

Synthesis of New Polymers Containing Tannin

MIN KIM, KYOICHI SAITO,* and SHINTARO FURUSAKI,
*Department of Chemical Engineering, Faculty of Engineering,
University of Tokyo, Tokyo 113, Japan,* and TAKANOBU SUGO and
JIRO OKAMOTO, *Japan Atomic Energy Research Institute,
Takasaki Radiation Chemistry Research Establishment, Takasaki,
Gunma 370-12, Japan*

Synopsis

A novel method for preparation of immobilized tannin on polyethylene has been suggested. A tannin-containing polymer was prepared by radiation-induced graft polymerization of glycidyl methacrylate onto porous polyethylene, followed by coupling tannin with the produced epoxide group. Reaction conditions for preparing immobilized tannin, such as the reaction temperature, pH, and the molar ratio of tannin to the epoxide group were investigated. The tannin content of the tannin-containing porous polyethylene was 20%, which is approximately equivalent to that of the conventional cellulose-based immobilized tannin. The adsorption isotherm for immobilized tannin and ferrous ion was determined.

INTRODUCTION

Tannin compounds have been used in a variety of industries, especially the leather industry, since ancient times. They can be classified as a hydrolyzable tannin or a condensed tannin.¹ Tannins, having a large number of phenolic hydroxyl groups, present an extremely high affinity to iron and protein.

Researchers of the Tanabe Seiyaku Co.²⁻⁴ have developed a tannin immobilized on cellulose. They have succeeded in its industrial application for the removal of unfavorable proteins in an aqueous solution such as Japanese rice wine, and for the removal of a trace amount of iron from water for brewing. Recently, Sakaguchi and Nakajima^{5,6} reported that tannin immobilized on various matrices, such as cellulose powder, Bemberg rayon fiber, and agarose gel, has a high adsorption capacity for uranium from seawater.

The conventional preparation process of immobilization of tannin, as shown in Figure 1, includes five procedures: (1) alkaline treatment of the matrix, (2) epoxy-activation, (3) interposition of the space arm, (4) epoxy-activation, and (5) coupling of tannin. This preparation method has two disadvantages: (1) Since the starting material is limited to cellulose matrices, the resulting immobilized tannin is a soft and compressible material; (2) the procedure of the interposition of the space arm is required to improve the adsorption characteristics.

*To whom correspondence should be addressed.

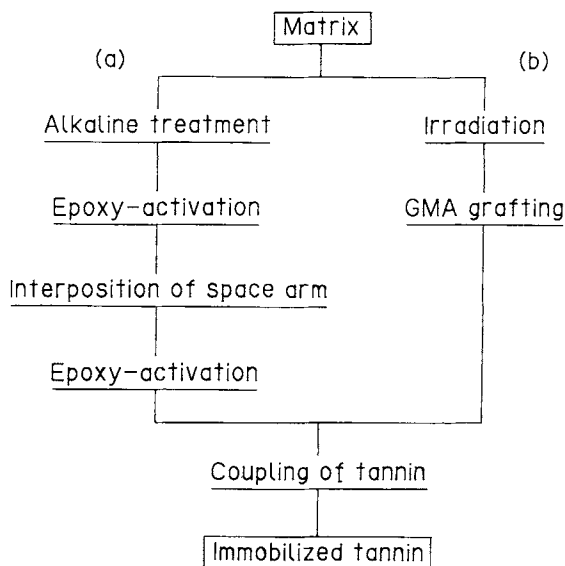


Fig. 1. Comparison of preparation method for immobilized tannin: (a) conventional method; (b) this study.

Radiation-induced graft polymerization is known to be especially useful to introduce functional groups into a variety of polymers.^{7,8} To overcome the above disadvantages, we attempted to apply radiation grafting to the immobilization of tannin for the following reasons: (1) Since physically and chemically stable polyethylene is used as the base polymer, the resulting immobilized tannin may be easy to handle. (2) The graft chains containing the epoxide group function not only as a precursor to introduce tannin, but also as space arms. Thus, the preparation procedure can be simplified. (3) Since the radiation-induced graft polymerization is performed in vapor phase without any catalysts, no treatment, such as repetitive washing after the reaction, is required.

The objectives of our study were twofold: (1) to suggest the novel preparation method of tannin immobilized on porous polyethylene by radiation-induced grafting and (2) to exhibit the ability to adsorb the iron ion by the immobilized tannin.

