NOTE

Preparation of Novel Gold-Coated Syndiotactic Poly(vinyl alcohol) Microfibrils by Sputtering

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ABSTRACT: To prepare a syndiotactic poly(vinyl alcohol) (PVA)/gold complex for various biomedical applications, ultrahigh-molecular-weight syndiotactic PVA microfibrils were directly prepared by the saponification of poly(vinyl pivalate) that was obtained through bulk polymerization of vinyl pivalate at 30°C. PVA microfibrils with a number-average degree of polymerization, syndiotactic diad content, and degree of saponification of 14,300, 61.7%, and 99.9%, respectively, were gold-coated by sputtering at 140 and 150 W (Watt) for 1, 2, and 3 min, respectively. A weight gain of up to 7% by the gold atoms for the PVA microfibrils treated at 150 W for 3 min was found. Morphological changes at the surface were observed by a microscopic method. A mechanism of gold coating on PVA microfibrils is suggested.
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Key words: syndiotactic PVA/gold complex; PVA microfibrils; sputtering

INTRODUCTION

Poly(vinyl alcohol) (PVA) cannot be prepared directly from the polymerization of monomeric vinyl alcohol because of its tautomerization, which means fast conversion to its aldehyde form and, rarely, the vinyl alcohol form. Therefore, PVA can be prepared by polymerization of monomeric vinyl esters such as vinyl acetate, followed by saponification of the precursor.[1–9] The resulting PVA, a crystallizable linear polymer of aliphatic chains, shows superior resistance to solvents and oil. Furthermore, PVA fibers have higher strength, modulus, and abrasion resistance, as well as alkali resistance than do other organic synthetic fibers.[10–16] The superior biocompatibility of PVA makes it possible for use as a hydrogel for organ substitution, drug delivery system, bioreactor, biosensor, and embolic materials for cancer killing and aneurysm treatment.[17,18]

Recently, Lyoo et al.[19–25] found that a PVA fiber with a well-oriented microfibrillar structure was formed by saponifying poly(vinyl pivalate) (PVPi) to PVA. These PVA microfibrils showed the appearance and characteristics of natural fibers, such as cotton and jute. In general, PVA microfibrils have enhanced mechanical properties compared with spun fibers. Furthermore, they have abundant microvoids, which are expected to enhance the surface area.

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PVA microfibrils have been a focus of studies, especially for their possible use in embolization, the operational therapy of controlling blood flow to a specific vein or portion of vein to prohibit the supply of nutrition to a certain kind of cell, such as a cancer cell. Another kind of embolization is physical treatment for blood circulation, such as aneurysm surgery. The cancer cell–killing embolic application has been paid attention to because of the possibility of effectively replacing commercial metallic coil–shaped embolic materials; these expensive metallic materials present some problems during operations because of their sharp cut faces. PVA microfibrils, in contrast, have superior properties, including enhanced biocompatibility and less risk of scratching but are hard to detect by X-ray during an operation because of a lack of radio-opacity, which is a very important characteristic for embolic materials because of the need for minute control in positioning materials in a human organ.

The most widely used method to make organic polymers detectable by X-ray is "doping" with a material that has a higher electron density. Iodine has been used for PVA. The intensity, however, is so low that it hardly can be used during surgery. Moreover, a higher amount of iodine might cause toxicity in humans.

Sputtering of a finish is the most recently developed finishing technology for attaching molecules or atoms to fiber or fabric in inert gas conditions. This technique enables the forming of a thin layer of metal on a fiber surface without losing any mechanical or functional characteristics. In this study, therefore, high-molecular-weight (HMW) syndiotactic PVA microfibrils were coated with gold atoms by sputtering to endow radio-opacity, as well to maintain biocompatibility. Morphological changes in the surface of PVA

microfibrils resulting from the attached gold atoms were also investigated.

EXPERIMENTAL

Materials

Vinyl pivalate (VPi) purchased from Shin-Etsu was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, followed by distillation under reduced nitrogen pressure. The initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), (Wako Co., Japan, 99%) was recrystallized twice from absolute methanol before use. PVA with a number-average molecular weight of 127,000 and a degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Other extrapure-grade reagents were used without further purification. Water used for all procedures was deionized.

Preparation of PVA microfibrils

In a three-necked flask 250 mL of VPi was flushed with anhydrous nitrogen that had passed through pyrogallol-aqueous alkali and calcium chloride dehydrating traps at 10°C for 3 h. Polymerization was carried out at 30°C for 10 h, after which 1×10^{-4} mol/mol of VPi of ADMVN was added. Unreacted monomer and initiator were removed by distillation under vacuum. The resultant PVPi was purified by reprecipitation, using methanol and benzene as precipitator and solvent, respectively, followed by drying at 40°C in a vacuum for a day. The conversion was calculated by measuring the weight of the polymer.

