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A low-cost, high-efficiency and high-flexibility surface modification technology for a black bisphenol A polycarbonate board

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ABSTRACT

In this paper, a low-cost, high-efficiency and high-flexibility surface modification technology for polymer materials was achieved at high laser scanning speeds (600–1000 mm s^{-1}) and using an all-solid state, Q-switched, high-average power, and nanosecond pulse ultraviolet (355 nm wavelength) laser. During the surface modification of a very important engineering plastic, i.e., black bisphenol A polycarbonate (BAPC) board, it was found that different laser parameters (e.g., laser fluence and pulse frequency) were able to result in different surface microstructures (e.g., many tiny protuberances or a porous microstructure with periodical V-type grooves). After the modification, although the total relative content of the oxygen-containing groups (e.g., C—O and COO^-) on the BAPC surface increased, however, the special microstructures played a deciding role in the surface properties (e.g., contact angle and surface energy) of the BAPC. The change trend of the water contact angle on the BAPC surface was with an obvious increase, that of the diiodomethane contact angle was with a most decrease, and that of the ethylene glycol contact angle was between the above two. It showed that the wetting properties of the three liquids on the modified BAPC surface were different. Basing on the measurements of the contact angles of the three liquids, and according to the Young equation and the Lifshitz van der Waals and Lewis acid–base theory, the BAPC surface energy after the modification was calculated. The results were that, in a broad range of laser fluences, pulse frequencies and scanning speeds, the surface energy had a significant increase (e.g., from the original of about 44 mJ m^{-2} to the maximum of about 70 mJ m^{-2}), and the higher the laser pulse frequency, the more significant the increase. This would be very advantageous to fabricate the high-quality micro-devices and micro-systems on the modified surface.

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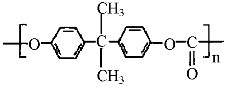
1. Introduction

The surface properties (e.g., surface wettability and surface energy) of a material are very important features for itself. Different kinds of materials usually have different surface properties, and, for the same kind of material, if it has different surface structures and states, it also has different surface properties. In other words, changing the surface structure and state of the material is able to change the surface properties. While the surface properties will play a very important part in the practical application of the material [1].

Thermoplastic polymer material, bisphenol A polycarbonate (i.e., BAPC, ), is a very important engineering plastic because of its low cost, excellent thermo-stability, good mechanical properties, and high electrical insulation. However, its low surface energy feature renders it a poor surface adsorption and adhesion capability to other films or coatings [2,3]. Thus, this greatly limits its direct applications in some high-tech fields, e.g., electronics, microelectronics, microfluidic system, microelectromechanical system (MEMS), lab on chip, and so on [4–6]. Therefore, in order to overcome these shortcomings, it is necessary to modify the BAPC surface and to improve the surface energy [7]. So far, many surface modification technologies including chemical modification, low-energy plasma modification, and laser irradiation/direct-writing modification have been widely used.

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Compared with other surface modification technologies, laser direct-writing modification has been the most promising and potential, because of its masklessness, feasibility to three-dimensional curved surface, region selection, and high flexibility [8]. Using femtosecond pulse infrared (IR)/visible laser, nano/microsecond pulse 1064 nm-wavelength Nd:YAG laser, or ultraviolet (UV)-wavelength (157–351 nm) excimer laser as the modification light source, many researchers had reported their research results from this technology [9–17]. Because femtosecond laser pulses can offer extraordinarily high peak powers in extremely short pulse durations [18], excimer laser can offer higher single photon energy (vs. IR/visible wavelength photon energy) [11], or nano/microsecond pulse Nd:YAG laser can result in photo–pyrolysis effect, it shows that this technology is able to change the wettability, adsorbability, chemical composition, and microstructure of some materials surface. However, so far, this technology is usually achieved in the condition of low laser scanning speeds (from several mm s^{-1} to several dozens mm s^{-1}) or static laser pulse irradiation. In addition, femtosecond laser is expensive and needs high maintenance cost, excimer laser needs toxic halogen gas, and nano/microsecond pulse Nd:YAG laser modification brings on larger and inevitable thermal-affected zone.

