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Exploring the polymerization of bioactive nano-cones on the inner surface of an organic tube by an atmospheric pressure pulsed micro-plasma jet

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ABSTRACT

In this paper, the successful deposition of acrylic acid polymer (PAA) nano-cones on the inner surface of a polyvinyl chloride (PVC) tube using an atmospheric pressure pulsed plasma jet (APPJ) with acrylic acid (AA) monomer is presented. Optical emission spectroscopy (OES) measurements indicated that various reactive radicals, such as •OH and •O, existed in the plasma jet. Moreover, the pulsed current proportionally increased with the increase in the applied voltage. The strengthened stretching vibration of the carbonyl group (C═O) at 1700 cm^{-1}, shown in the ATR-FTIR spectra, clearly indicated that the PAA was deposited on the PVC surface. The maximum height of the PAA nano-cones deposited by this method ranged from 150 to 200 nm. FTIR and XPS results confirmed the enhanced exposure of the carboxyl groups on the modified PVC surface, which was considered highly beneficial for successfully immobilizing a high density of biomolecules. The XPS data showed that the carbon ratios of the C—OH/R and COOH/R groups increased from 7.03% and 2.6% to 18.69% and 6.81%, respectively (more than doubled) when an Ar/O_2 plasma with AA monomer was applied to treat the inner surface of the PVC tube. Moreover, the enhanced attachment density of MC3T3-E1 bone cells was observed on the PVC inner surface coated with PAA nano-cones.

1. Introduction

In the medical field, the autologous saphenous veins are widely considered to be the best choice for vascular prostheses, and their limited availability has shifted the focus to artificial vascular materials [1]. Successful clinical applications of the artificial vascular materials, however, would typically require extensive pretreatment of the prosthetic surface due to the fact that the vascular grafts have been shown to provide very poor adherence to the endothelial cells [2]. Recently, a critical area of interest for developing artificial vascular materials has emerged which focuses on coating bioactive materials on the inner surface of the organic tubes [1], whose inner diameters are generally in the range of 4–5 mm. Generally, the cellular adhesion strength is proportional to the surface energy, and it has been shown that the polymeric materials with increased surface roughness would provide significantly improved adhesion strength [3,4], especially when the polymeric materials surface are rich in the carboxylic or hydroxyl groups [5–7]. Various wet chemical treatment processes have been widely used to increase the polymer surface energy and roughness, but such methods are of significant environmental concerns.

Recently, many works indicate that the plasma deposition of composite materials is a highly promising method for such a task because of its simplicity, all-dry processing, and one-step processing nature [7]. Because of these advantages, various plasma processes have been widely investigated for inner surface modification of polymer tubes [8,9]. For example, Cho et al. [1] modified the inner surface of a PTFE tube with H_2 and O_2 plasmas, and the treated PTFE tube showed a higher bioactivity for attaching smooth muscle cells. Lackner et al. [8] used a pulsed discharge to modify the inner surface of several different types of polymer tubes. However, certain drawbacks limited their applications, i.e., such plasmas require vacuum systems and their operation can be quite cumbersome. Moreover, when the inner surfaces of microtubes need to

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be modified, it is very difficult to achieve satisfactory results using such vacuumed plasma systems.

Because of these concerns, the atmospheric pressure plasma jet (APPJ) has recently attracted considerable attention because of its ability to generate highly reactive chemical species at room temperature [10,11]. The APPJ has shown some potential applications in several areas, such as surface modification [12–16], sterilization [17–19], and decontamination [20,21]. In our previous work, we performed a number of studies on polymeric modification by APPJs, generated using an AC power supply, and successfully investigated the different discharge and polymerizing characteristics of Ar and He APPJs [22–25]. In one mode of operation, the APPJ can modulate the plasma formation by continuously alternating the plasma on-time (discharge) and off-time. Moreover, the pulsed plasma not only has high instantaneous power, which can increase the density and energy of ions and electrons, but also has the ability to homogenize the monomer density above the substrate surface during the off-time phases, which can improve the uniformity, and control the thickness, composition and structure distribution of the plasma-deposited film [26,27]. APPJ has been shown to conveniently tune the functional group density on the deposited film surface [28] and to change the hydrophobic/hydrophilic characteristics of the surface. For example, Onyshchenko et al. [29] studied the penetration characteristics of an argon APPJ plasma in LDPE tubes (with diameters in the range of 0.28–3.00 mm), and had demonstrated that the LDPE surface was transformed from hydrophobic to hydrophilic.

However, the aging defect of plasmatic treatment generated with inert gases with/without oxygen has posed a major challenge for the polymeric modification with APPJ system. It was therefore of great interest to look into the feasibility of combining the pulsed APPJ with organic monomer to circumvent the aging defect concern and potentially also tune the chemical groups, especially when the application such as coating bioactive film on the inner surface of micro-polymer tube was concerned. To the best of our knowledge, however, open reports on pulsed APPJ polymerization at room temperature, especially regarding the treatment of the inner surface of tube materials, are scarce.

