Surface Wettability Improvement of Heat Curing Acrylic Resin by Direct Current (DC) Non-thermal Atmospheric Pressure Plasma

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Abstract: Ar/O₂/N₂ cold plasma was employed to treat the surface of heat-curing acrylic resin, and the wettability changes were evaluated. After plasma treatment, the contact angle reduced significantly. XPS results indicated that the C/O ratio reduced and a new hydrophilic group C–OH was generated on the surface of acrylic resin.

Key words: heat-curing acrylic resin, cold plasma, contact angle, XPS

1. Introduction

Heat-curing acrylic resin is a widely material used in prosthetic dentistry, particularly in complete denture bases and partial denture bases due to its suitable color and acceptable price. However, in clinical, the poor surface hydrophilicity of heat-curing acrylic resin may result in bad retention. It has been clearly suggested that the improvement of surface wettability can increase the retention power of denture[1, 2].

Actually, there is a high incidence of denture-induced stomatitis in denture wearers, approximately 11% to 67% of healthy denture wearers[3]. Candida albicans is a potential causative agent in denture-induced stomatitis[4]. As the adherence of C. albicans cells to denture surfaces is now recognized as an important step in colonization and pathogenesis of infection, inhibiting the early adherence process could represent a significant advance in the prevention of stomatitis[5]. Previously, the adherence of C. albicans to biomaterial surfaces is affected by their relative hydrophobicities. With regard to the hydrophobic interaction, Klotz et al observed a nearly linear relationship between the number of C. albicans adhering per unit area and the hydrophobicity of polymers[6].

Plasma is a complex mixture composed of ions, energetic free radicals, atoms, electrons, and molecules generated by gas discharge. Atmospheric pressure cold plasma have recently attracted much interest in biomedicine owing to their applications in bacteria inactivation[8-10], tooth whitening[7, 11], blood coagulation[12] and cancer therapy[13]. In recent years, researchers have reported that plasma can be used as an economical and effective technology in surface modification in the biomedical field[14-17]. Duske et al found that plasma treatment supported spreading of osteoblastic cells on the titanium discs[16]. It has been confirmed in previous research that cold plasma treatment is able to increase shear bond strength between heat-curing acrylic resin and self-curing acrylic resin[17].

Thus, the purpose of this study was to investigate whether surface modification by atmospheric pressure cold plasma treatment would improve the surface wettability of denture base acrylic resin, and explore its possible mechanisms.
2. Materials and Methods

2.1 Sample fabrication

Two different sizes of heat-curing acrylic resin specimens (specimens A: d=12 mm, h=1 mm, n=54; specimens B: 3 mm×3 mm×1 mm, n=2) were fabricated according to the manufacturer's instructions (Vertex, Netherlands). Specimens A were used for contact angle measurements. They were polished with 600 grit silicon carbide paper to achieve smooth surfaces prior to further treatment. Specimens B were used for XPS measurement. Each specimen was kept in distilled water at 37 °C for 48 h to release residual monomer before experiments.

2.2 Plasma treatment

Fig. 1 (a) Photograph of sample treated by the non-thermal atmospheric pressure plasma jet (b) Schematic diagram of the experimental arrangement.

![Image](https://via.placeholder.com/150)

The plasma device used in this paper was consisted of two coaxial copper cylinders as electrodes, which were separated by a dielectric layer with a thickness of around 0.5 mm, as shown schematically in Fig. 1(b). The inner electrode was powered by a dc high-voltage power supply (negatively biased) while the outer electrode was grounded for safety considerations. The nozzle opening of the plasma device had a diameter of around 0.8 mm. Ar/O\textsubscript{2}/N\textsubscript{2} (88%Ar+2%O\textsubscript{2}+10%N\textsubscript{2}) was used as the working gas and was forced through the inner electrode. The high-voltage electrode was completely embedded in the device and powered by a DC power supply (Matsusada AU5R120)[7, 9]. The sustaining voltage of the plasma microjet (PMJ) was in the range of range of 400-600 V, with an operating current of 30 mA, and the gas flow rate was 5 L/min. Fig. 1(a) shows a picture of the PMJ working in Ar/O\textsubscript{2}/N\textsubscript{2} with a typical length of the plasma plume of about 10 mm. The temperature of the end of plasma flame was about 38 °C[18].

