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Enhancing surface energy of polycarbonate by atmospheric pressure plasma jet

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ABSTRACT

A plasma jet system with floating electrode configuration was setup to treat polycarbonate (PC) surface. Enhancement in energy surface and the duration of the effect by plasma treatment were characterized by water contact angles (WCA) of water droplets on the PC surface. Morphological changes of the surface were examined by AFM. The results show that after 60 seconds of treatment by plasma, the WCA decreased from 74° to 38° and the PC surface was not physically damaged. The average change of WCA by plasma treatment is 40% and remained at 20% after 14 days with a treatment time greater than 180 seconds.

Introduction

Non-thermal plasma technology is applied in many different fields such as water purification, bio-sterilization, and decontamination [1]. It can also be applied in surface treatment of different materials such as carbon nanotubes, carbon fiber composites, polymers [2-4] to enhance their surface energy for stronger binding with other coating layers. Thanks to its high temperature resistance, toughness, optically transparent [5], polycarbonate (PC) was used in many different areas such as medical equipment, food, optic [6]. However, the PC surface is quite soft to resist scratches [7] and its surface energy is low. Therefore, it is difficult to coat another material onto PC surface to enhance its scratch-resistance property. In this work, we mainly study and optimize the effect of increasing energy surface of the PC by plasma treatment. This approach will allow enhance binding of different coating layers on the surface of PC.

Experimental and methods

Materials

Polycarbonate (PC) with 50mm thickness was purchased from Xilong company. It was cut out with dimensions of 10mm × 100mm and divided into cells of size 10mm × 10mm to treat in different experiments. Ethanol (>95%) was used to clean the PC surface before experiments.

Set up of plasma jet system

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The plasma jet system setup was shown in Figure 1. A schematic with two main components including: (1) a high voltage, high frequency power supply and (2) a plasma emitter.

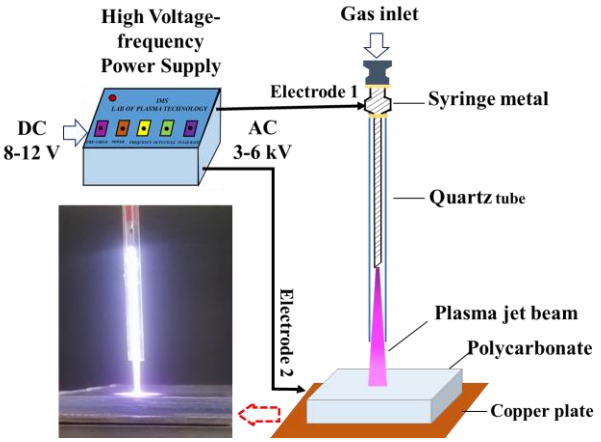

Figure 1: Schematic setup of the plasma jet system for treatment of the polycarbonate surface and a photo during plasma treatment process

The power source used a direct input of 8 to 12 V and could be transformed to a voltage of 3 – 6 kV with a frequency of 35kHz. The plasma emitter was composed of a capillary gas tube, a nozzle and a gas inlet. The capillary was made by a 70 mm – length quartz tube with an internal diameter of 5 mm and an external diameter of 7 mm. The nozzle was made by a pointed-tip metallic syringe in 55-mm length and 1.5-mm diameter. Argon gas was flown inside a nozzle from a mass flow control (MFC) with flow rate of 1 L/min. In floating electrode configuration, the first electrode is placed in a metal syringe. The second electrode is placed into a copper plate with an area of 50mm × 70mm. The PC samples were placed onto the copper plate at 1 cm away from the nozzle.

Contact angle measurement

Contact angle measurement is widely used in demonstrating surface energy changes on the surface of materials treated by various methods, including plasma.[8] The smaller contact angle translates to the stronger energy surface potential. 10 µL distilled water was dropped on to PC's surface and a macro camera used to measure water contact angle (WCA). After capturing, the WCA images were processed with ImageJ software to derive precisely the contact angle.

Surface characterization by AFM

Atomic Force Microscope (AFM) (model: Pico Scan 2500) was used to determine the surface images of the untreated and plasma-treated PC. An AFM tip (model TAP190AI-G) was used to analyze images with resonant frequency at 190 kHz and a force constant of 48 N/m. The scanning area was chosen to be 10µm × 10µm.