Therefore, in this paper, a high voltage pulsed power supply was used to generate a micro-plasma jet with He/O_2 gas or Ar/O_2 gas at room temperature, and the inner surfaces of polyvinyl chloride (PVC) tubes were modified with AA monomer by the pulsed APPJs. The pulsed He/O_2 and Ar/O_2 plasmas with acrylic acid monomer were used to explore the discharge and polymerizing characteristics of the inner surface of the polymer tube. Additionally, the preliminary bioactive properties of the modified PVC tube were investigated using Fluorescence Microscopy to observe the cultured MC3T3-E1 bone cells.

2. Experimental

The micro-APPJ system used for medical-grade PVC tube modification (see Fig. 1) was similar to that reported in the previous work [24], except that in this work, the outer diameter of the jet nozzle was reduced to 4 mm, so that it could be fitted inside the PVC tubes with a length of 15 cm and an inner diameter of 4 mm. It should be noted that this work was mainly aimed at determining the feasibility, and consequently, instead of the vascular materials actually used in the medical field, the PVC tube was used as the modification target. The copper tube (length: 45 cm, inner diameter: 4 mm, outer diameter: 6 mm) centered in the quartz tube acted as one electrode, and the channel was used to inject the acrylic acid monomer to the jet center. The potassium chloride (KCl) electrolyte solution having a conductivity of 0.12 S cm^{-1} contained in the outside of the quartz tube functioned as the second electrode. Both electrodes were connected to a pulsed power that provides a

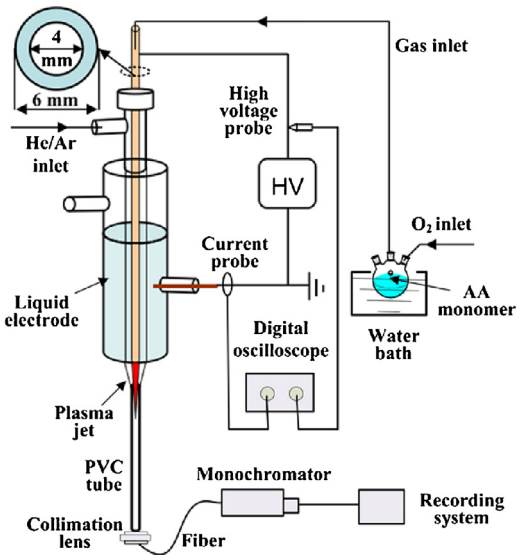

Fig. 1. Schematic illustration of the plasma jet system.

maximum peak voltage of 40 kV with adjustable frequencies ranging from 50 to 500 Hz. The AA monomer (Tianjin Kemiou Chemical Reagent Company, China) was placed in a separate flask, which was heated in a water bath. Then, the monomer vapor was transported to the plasma jet through the copper tube by the oxygen (O_2) gas. Applying such settings, the acrylic acid was then ionized by the He/O_2 or the Ar/O_2 plasma, and the PAA nano-cones were subsequently deposited on the inner surface of the PVC tubes. It should be noted that the He/O_2 or the Ar/O_2 plasma could increase the hydrophilic property of PVC tube, which in turn enhanced the binding intensity between the PAA and the inner surface of the PVC tube. The discharge voltage and current were monitored using a high voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021). The measured values were recorded with a digital oscilloscope (Tektronix TDS1012B). The optical emission spectrum from the discharge was obtained through a UV–vis optical emission spectrophotometer (Andor, SR-500i-A, USA) with a charge-coupled device, and an optical fiber probe with an inner diameter of 1 mm was connected to the incident slit of the monochromator. It should be noted that the APPJ light was focused by a collimation lens facing the jet outlet. The processing parameters are summarized in Table 1, and the flow rate of the AA monomer was estimated based on the weight change in the polymerization process.

The modified PVC tube was then dissected into small fragments, and the samples were flatted on the silicon wafer by applying the gum for the AFM and WCA measurements. The morphology of PVC inner surface was examined using AFM (XE-100E, Korea). All images were acquired in air using the tapping mode to prevent significant deterioration of the film surface, and the average diameter of nano-cones was determined by the software Image-Pro Plus 6.2 for 20 counts in AFM pictures. The surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) (Kratos,

Table 1
The plasma parameters for AA polymerization.

Parameter	Values
Input voltage (kV)	30
Pulsed width (μs)	12
He or Ar flow rate ($m^3\ h^{-1}$)	0.4
O_2 flow rate ($m^3\ h^{-1}$)	0.1
Depositing time (min)	20
Temperature of water bath (°C)	60
AA monomer flow rate ($g\ min^{-1}$)	0.2