The following is a typical example of the PVA fibrillation experiments that were done. In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 3 g of PVPi was dissolved in 300 mL of tetrahydrofuran. The PVPi solution in the flask and a 20% potassium hydroxide/methanol/water (90:10 v/v) solution in the dropping funnel were flushed with nitrogen. The ratio of saponification agent/PVPi solution was 0.05:0.25 (v/v). The alkali solution was added to the PVPi solution while being stirred at 50°C–60°C. After the saponification reaction was completed, the solid saponification product was beaten mechanically, filtered, and washed several times with methanol. A quantitative yield of PVA microfibrils was obtained.

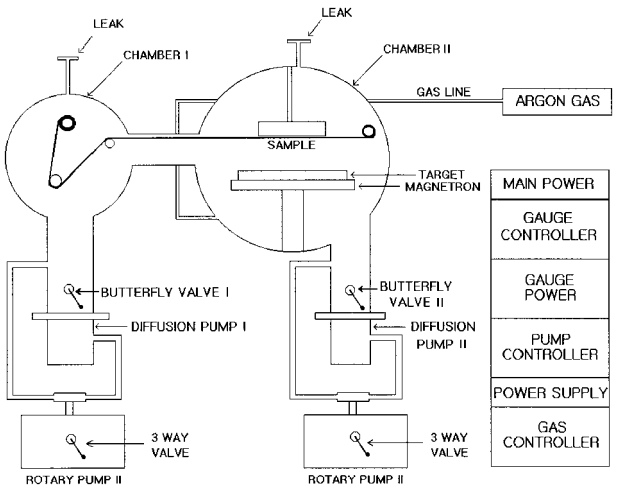

Figure 1 Schematic presentation of sputtering apparatus.

TABLE I
Sputtering Conditions of PVA Microfibrillar Fiber

Sputtering gas	Argon
Reactor pressure	3×10^{-3} Torr
Power supply	140 and 150 W
Target	Stainless steel
Distance between electrodes	6 cm
Treatment time	1, 2, and 3 min

To determine its molecular weight, PVA was reacetylated into poly(vinyl acetate) (PVAc), and the number-average degree of polymerization (P_n) of PVAc was calculated by using eq (1)[20]:

$$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62} \text{ (in benzene at 30 °C)} \quad (1)$$

where $[\eta]$ was the intrinsic viscosity of the PVAc/benzene solution. The syndiotactic diad content and degree of saponification were determined from the spectrum of PVA obtained by proton-nuclear magnetic resonance (^{1}H-NMR) spectroscopy (Varian, Sun Unity 300). Residual ester groups could not be detected in the ^{1}H-NMR spectrum of the specimen. The P_n, syndiotactic diad content, and degree of saponification of PVA in this study were 14,300, 61.7%, and 99.9%, respectively.

Sputtering of PVA microfibrils

Figure 1 shows the schematic presentation of the sputtering apparatus. A gram of PVA microfibrils was gold-coated by sputtering at 3×10^{-3} torr of argon gas. Supplied power was controlled to 140 and 150 Watt (W) at predetermined time intervals of 1, 2, and 3 min. Detailed experimental conditions are listed in Table I.

Characterization

The amount of attached gold atoms was determined by weight gain (%) in eq. (2). Weight measuring was conducted after sputtering to avoid possible weight loss.

$$W(\%) = \frac{N - N_0}{N_0} \times 100 \quad (2)$$

where N_0 and N are the weights of the PVA microfibrils before and after sputtering, respectively.

The surface morphologies of the PVA microfibrils were observed using a scanning electron microscope (JSM 5800-LV, Jeol, Japan) with a magnification of 1 K.

RESULTS AND DISCUSSION

The structure and physical properties of gold-coated fibers may vary with the molecular parameters of the fibers such as molecular weight and stereoregularity and with process-

ing parameters such as sputtering conditions. In this study, because only one specimen (PVA with a P_n, syndiotactic diad content, and degree of saponification of 14,300, 61.7%, and 99.9%, respectively) was adopted for use in the sputtering experiments, sputtering conditions affecting the structure and physical properties of the PVA microfibrils were varied to identify the gold-coated fibers.

Figure 2 shows the weight gains of the sputtered PVA microfibrils. Weight gains of PVA microfibrils as a result of the combined gold atoms increased with increasing sputtering time at either supplied power, 140 and 150 W. The weight gain of PVA microfibrils treated at 140 W for 3 min was under 4%. On the other hand, a weight gain of more than 7% was observed for PVA microfibrils treated at 150 W for 3 min. The difference in weight gain for PVA microfibrils treated at 140 and 150 W increased with increasing sputtering time. Therefore, it can be concluded that high power is needed for effective gold coating on PVA microfibrils. The linearity in the increasing tendency of weight gain of PVA microfibrils with increasing sputtering time indicated that there was no difference between fiber–gold and gold–gold interfaces. This tendency of increasing linearity was also noted for the sputtering of spun fibers of smooth surfaces. In the current results there was no difference in the etching and activation mechanism through sputtering for both microfibrillar and spun fibers. Gold-coated PVA microfibrils, however, were not detected by X-ray up to a 7% weight gain. From this result, it is thought that much more severe sputtering conditions or modification of crystalline structure of PVA microfibrils should be applied for using this as a radio-opaque embolic material. But an excessive amount of gold coating would toughen PVA microfibrils, making it impossible for PVA microfibrils to be used in the human body. Therefore, the sputtering conditions of PVA microfibrils should be defined for application to the human body.