Results and discussion

Enhancement of PC energy surface by plasma treatment

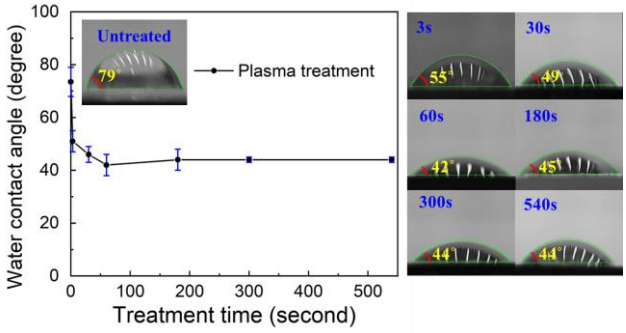

Figure 2: Left: dependence of water contact angle on PC surface on plasma treatment time. Right: photos of the water droplets on PC surface in various plasma treatment duration

Polycarbonate samples was treated by plasma jet system with 3s, 30s, 60s, 180s, 300s and 540s duration (Figure 2). We divided all PC samples into 7 sets (each sample were repeated 5 times): right after (0), after 1, 2, 3, 7, 10 and 14 days of plasma treatment (Figure 3). After treating, samples were stored in a black box and at room temperature. Untreated samples have a contact angle of 74°. This value is also agreed with previous measurement [9]. After 3 seconds of treatment, the contact angle was reduced from 74° to 51°. The WCA of 60s-treated samples were lowest at 42° ± 4°. For 180s, 300s and 540s plasma-treated samples, the contact angles saturated to nearly 44°.

Duration of the surface energy enhancement effect of various plasma treatment time

The effect of plasma on the PC surface was calculated by Equation 1:

$$H = \frac{WCA_{untreated} - WCA_{treated}}{WCA_{untreated}} x100\% \quad (1)$$

The stronger energy surface induced by plasma treatment leads to the higher percentage of change in

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WCA. Hence, monitoring the percentage of change in WCA as a function of time (0 to 14 days) allow studying the lasting effect of plasma treatment. After 14 days, the percentage of change in WCA of the 3s, 30s and 60s-treated samples decreased quickly from ~40% to less than 10%. While the 180s, 300s, 540s-treated samples showed the same trend in decreasing linearly to about 20% after 7 days treated and remained at this value for the next 7 days (Figure 3).

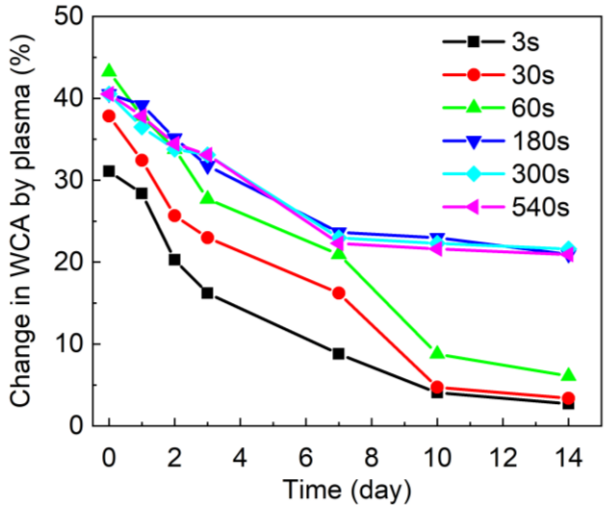

Figure 3: Lasting effect at various plasma treatment time (3s, 30s, 60s, 180s, 300s, 540s) on PC surface from immediately (0 day) to 14 days

Duration of 60 seconds is the most optimal time to obtain the highest surface energy right after plasma treatment but treatment time of 180 seconds led to the longer lasting effect. By this long-lasting effect, it is very convenient to coat other layers of different materials such as anti-fog, anti-scratching, anti-fingerprint, anti-bacteria, anti-glare on PC surface for various applications.

