using a SL200B contact angle meter (USA Kino Industry Co., Ltd, USA). The sessile drops were comprised of 2 μL redistilled water and were released onto the surface through a 500 μm diameter micro-liter syringe. For each sample, the measurements were performed at three different locations, and at each location, they were repeated twice. Then the results were averaged.

The surface microstructures were observed using scanning electron microscopy (SEM) (Quanta 200 scanning electron microscope, FEI Company, Holland) after surface metallization with gold. To quantify the surface microstructure change before and after the UV laser direct-writing modification, a KLA Tencor P-16+ surface probe profiler (KLA Tencor Corporation, USA) was used to measure the surface roughness (Ra, μm). During the measurement, the probe scanning length was set as 200 μm. For each specimen, the measurements were performed in two different directions, i.e., parallel and perpendicular to the raster scanning direction, and in each direction, the measurements were repeated three times. Then the results were averaged.

The surface elemental composition was analyzed with a VG Multilab 2000 X-ray photoelectron spectrometer (VG Instruments Corporation, UK) using a standard Al-K_α radiation ($h\nu = 1486.6$ eV) as the excitation source. The vacuum degree of analysis room was kept below 10^{-8} Pa. To acquire survey-scan or high-resolution XPS spectrum, the pass energy of 100 eV or 25 eV was applied, respectively.

FT-IR spectra were obtained on an FT-IR spectrophotometer (EQUINOX 55, Bruker Corporation, Germany) via the attenuated total reflectance (ATR) method.

3. Results and discussion

3.1. Effect of the UV laser fluence and pulse frequency on the water contact angle of the modified BAPC surface

The water contact angles on the BAPC surface modified with different UV laser fluences and pulse frequencies are listed in Table 1. Additionally, in order to more directly view their change trend, they are also displayed in Fig. 1. From Table 1 and Fig. 1, one can see that the UV laser fluence and pulse frequency were able to significantly affect the contact angle. Moreover, for different laser pulse frequencies (here, 30 kHz, 60 kHz, or 100 kHz), there existed a certain critical laser fluence (F_c, Fig. 1II, F_c = about 4.1 $J \cdot cm^{-2}$, about 3 $J \cdot cm^{-2}$, or about 1.2 $J \cdot cm^{-2}$, respectively) that was obviously different from the threshold fluence (usually from tens of $mJ \cdot cm^{-2}$ to hundreds of $mJ \cdot cm^{-2}$) of the UV laser ablation polymer materials [24].

When the applied laser fluences were less than or equal to F_c, the water contact angle tended to decrease (Fig. 1II), i.e., the hydrophilicity of the BAPC surface increased. However, when the applied laser fluences were larger than F_c, the water contact angle increased with increasing laser fluence. When the laser fluences were larger than about 11 $J \cdot cm^{-2}$ (30 kHz pulse frequency), about 6.5 $J \cdot cm^{-2}$ (60 kHz), or about 3 $J \cdot cm^{-2}$ (100 kHz), respectively, the water contact angle on the modified BAPC surface was larger than 90°. These findings indicated that the BAPC surface became hydrophobic. With a continuous increase of the laser fluence, the water contact angle showed a maximum value (Fig. 1I, i.e., about 129° (30 kHz), about 125° (60 kHz), or about 122° (100 kHz), respectively). Then, the water contact angle gradually decreased and tended toward a constant. Here, the BAPC surface was still hydrophobic.

Given conditions of an appropriate laser fluence and pulse frequency, the low-cost and efficient (800 $mm \cdot s^{-1}$) nanosecond pulse UV laser direct-writing modification was able to change the wettability (in particular, from hydrophilicity to hydrophobicity) of the BAPC surface. Although both excimer laser and femtosecond laser