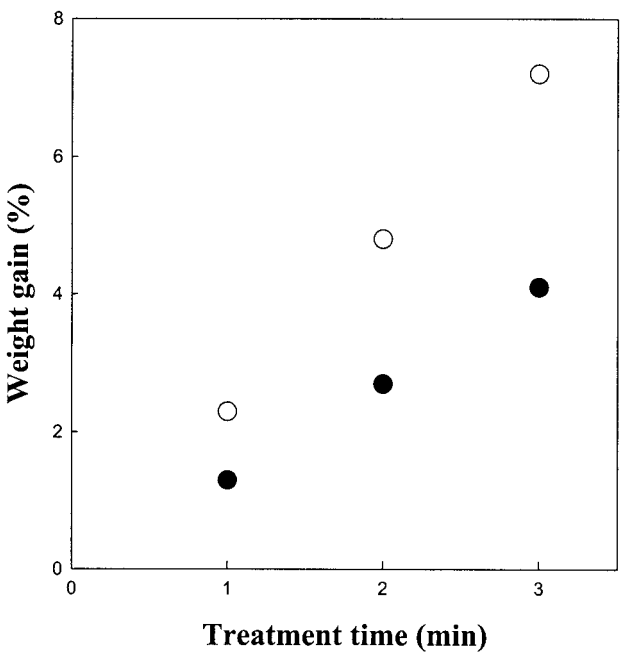

Figure 2 Relationship between treatment time and weight gain (%) of sputtered PVA microfibrils treated at (●) 140 W and (○) 150 W.

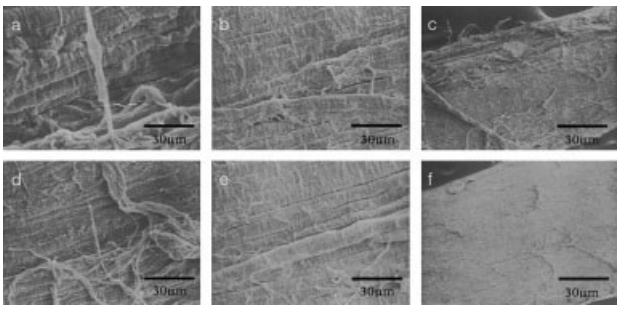

Figure 3 Scanning electron micrographs of gold-coated microfibrillar PVA fiber. Supplied power and sputtering times: (a) 140 W, 1 min; (b) 140 W, 2 min; (c) 140 W, 3 min; (d) 150 W, 1 min; (e) 150 W, 2 min; (f) 150 W, 3 min.

The surfaces of PVA microfibrils sputtered at various conditions are shown in Figure 3. PVA microfibrils treated at 150 W showed a smoother surface than that treated at 140 W. In considering the chemical vapor deposition mechanism,[26] it can be assumed that the development of crystals of gaseous metallic atoms first occurred in an irregular layer. Therefore, it was assumed that as more gold atoms were attached to PVA microfibrils at 150 W, this would result in more regular surfaces of the PVA microfibrils.

Smoothness of the surface increased with sputtering time at the same power supply. There was a sharp change in the surface at sputtering times between 1 and 2 min. This was ascribed to the transition of the binding sites from fiber–gold to gold–gold interfaces. From these results it can be concluded that the combining of PVA microfibrils with gold by sputtering proceeds in two steps: first, between the PVA microfibrils and the gold atoms and, then, following the combination of the gold atoms with the gold layer formed on the PVA microfibrils. Maintaining the natural touch of PVA microfibrils can increase their usability as an embolic material. Therefore, the degree of gold coating should be controlled to maintain the flexibility and radio-opacity of PVA microfibrils.

CONCLUSIONS

Syndiotactic PVA microfibrils were coated by gold atoms through a sputtering finish in a high vacuum. The weight gain of the PVA microfibrils increased with an increase in the power supplied and in the sputtering time. The smoother surfaces of the PVA microfibrils with more gold coating indicates that the gold-coated atoms first filled irregular surface defects and were combined with the gold layer afterward. The small increase in X-ray detectability, however, calls for improved sputtering methods or structural modification of PVA microfibrils. In the near future we will report on the effects of the degree or layer of coated gold on the embolic and thrombogenic properties of PVA microfibrils.

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