Polymerization of acrylic acid using atmospheric pressure DBD plasma jet

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Abstract. In this paper polymerization of acrylic acid was performed using non thermal atmospheric pressure plasma jet technology. The goal of this study is to deposit organic functional coatings for biomedical applications using a low cost and rapid growth rate plasma jet technique. The monomer solution of acrylic acid was vaporized and then fed into the argon plasma for coating. The discharge was powered using a laboratory made power supply operating with sinusoidal voltage signals at a frequency of 10 kHz. The optical emission spectra were collected in order to get insight into the plasma chemistry during deposition process. The coatings were characterized using Fourier transform infrared spectroscopy, atomic force microscopy and growth rates analysis. A high retention of carboxylic functional groups of the monomer was observed at the surface deposited using this low power technique.

1. Introduction
Recently the use of atmospheric pressure non thermal plasmas for coating of organic materials has gained much attention due to their low cost and low temperature operation [1-4]. Atmospheric pressure cold plasmas can be generated using different type of sources: pulsed DC, inductively coupled plasma, radio frequency AC and dielectric barrier discharge (DBD) [5-7]. Among these the dielectric barrier discharges are the most suitable sources for the generation of non thermal plasmas at atmospheric pressure due to their cold, robust and low frequency operation. Plasma jet devices based on DBD can produce non thermal atmospheric pressure plasma which is low cost, safe to use and extremely stable for longer operation.

Acrylic acid (AA) is a commonly used precursor for plasma polymerization as it is easily available and low cost material. Thin films of the plasma polymerized acrylic acid (PPAA) have been a dynamic research for applications in biomedical, biosensors and micro fluidics [8-9]. Plasma deposition of acrylic acid using low pressure vacuum systems has been extensively studied [10-11]. However, low pressure coating systems are associated with practical limitations due to the expensive vacuum technology and their low deposition rates. The development of new technology based on atmospheric pressure deposition has gained much interest due to its flexibility in terms of low cost and ease of operation. Few studies have been made that address the use of atmospheric pressure plasma for polymerization of acrylic acid [12-13].
### Table 1. Deposition conditions for plasma polymerization of acrylic acid

| Processing parameters | Quantity     |
|-----------------------|--------------|
| Ar gas flow rate (sccm) | 500          |
| Monomer flow rate (sccm) | 10 - 20     |
| Monomer temperature (°C) | 80          |
| Deposition time (min)   | 5 - 15       |
| Plasma power (W)        | 25           |

This paper presents the deposition and characterization of polyacrylic acid films using an atmospheric pressure DBD plasma jet. The aim of the current investigation is to study the potential of this specific DBD plasma technique for deposition of organic functional films. The properties of the deposited surfaces were studied using atomic force microscopy, Fourier transform infrared spectroscopy and growth rate analysis. The paper is structured as follows. The experimental methods are described in the section 2. The results with discussion are presented in the section 3 and the conclusions of this study are drawn in section 4.

### 2. Experimental methods

#### 2.1. Polymerization setup

The experimental setup used for atmospheric pressure plasma deposition is shown in Figure 1. A 99.9% pure argon (Ar) gas was used for plasma generation and to carry the monomer vapours in reactor. The setup consists of two mass flow controllers to control the flow rate of Ar gas. A custom made glass bubbler was heated at 80 °C for vaporizing the monomer solution. A low flow rate Ar gas was connected from the ground side of the reactor for measuring plasma power.

#### 2.2. Electrodes configuration for plasma jet

The DBD plasma jet was generated in a flask made from Pyrex glass (Figure 1). The high voltage (HV) electrode is a steel tube with inner diameter of 5 mm and outer diameter of 7 mm. The steel tub was fixed at the centre of the flask by inserting into a rubber bang at the top of the flask. The rubber bang seals the flask in order to create the vacuum. The steel tube serves as a HV electrode for plasma generation and also as an inlet for gas flow. The ground electrode, made of aluminium sheet, was placed underneath the flask. The bottom glass wall of the flask acts as a dielectric barrier for plasma generation. The distance from the lower end of the steel tube to the bottom of the flask was fixed to 2.5 cm in order to accommodate the substrate. A concentrated high voltage electric field that breaks down the gas in the flask is emitted from the lower end of the high voltage electrode. Plasma was produced in the form of a jet. The glass substrate was placed under the HV electrode in the flask before starting the polymerization process. In the next step the flask was evacuated to a pressure of 100 mTorr using a rotary pump. The discharge flask was then filled with Ar gas to atmospheric pressure. When the pressure in the flask is reached to atmospheric the high voltage electric field was applied for generating plasma in the flask. Finally a mixture of gas containing Ar and monomer vapours was introduced to Ar plasma for deposition.
Figure 1. Schematic diagram of the experimental setup used for plasma polymerization at atmospheric pressure. Photograph of DBD plasma jet generated in a Pyrex flask (bottom)

