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Effects of gas atmospheres on poly(lactic acid) film in acrylic acid plasma treatment

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ABSTRACT

Plasma polymerized acrylic acid (AA) coatings were deposited on poly(lactic acid) (PLA) films in various gas atmospheres during the pre-treatment of PLA and the deposition of AA, respectively. Therefore, this work was twofold: the argon pretreated PLA films followed by a deposition in argon were investigated against the mixture of argon and oxygen pretreated ones under the same deposition conditions; the plasma deposition of AA operating in different atmospheres (argon, oxygen and nitrogen) was employed to modify the pretreated PLA in oxygen. Chemical and physical changes on the plasma-treated surfaces were examined using contact angle, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM) and attenuated total reflection infrared (ATR-FTIR) analysis. The results showed that the discharge gas can have a significant influence on the chemical composition of the PLA surfaces: oxygen plasmas introduced oxygen-containing groups in company with surface etching in pre-treatment and deposition, while argon discharges was able to achieve much better hydrophilic behavior and high retention ratio of poly(acrylic acid) (PAA) coating before and after washing in water.

1. Introduction

Poly(lactic acid) (PLA) is a well-known biodegradable aliphatic polymer and has been previously used for several biomedical applications [1,2]. Owing to its excellent properties in processibility, degradability and compostability, PLA has been widely applied in industry, especially in food packaging [3–5]. However, some drawbacks have inhibited its further application in immobilizing bioactive molecular field, e.g. poor surface hydrophilicity and chemical reactivity which should be altered to create functional groups for PLA surface [6–9]. Meanwhile, hydrophobicity and insufficient reactive side-chain groups on surface usually lead to low performances in antimicrobial active packaging whose surface is demanded to carry the coating layer of bioactive antimicrobial agent [10,11]. Therefore, surface modification by cold plasmas is usually necessary to achieve satisfactory surface properties without altering the bulk performances [12–16]. Plasma-polymerization deposition of acrylic acid (AA) has been an effective pre-treatment approach for the modification of covalent immobilization of biomolecules [17,18]. Furthermore, PAA deposition on various polymers through plasma has been extensively reported in the literature, for instance, polypropylene [19], polyethylene [20], poly(ethylene terephthalate) [21], and polystyrene [22]. These works have extensively investigated the effects of ratio of mixture composition, reactor geometry and treating pressure on film surface behaviors. Recently, cold plasmas have been used to modify the surface properties of biodegradable polymers, such as polylactic acid (PLA) [23–26]. However, few articles have reported the effects of gas types on film surface state in AA polymerization, which can play a critical role under certain conditions. For instance, it has been reported that gas atmosphere effects on surface properties in terms of weight loss, surface wettability, surface chemical composition and electrical resistance in surface layer [27–32]. In addition, noble and reactive gases improved organic reagents polymerization and deposition [33–35], and the coating stability became higher simultaneously [36].

The present work explored the potential effects of various gas atmospheres at the pre-treatment of PLA and the deposition of AA on surface modification of PLA, respectively. Therefore, this work was twofold: the argon pretreated PLA films followed by a deposition in argon were investigated against the oxygen pretreated ones under the same deposition conditions; the plasma deposition of AA operating in three different atmospheres (argon, oxygen and nitrogen) was employed to modify the pretreated PLA in oxygen. The differences in surface modifications among the different discharges were investigated by contact angle measurements, XPS, FE-SEM and ATR-FTIR. Contact angle measurements were used to evaluate the wettability of the untreated and plasma-treated PLA films, while the chemical composition of the films were studied

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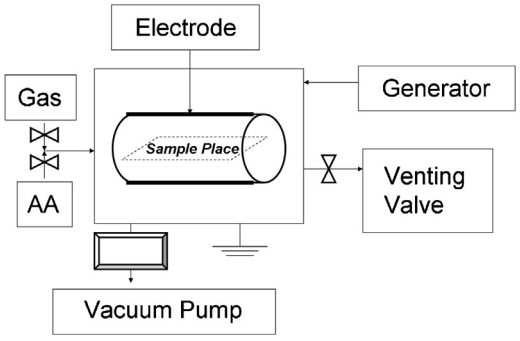

Fig. 1. Schematic illustration of plasma system utilized in this experiment.

using XPS and ATR-FTIR, respectively; FE-SEM was employed to capture the surface morphology of untreated and plasma-treated PLA surfaces.

2. Experiments

2.1. Materials

PLA foils with a thickness of 200 μm were produced by PLA2002D (NatureWorks, U.S.A.) pellets as raw material with casting extruded internally and were not subjected to any pre-treatment step before plasma modification. AA, from Sigma–Aldrich (Italy), was purified by vacuum distillation before usage.

