



Surface functionalization of polytetrafluoroethylene substrate with hybrid processes comprising plasma treatment and chemical reactions

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ABSTRACT

Polytetrafluoroethylene (PTFE) exhibits excellent mechanical properties and chemical stability and has been widely used in medical fields for the preparation of implantable medical devices. However, the implantation of PTFE in living systems results in inflammation reactions and infections at the surface thus limits its long-term applications. For PTFE surface modification, we examined the effects of mussel-inspired polydopamine (PDA) coating and the further introduction of functional groups. During PDA coating, the plasma pretreatment on PTFE enhanced the stability of the PDA coating layer. Furthermore, the introduction of functional groups on the PDA layer was carried out using reactive functional groups for the photoinduced graft polymerization of methacrylate. For instance, 2-methacryloyloxyethyl phosphorylcholine (MPC) could be polymerized from the surface of the substrate. These chemical modifications were confirmed step by step using spectroscopes to obtain the hydrophilic surface of the poly(MPC)-modified PTFE. The protein adsorption behaviors on PTFE and poly(MPC)-modified PTFE were compared to understand biocompatibility characteristics of these substrates. The surface of PTFE was immediately covered with albumin and the contact between the substrate and the serum resulted in an increase in the fibrinogen composition with time. On the other hand, fewer proteins were adsorbed on the poly(MPC)-modified PTFE substrate. Thus, this modification procedure would serve as a strategy for safer alterations in PTFE surfaces to expand the life span of the PTFE-carrying medical devices in living systems.

1. Introduction

The favorable mechanical properties and chemical stability of polytetrafluoroethylene (PTFE) under biological conditions have encouraged its applications in various industrial fields, including biomedical applications in the form of medical devices. For instance, physically expanded PTFE has been used as artificial heart valves [1], vascular prostheses [2], and artificial ligaments [3]. Although PTFE substrates have been thought to be resistant to biological reactions once implanted into a living system [4], unexpected inflammation and infections are common [5,6]. The uncontrollable adsorption of proteins on the surface induces the adhesion of cells and bacteria on PTFE substrates. Thus, surface functionality to prevent these bio-interactions on PTFE substrates is important to obtain safer and effective implantable medical devices for long-term applications. To overcome the aforementioned limitations, several efforts have been directed for the modification of PTFE substrates through physical and chemical treatments [7–13]. The surface-reducing agent like sodium hydrate/benzo-phenone complex was used to chemically change the C–F bond into

C–H bond on PTFE surfaces [14]. However, this wet-chemical process is hazardous, which needs a careful handling. Plasma treatments have also been used to introduce reactive functional groups such as peroxides and –OH on PTFE surfaces to trigger further modifications [15–17]. But actually, the grafted layer upon the PTFE is of low density that cannot fully cover the surface. So far, pretreatments such as plasma etching or wet chemical etching of PTFE surface are deemed necessary for high performance modifications, but the effectiveness seems to be unsatisfied.

In recent years, polydopamine (PDA) coating has attracted attentions of researchers owing to the convenience and material independence [18,19]. PDA coating was mainly carried out on metal and inorganic substrates at first [20–22]. Since then, PDA coating has been performed for the successful modification of polymer substrates [23,24]. Studies have been performed to introduce the PDA layer on PTFE surfaces to achieve surface functionality; however, the general PDA coating procedure fails to form stable layers on PTFE surface, owing to the chemical inertness and highly hydrophobic nature of PTFE [25]. Therefore, hybrid surface modification procedures with physical

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and chemical reactions have been considered.

An effective PTFE surface modification method with the combination of plasma pretreatment and PDA coating has been reported [25]. The process of PDA coating on PTFE surfaces and the stability of PDA coating layer under sonication were monitored by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR/FTIR) and X-ray photoelectron spectroscopy (XPS). Further functionalization on the PDA-modified PTFE surfaces was examined. The amine groups in the PDA coating layer on PTFE surfaces were used to fabricate a thiol-functionalized PTFE surface (Thiol-PTFE) using ethylene sulfide [20,26]. Furthermore, photo-induced surface-initiated graft polymerization of a functional methacrylate was performed to prepare a hybrid polymer material comprising the PTFE substrate and functional polymer layer.

Surface modification with zwitterionic polymers is confirmed as a precious and effective procedure to obtain highly hydrophilic and biocompatible surfaces [27–35]. Of these, a polymer composed of 2-methacryloyloxyethyl phosphorylcholine (MPC) units is an approved biomedical polymer that reduces unexpected biological reactions from medical devices when implanted in living systems [36–41]. MPC polymers have been used for the preparation of various medical devices, which may have longer life span once implanted into patients. The basic mechanism underlying the biocompatibility of the MPC polymer surface involves the reduction in the protein adsorption. Photoinduced grafting of poly(MPC)(PMPC) is one of the efficient and effective ways to improve the hydrophilicity and biocompatibility of ultra-high-molecular weight polyethylene and poly(ether ether ketone) [42–47]. In this research, we propose a novel hybrid process for the functionalization of PTFE substrates and discuss the effectiveness of the PDA coating layer on PTFE substrates. In addition, we discuss the differences in the mechanism underlying the *in vivo* compatibility of PTFE substrates and that modified with the PMPC layer through PDA coating.