During the last ten years, with the rapid development of laser technology, high-average power DPSS (i.e., diode pumped solid state) UV laser has become a reliable laser apparatus. It adopts Q-switched technology, and has the output wavelength of 355 nm (i.e., the third harmonic of Nd:YAG laser), the pulse widths of from ten nanoseconds to several dozens nanoseconds, a high electro-optical conversion efficiency, a low cost, a convenient maintenance, a small volume, a good beam quality, and a stable output power. It has been widely used in the fields of cutting, drilling, electronic packaging, and so on [19,20]. If the nanosecond pulse UV laser with higher single photon energy, higher average power, and lower thermal effect is used to modify the surface of polymer materials, it will be low-cost, and can acquire high-speed and high-light/space-resolution modification effect. Thus, this surface modification technology will have a great industrialization potential. However, the previous research on this is still very limited.

In this paper, using a low-cost, 355 nm-wavelength, all-solid state, Q-switched, high-average power, and nanosecond-pulse width UV laser, the surface modification on a black BAPC board was achieved. The microstructure, chemical composition, and contact angle of the BAPC surface before and after the modification were analyzed and measured. At last, according to the Lifshitz van der Waals and Lewis acid–base theory, the BAPC surface energy after the laser modification was calculated and evaluated.

2. Experimental

2.1. Materials and sample preparation

Chemicals including ethylene glycol and methylene iodide were of analytical reagent (AR)-grade, obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used as received without further purification.

The black BAPC boards with the thickness of 1 mm, obtained from Jiangsu Dimai plastic Co., Ltd. (Suzhou, China), were cut into the samples with appropriate sizes. Then, they were ultrasonically washed in distilled water and in ethanol for 10 min, respectively. Next, they were dried for use.

2.2. Nanosecond pulse UV Laser surface modification equipment and process

In this research, a nanosecond pulse UV laser 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 $Nd:YVO_4$ laser (DPSS type, 355 nm wavelength, TEM_{00} mode, and Gaussian beam), (3) an optical system, (4) a vacuum unit, and (5) a x–y–z three-dimensional workstation (460 mm × 310 mm × 100 mm).

The pulse frequency (i.e., pulse repetition frequency) of the laser was adjustable from 20 kHz to 100 kHz, the corresponding pulse width was from 10 ns to 60 ns, and they had an approximately linear relationship. At 30 kHz pulse frequency, 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 30 kHz pulse frequency. The depth of focus (DOF) was 114 μm and the lightspot size of focused beam was 10 μm in diameter.

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

2.3. Measurements and characterization

At room temperature and in air, the static contact angles of the BAPC samples surface were measured using a SL200B contact angle meter (USA Kino Industry Co., Ltd). Three liquids including water, ethylene glycol, and methylene iodide were selected. For each specimen, the contact angles were separately measured three times and then averaged. Five specimens were tested separately.

The surface microstructures were observed using a Quanta 200 scanning electron microscope, the surface elemental compositions were analyzed by a VG Multilab2000 X-ray photoelectron spectrometer, and Fourier transform infrared spectra were obtained on an Equinox 55 Fourier transform infrared spectrophotometer by attenuated total reflection (ATR) method.

3. Results and discussion

3.1. Microstructure of the BAPC surface after the nanosecond pulse UV laser modification

Experiments showed that laser fluence, pulse frequency, and scanning speed were the three main parameters affecting the microstructure of the modified BAPC surface. Fig. 1 was the scanning electron microscopy (SEM) images of the BAPC surface modified with different UV laser fluences and pulse frequencies, respectively. It could be seen that, when the laser fluences applied were low, many tiny protuberances appeared on the BAPC surface (Fig. 1(a–c)). Whereas, when the laser fluences applied were high, a porous microstructure with periodical V-type grooves was generated on the surface (Fig. 1(d–h)). Furthermore, in the case of lower laser frequencies, the V-type groove was not very continuous and many small dents appeared (Fig. 1(f and i)). The reason was that different laser pulse frequencies resulted in different lightspot coupling ratio.

If the laser fluences applied were too low, the surface microstructure change would not be found; On the other hand, if the laser fluences applied were too high, the BAPC surface would be badly carbonized and damaged, and this would be beyond the field of laser surface modification.

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