2.2. Surface modifying process

The cold plasma system used for the surface modification was Pico 1.1.2 semi-automatic system from Diener Electronic GmbH. Its structure was schematically shown in Fig. 1. Before plasma treatments, the pristine PLA film was first hold by an aluminum rectangular frame which was then inserted into the working chamber (length = 320 mm and diameter = 150 mm). Owing to this sample holder, the two sides of the PLA film can be treated simultaneously. Next, the reactor was pumped to the desired pressure using a rotary vane pump, followed by filling the chamber with the discharge gas at the certain rate. During the plasma discharge, the gas flowing rate was kept constant, and the frequency of plasma discharge was 40 kHz with the pressure ranged from 10 to 100 Pa throughout the present study. In present work, we first activated the PLA surface using plasma in argon or the mixed oxygen and argon before the deposition of AA in three different atmospheres (argon, oxygen and nitrogen) in order to investigate the effects of gas atmospheres. During the pretreatment, the chamber was vacuumized until the pressure lower than 10 Pa for 5 min, and then the needle valve of gas was open to let the gas (Ar or O_2) into the reactor. In the following deposition process, the gas and acrylic acid were introduced by the valve and they were contained by gas cylinder and a bubbler bottle containing the purified monomer, respectively. In such conditions, the flow rates of both the acrylic acid and gas were fixed to about 15 sccm. In this work, three different feed gases are used for the plasma deposition treatments: oxygen, nitrogen and argon. The detailed parameters for pretreatment and deposition were listed in Table 1.

In the following analyses, these treated samples were divided into two parts: one portion was further washed by distilled water, denoted as group WPLA-X; the other one was exempt from water washing, referred to group PLA-X. The meaning of the sample's acronym, X, included the gas information used in pre-treatment (O represented used both Ar and O_2) and depositing course (Ar, O_2 and N_2).

2.3. Surface characterization

The surface contact angles (SCA) were measured at room temperature by Theta Optical Tensiometer (KSV Instruments Ltd.) immediately after plasma treatment. The deionized water droplet with 5.0 μl was placed on the films surface. There was one water droplet for each tested sample. The obtained contact angle values were the average of three samples treated under the same condition.

The morphology was characterized by FE-SEM (model JEOL JSM 6700F), and the surface of PLA film was coated with chromium high concentration solution before test.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) for film-surface-composite measurements was performed on the Bruker Tensor 27 spectrometer equipped with a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector and a variable angle multi-reflection ATR accessory (ATRMaxII-Pike). The spectrometer was continuously purged with dry, carbon dioxide gas. For each sample, 32 scans with a resolution of 2 cm^{-1} were taken for spectrum integration in the wavenumber ranging from 600 to 4000 cm^{-1}.

The surface chemical composition of the plasma-treated polymer films was investigated by Physical Electronics PHI 5800 (USA) multi-technique ESCA X-ray photoelectron spectroscopy (XPS), equipped with a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV) with a power of 250 W. The pressure of the chamber kept under the ultra high vacuum condition maintained at 2.67×10^{-8} Pa. The survey and narrow spectra were acquired by passing energy of 187.85 and 58.7 eV, respectively. Binding energies were calibrated with respect to C1s at 285.0 eV with accuracy within ±0.2 eV.

The optical properties of untreated and treated films were tested by UV–vis spectrophotometer (Varian Cary-500 UV–vis–NIR spectrophotometer) in the range of 200–800 nm. The spectra were chosen in 400–700 nm to record the transparency of each sample; three points were randomly selected in the test for each sample.

3. Results and discussion

3.1. Surface wettability analyses

Although plasma modification can improve surface wettability, it was found that the surface treatment was not permanent, and to the plasma-treating materials, the aging behavior had remarkable effects on the material properties [37–39]. In this work, the aging behavior was examined by the contact angle measurements. Before treatment, the PLA water contact angle was equal to approximately 79 ± 1°. After the surface modification, the PLA samples were tested in air at room temperature, and the measurement for each sample was in the continual time ranging from 10 to 100 s with the interval of 10 s.

Fig. 2 shows the evolution of the contact angles of PLA films as a function of elapsing time after plasma deposition in argon, oxygen and nitrogen following pretreatments in argon or oxygen and argon. It was clearly observed in Fig. 2 that the contact angles of the PLA films without water washing (PLA-X) significantly decreased from the original value, and no obvious aging effect was present. Among the samples in group PLA-X, the lowest contact angle was obtained for PLA-O-Ar (pretreatment in the mixture of argon and oxygen and deposition in the argon plasma) in contrast to PLA-O (both pretreatment and deposition in the mixture of argon and