3. Results and discussion
Plasma deposition was performed using a laboratory made DBD jet plasma configuration as described in section 2.2. A circular area with an average diameter of 1.5 cm was deposited on the substrate. The commercially available glass microslides were used as a substrate for deposition. They were cleaned using methanol and deionized (D.I.) water. The substrates were pre-treated with Ar discharge for 2 minutes. The deposition conditions for plasma polymerization are summarized in Table 1. The monomer flow rate of 10 sccm, Ar gas flow rate of 500 sccm, deposition time of 10 minutes and plasma power of 25 W were optimized and kept constant throughout the observation until otherwise stated.

Figure 2. Typical voltage and current signals of plasma jet. Voltage $V_p = 8.4$ kV, current $I_p = 6$ mA
3.1 Electrical characterization of plasma
The electrical characterization of plasma was performed by measuring the applied high voltage and the resultant current. An oscilloscope, a high voltage probe and a current probe was used to perform the electrical characterization of the discharge. The characteristics current-voltage signals were recorded simultaneously on the oscilloscope and are shown in Figure 2. Typically the atmospheric pressure DBD plasmas operating in filamentary mode consist of a large number of current spikes appearing on each half cycle of voltage [14]. These current spikes are diminished in the case of glow discharge plasma and get the shape close to the sinusoidal waveform which corresponds to the capacitive current [15]. Also, the current signal is leading the voltage with a phase shift of $< 90^\circ$ (Figure 2) which characterizes the capacitive load. Hence, the DBD jet plasma used here for polymerization of acrylic acid operates in glow mode.

3.2. Plasma emission spectroscopy
The optical emission spectroscopy (OES) was used in order to get insight into the plasma chemistry during deposition process. The emission spectra were collected using a USB2000 spectrometer (Ocean Optics). The signals were recorded by placing the lens of fibre optic cable close to the plasma jet. Figs. 3a and 3b show the emission spectra of argon discharge before deposition and argon mixed with acrylic acid during deposition process respectively. The discharge was generated at a power of 25 W and a monomer flow rate of 10 sccm. The emission peaks were identified and assigned with reference to previous studies [16-17] and to the online data available from the National Institute of Standards and Technology (NIST) [18]. The spectrum of the Ar discharge shows the presence of OH (309 nm), N$_2$ band (310 nm - 440 nm) and Ar band (695 nm - 850 nm). The spectral lines intensities of pure Ar were decreased by introducing the monomer precursor into the plasma jet as shown in Figure 3b. The decrease in the emission intensities of Ar plasma by introducing monomer vapours is most probably due to the utilization of plasma energetic species (Ar metastables etc.) for dissociation of organic molecules. This reduction in Ar metastables is caused by the plasma quenching due to the additional reactions related to the increase of monomer content into the discharge volume. The peaks of NH at 337 nm, CN at 359 nm and CO at 457 nm appeared in the emission spectrum when the acrylic acid was mixed with Ar plasma in order to achieve deposition. Similar peaks of NH and CN have been reported by Tran et al. [19] during plasma deposition at atmospheric pressure. The presence of strong peaks corresponding to NH, CN and CO indicated that the monomers were fragmented during the plasma polymerization process. Moreover, the emission of the lines from hydroxyl (OH) radicals and N$_2$ indicates the presence of excessive air in open to atmosphere plasma jet.