2.3 Contact angle measurement

The surface wettability of all test samples was evaluated by measuring water contact angle. An automated goniometer system (OCA 15 plus; Dataphysics Instruments, Germany) in combination with SCA-20 software was used to analyze and calculate specific contact angles. Ultrapure water was used as test liquid. An image of the water droplet on the surface of the specimen was taken immediately after the contact. A single droplet (2.0 μl) was assessed with two measures (right and left contact angle) for each droplet on each sample. The values before and after plasma treatment were measured.

2.4 XPS measurement

The surface elemental composition was monitored by X-ray photoelectron spectroscopy (Axis Ultra, Kratos, England). The operating power was 225 W (working voltage—15 kV, emission current—15 mA), the minimum energy resolution is 0.48 eV; the minimum sample analysis area was 15 μm. XPS peak position was calibrated using the C1s peak at 284.8 eV to compensate for residual charging effects. Data for percent elemental composition, elemental ratios, and peak fit analysis parameters were calculated using software supplied by Kratos with the XPS. Samples were measured and analyzed before and after plasma treatment.

2.5 OES analysis

A conventional fiber optics spectrometer (AVANTES AvaSpec-2048-8) was employed to record the emissions arising from the major excited plasma species in the 200–825 nm range.
The output power was 24 W, and the operating temperature was 60 °C. The distance between the exit nozzle of the plasma device and the receive port was 5 mm. The recorded spectra were transferred to a computer for further analysis.

2.6 Statistical analysis

The differences in the water contact angle changes among the groups were analyzed with Pair-Sample T Test and one-way ANOVA in Origin8.0.

3. Results

3.1 Contact angle results

The contact angle results are shown in Fig. 2. After plasma treatment, the contact angle reduced significantly ($P<0.001$), especially in the first 1 minute. There are no significant differences ($P>0.05$) among the contact angle of 2, 4, 6, 8, 10 mins treatment. Generally, after the Ar/O$_2$/N$_2$ plasma treatment, the water contact angle reduced, which means the wettability improved remarkably.

Fig. 2 Changes of contact angle after non-thermal atmospheric pressure plasma treatment (n=9)

3.2 XPS results

XPS analysis has been applied to analyze the surface chemical modifications. The XPS scan spectra of control group and the treatment group is presented in Fig. 3. The ratio of C/O decreased from 4.32 (Fig. 3a) to 1.86 (Fig. 3b). Fig. 4 shows the carbon peak fitting in the XPS narrow scan spectra of the test samples. Peak fitting can be used to help identify the grafted components. Spectra were fitted to elucidate the change of chemical bonds. The C 1s spectra of untreated sample could be resolved into three components, as shown in Fig. 4a. The peaks near 284.8 eV.
Fig. 4 Carbon peak fitting of the XPS narrow scan spectra (a) control sample; (b) sample after Ar/O₂/N₂ plasma treatment.

286.1 eV and 288.5 eV are assigned to the functional groups of C-C-H, O-CH₃ and O-C=O on the surface of acrylic resin[19-21]. After plasma treatment, the structures of the C 1s spectra are affected (Fig. 4b). It is observed that compared with the untreated acrylic resin, the intensity of the C 1s spectra around 286.5 eV show a significant increase, which probably attributed to the new functional group: C-OH bond [22]. The C-OH bond was not discovered in the untreated acrylic resin (Fig. 5). In fact, researchers have realized that the C-OH bond can offer improved wettability [23], and it brings a reasonable explanation why plasma is able to implement surface modification of acrylic resin.

\[ \begin{align*}
\text{O} & \quad \text{C} \quad \text{C} \\
& \quad \text{C} \quad \text{H} \quad \text{H} \\
& \quad \text{C} \quad \text{O} \quad \text{H} \\
& \quad \text{O} 
\end{align*} \]

Fig. 5 Molecular formula of the untreated acrylic resin

3.3 OES result

The OES result of the Ar/O₂/N₂ plasma jet was showed in Fig. 6. There are plenty of active components in plasma, such as O (777 nm), •OH (304-309 nm) and N₂ (372 nm).

Fig. 6 Optical emission spectrum (OES) of Ar/O₂/N₂ plasma jet

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References