Moreover, the lasting effect of plasma treatment in Figure 3 revealed that plasma caused both the chemical (surface energy – chemical bonding) and physical (cracks owing to the bombardment of electrons and ions in the plasma beam on PC surface) changes on PC surface. Probably, only surface energy change is induced by plasma treatment in the first 3 to 60 seconds and the change decreased linearly in 7 days to zero due to reaction with water vapor or oxygen agents. Since all plasma treatment time of 180s, 300s and 540s lead to longer lasting effect of changing the WCA (Figure 3), they should induce both chemical and physical change of PC surface. While plasma treatment time greater than 180 seconds leads to both chemical and physical change of PC surface and the physical change remain at 20% of the effect even after 14 days.

Morphological changes of PC surface by plasma treatment

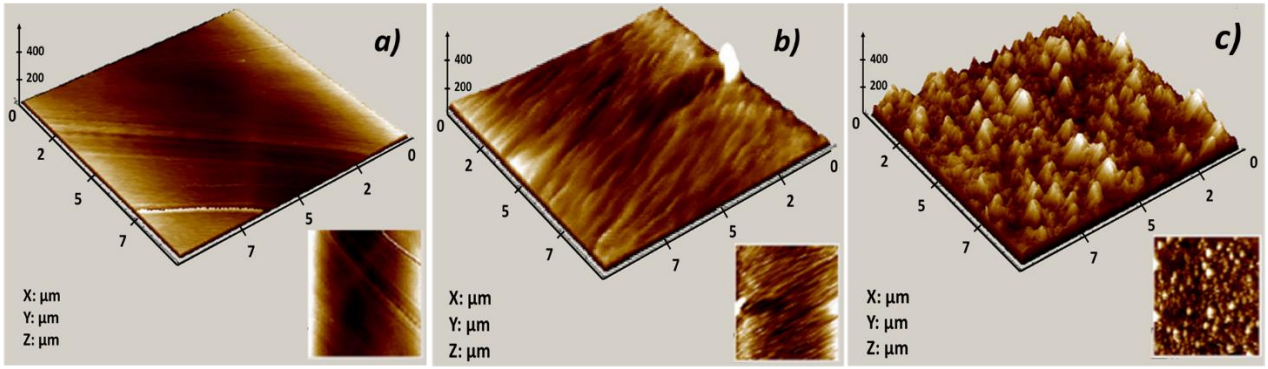

Figure 4: AFM images of PC surface: a) untreated; b) 60s and c) 540s plasma treatment time

The changing of PC surface by the plasma jet system is clearly demonstrated through AFM images shown in Figure 4. The photo of untreated (Fig.4.a) and 60s-treated sample (Fig.4.b) showed that PC surface was not damaged during the first 60 seconds of plasma. Roughness surface of 540s-treated samples (Fig.4.c) clearly showed cracks – the physical damage of the plasma beam – after 540 seconds interaction with the PC surface. The ratio of chemical bonds on the surface explains exactly the change in surface energy. The change between C-O, C-O=C, C=O; C-C/C-H bonds were found (specifically the O's ratio increased and the C's ratio decreased) when performing X-ray Photoelectron Spectroscopy (XPS) measurement on the PC surface before and after plasma treatment [10,11]. The main components of plasma beam include ions, electrons and UV radiation can split the polymer structure of the PC surface, causing oxygen to come in.

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The increasing of oxygen inside polar functional groups lead to enhancement of surface energy and surface hydrophilicity of the PC surface, which explains the decrease in contact angle after plasma treatment. However, if the plasma irradiation time is too long, it can lead to the process of changing the O:C ratio to be saturated, causing the contact angle of the PC to only decrease to a certain value (42° in our experiment).

Conclusion

We have successfully set up a plasma jet system with a floating electrode configuration to treat and study the changes in surface energy and the duration of the effect on polycarbonate. The PC samples were treated in 3s, 30s, 60s, 180s and 540s. The effect of plasma treatment was analyzed by water contact angles and AFM images. Accordingly, 60 seconds is the most optimal time to obtain the highest surface energy without physical damage right after plasma treatment. Plasma-induced chemical change can cause the WCA to reduce quickly up to 40%, and then gradually restore to 100% in 14 days, while plasma-induced physical change, which is – only present in cases of plasma treatment time more than 60 second – can reduce the WCA up to 20% with long lasting effect.

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