2. Material and methods

2.1. Materials

PTFE substrates were purchased from SANPLATEC Co. Ltd., Osaka, Japan. Tris(hydroxymethyl)aminomethane, 3-hydroxytyramine hydrochloride (dopamine), and ethylene sulfide were obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. MPC was synthesized as previously reported [39] and supplied by NOF Co., Ltd., Tokyo, Japan. Anti-bovine albumin rabbit immunoglobulin (IgG) (#B1520), anti-rabbit IgG goat IgG labeled with a 10-nm gold colloid (#G7402), and ovalbumin (#A5503) were obtained from Sigma-Aldrich, St. Louis, MO, USA. Anti-bovine fibrinogen rabbit IgG (#BS-10361R) was procured from Bioss Antibodies, Boston, MA, USA. Fetal bovine serum (FBS) for cell culture medium (Gibco®) was purchased from Thermo Fisher Scientific Inc., IL, USA. Other reagents and solvents used were pure-grade commercial reagents.

2.2. Plasma treatment and PDA coating on PTFE substrate

The overall process of the surface modification of PTFE substrates is shown in Fig. 1. PTFE substrates were washed with ethanol in an ultrasonic cleaner (US-2R; ASONE CO., Ltd. Osaka, Japan) for 15 min. A plasma reactor (PR500; Yamato Scientific Co. Ltd., Tokyo, Japan) was used to treat PTFE surfaces under oxygen atmosphere for different treatment times and at a constant pressure of 20 Pa. The frequency of plasma generation was 13.56 MHz, while the plasma energy was controlled by the change in the electric power of the plasma generator from 10 to 100 W. In addition, plasma treatment under argon gas atmosphere was used, followed by a 20 min exposure to atmosphere [48]. Conditions of plasma treatment are summarized in Table 1.

After plasma treatment, coating of PDA on the substrate was carried out. The obtained Plasma-PTFE substrates were dipped into a freshly

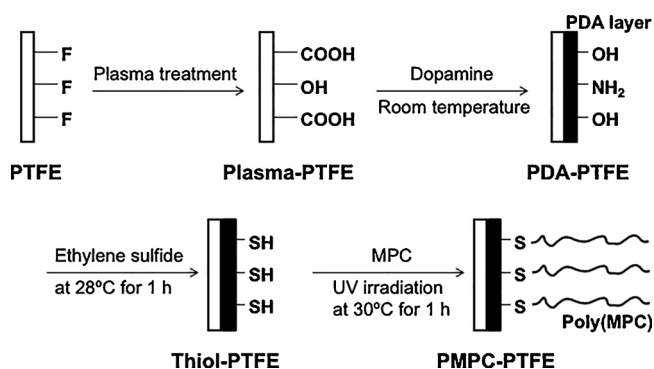


Fig. 1. Overall procedure of the surface modification of the PTFE substrate.

Table 1

Conditions of plasma treatment.

Conditions	Plasma energy (W)	Plasma treatment time (s)
I	10	5
II	20	5
III	30	5
IV	40	5
V	100	60

prepared aqueous solution of 2.0 g/L dopamine at pH 8.5 [18]. The reactions were performed on a shaking plate for different time points (up to 30 h) at room temperature. The substrates were thoroughly washed with ethanol and water and dried in a vacuum desiccator to obtain PDA-PTFE substrates.

2.3. Evaluation of the stability of the PDA coating layer on PTFE substrates

The PDA-PTFE substrates were sonicated in the ultrasonic cleaner in the presence of ethanol to examine the stability of the PDA coating layer. The sonication time varied from 5 to 90 min. The PDA coating layer retained on the substrate was analyzed by ATR/FTIR spectroscopy. The states of sonicated surfaces of the substrates were observed by naked eyes.

2.4. Preparation of PMPC-grafted PTFE substrates

The preparation procedure for PMPC-grafted PTFE (PMPC-PTFE) substrates is shown in Fig. 1. The PDA-PTFE substrates were removed from the desiccator and washed with ethanol in the ultrasonic cleaner for 5 min. A Thiol-PTFE substrate was prepared as previously reported through the reaction between ethylene sulfide and the amino groups from the PDA coating layer [21]. In brief, the PDA-PTFE substrate (2.0 cm²) was dipped into 5.0 mL of degassed ethanol. Ethylene sulfide (130 μ L, 0.84 mmol) was added into the solution and the reaction was performed at 28 °C for 1 h with constant stirring. The substrates were thoroughly washed with ethanol and double distilled water and dried in the presence of flowing nitrogen gas. Graft polymerization of MPC was performed by the photoinduced thiol-ene polymerization method using the Thiol-PTFE surface as follows [21,26,49]: The Thiol-PTFE substrate was placed in a reaction glass tube with an aqueous solution of MPC at a concentration of 0.50 mol/L. The reaction solution was degassed for 15 min to eliminate oxygen and the solution was subjected to UV irradiation at 30 °C for 1 h using an ultra-high-pressure mercury lamp (UV intensity; 21 mW/cm², wavelength; 360 nm, ML-251 A/B, USHIO, Tokyo, Japan). The substrates were thoroughly washed with distilled water and ethanol, followed by their washing with ethanol in the ultrasonic cleaner for 5 min. The substrates were dried in a desiccator to obtain PMPC-PTFE substrates.

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