Figure 3. Optical emission spectroscopy. (a) Ar plasma and (b) Ar plasma mixed with acrylic acid
3.3. FTIR spectroscopy
The chemical properties of the plasma polymerized acrylic acid films have been studied using Fourier transform infra red (FTIR) spectroscopy. The spectra were obtained by using FTIR spectrometer (Perkin Elmer USA) at a resolution of 4 cm$^{-1}$. Multiple scans (32) were performed and then averaged for each sample. Since the absorption depth of infrared beam is typically 1 μm the relatively thick samples were selected for FTIR analysis. Therefore, the samples for FTIR spectrum were prepared at a monomer flow rate of 20 sccm and deposition time of 10 minutes. Figure 4 shows the FTIR spectra of AA monomer and plasma polymerized acrylic acid. The comparison of the monomer spectrum with plasma polymers provide the evidence that the monomers have actually been polymerized in the plasma and are deposited on the glass substrate. The bands in the monomer spectra are well resolved compared to the broad bands obtained from the plasma polymers [20]. The spectral peaks were identified using data previously reported in the literature [12, 21, 22]. The spectrum of PPAA exhibits a dominant absorption band at 1720 cm$^{-1}$ which can be assigned to stretching vibration of the C=O group. The spectrum contains a very broad band ranging from 3600 cm$^{-1}$ to 2400 cm$^{-1}$ which can be assigned to the stretching vibrations of the hydroxyl group OH. A smaller peak at 2945 cm$^{-1}$ which can be attributed to stretching vibrations of the CH bond is also superimposed on a broad band of OH. At low wave numbers, two other significant bands appeared at 1200 cm$^{-1}$ and 1112 cm$^{-1}$ which can be assigned to the stretching vibrations of C-OH and C-O groups respectively [22]. Hence, a high retention of carboxylic functional groups of the monomer was observed at the surface deposited using this low power technique.

3.4. Coating morphology
The surface morphology of plasma polymerized acrylic acid films was observed using atomic force microscopy (AFM). The images of surface were recorded by adopting the tapping mode of AFM. The scans were performed by selecting an area of 5 μm$^2$ at the surface of the PPAA films. Figures 5a, 5b...
show 3D and 2D AFM images for PPAA surfaces respectively. AFM analyses showed that the surfaces deposited using jet plasma were continuous and free from pinholes. However, the average value of the surface roughness (20.5 nm) was found to be higher than the previous reports [20] according to which the films prepared using plasma enhanced chemical vapour deposition (PECVD) method are smooth with lower surface roughness. This roughness is an indication of the surface etching due to bombardment of energetic species at the substrate in the plasma jet. The continuity of the plasma coatings was further confirmed under an optical microscope using CCD camera (Figure 5c).

![AFM images of PPAA films](image)

**Figure 5.** Atomic force microscopy of the films, (a) 3D and (b) 2D images of the PPAA films. (c) CCD image under optical microscope with 10X resolution

### 3.5. Thickness and growth rate measurements

The film thickness was determined using step height method in atomic force microscopy (AFM). The microscope glass slides were masked during jet plasma deposition in order to measure the film thickness. Figure 6a shows the film thickness as a function of deposition time at two different flow rates of 10 sccm and 20 sccm of the monomers. A linear relationship was observed for a polymerization time of 15 minutes. The plasma power was kept constant at 25 W during this analysis. The average growth rates were calculated from the slope of the linear curves in Figure 6a. The average growth rates of 69.3 nm min⁻¹ and 150.8 nm min⁻¹ were found for monomer flow rates of 10 sccm and 20 sccm respectively. The increase in monomer concentration increases the number of monomer molecules in the plasma and hence, enhances the rate of reactive species reaching to the substrate.
Thus, the film growth rate in plasma polymerization process depends mainly on the plasma processing conditions. Figure 6b shows the step height for measuring thickness of the PPAA film.

![Graph showing film thickness as a function of deposition time for two different concentrations of monomers.](image)

**Figure 6.** (a) Thickness of the films as a function of deposition time for two different concentrations of monomers. (b) The image shows the step height for measuring film thickness through AFM

4. **Conclusions**
The plasma polymerized acrylic acid films deposited using an atmospheric pressure plasma jet are presented in this paper. The FTIR spectrum indicated a high retention of carboxylic functional groups at the surface when the films were deposited at a discharge power of 25 W, monomer flow rate of 20 sccm and a treatment time of 10 minutes. AFM results showed that the films were continuous and free from pin holes. An average growth rate of 150.8 nm min\(^{-1}\) was obtained for a monomer flow rate of 20 sccm. Hence, the films with promising characteristics can be obtained by the technique of atmospheric pressure DBD plasma jet.

5. **Acknowledgment**
M.B. would like to acknowledge the Higher Education Commission of Pakistan for financial support through its TTS program.

6. **References**
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