EXPERIMENTAL

Immobilization of Tannin on Porous Polyethylene

A commercially available hollow fiber (Asahi Chemical Industry Co., Japan) was used as the base polymer for grafting. The inner and outer diameters of this hollow fiber were 0.62 and 1.24 mm. The hollow fiber was made of a porous polyethylene with nominally sized pores of 0.1 μm diameter and 75% porosity. Reagent-grade glycidyl methacrylate (GMA) was used without further purification. Chinese gallotannin was obtained from the Dai-Nippon Pharmaceutical Co. Its presumed structure is shown in Figure 2. Other chemicals were of reagent grade and used without further purification. Figure

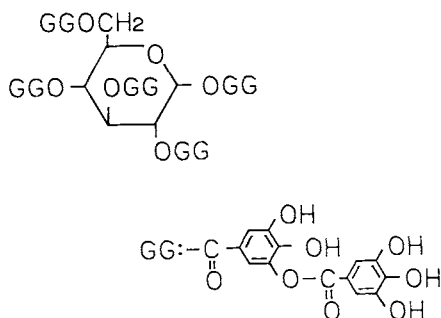


Fig. 2. Presumed structure of tannin.

3 shows the preparation process of tannin immobilized on porous polyethylene. Details of the irradiation and grafting are described in our previous reports.⁷⁻⁹ The porous polyethylene hollow fiber (PE-C fiber) was irradiated by an electron beam from a cascade-type accelerator (Dynamitron, Model IEA 3000-25-2, Radiation Dynamics) at ambient temperature in a nitrogen atmosphere. The accelerator was operated at a beam energy of 2 MeV with a current of 1 mA. The dose was 20 Mrad. Immediately after irradiation, the bundle of hollow fibers was put into an ampule and reacted in a vapor of deaerated GMA at high vacuum. Vaporized GMA was reacted with the trapped radicals in the base polymer. The degree of grafting (d.g.) is defined as follows.

$$\text{d.g.} = [(W_1 - W_0)/W_0]100 \quad (1)$$

where W_0 and W_1 are the weights of starting hollow fiber and GMA-grafted hollow fiber. The GMA-grafted hollow fiber is henceforth designated as GMA-C fiber. In this study GMA-C fibers with a degree of grafting ranging from 70 to 130% are used.

The epoxide group of the graft chains was coupled with a tannin aqueous solution as follows. The GMA-C fiber was suspended in 0.2 L of a 3% Chinese gallotannin aqueous solution. The initial pH of the solution was adjusted

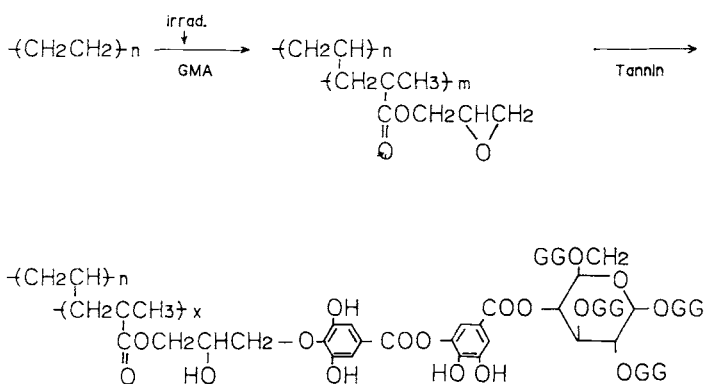


Fig. 3. Preparation process of the TA-C fiber.

TABLE I
Reaction Conditions for Immobilization of Tannin on Porous Polyethylene

Radition-induced graft polymerization	
Irradiation dose	20 Mrad
Reaction temperature	313–323 K
Coupling Reaction	
Concentration of tannin	3%
Initial pH	3.5, 7, 9
Initial molar ratio	2–20
Reaction temperature	323–335 K
Reaction time	1–6 h

between 3.5 and 9 with a sodium hydroxide solution. Nitrogen was bubbled into the suspension at a prescribed flow rate up to 0.12 L/h. The initial molar ratio of tannin in the feed solution to the epoxide groups ranged from 2 to 20.

After the reaction, the resulting hollow fiber was rinsed repeatedly with deionized water until the pH of the washings was about 5. Then it was dried at room temperature under reduced pressure and the weight was measured. The tannin content and the conversion in coupling were calculated as

$$\text{tannin content} = [(W_2 - W_1)/W_2]100 \quad (2)$$

$$\text{conversion in coupling} = [(W_2 - W_1)/1701]100/[(W_1 - W_0)/142] \quad (3)$$

where W_2 is the weight of the tannin-immobilized hollow fiber. The factors 1701 and 142 in eq. (3) correspond to the molecular weight of tannin and GMA, respectively. Thus, the conversion in coupling is based on the assumption that tannin has the structure as shown in Figure 2. The tannin-immobilized, porous polyethylene hollow fiber will hereafter be referred to as the TA-C fiber. The reaction conditions for grafting and coupling are summarized in Table 1.

Properties of Porous Polyethylene-Based Immobilized Tannin

The cross section of PE-C and TA-C fibers were observed by scanning electron micrography (SEM). To examine the distribution of the introduced functional group across the TA-C fiber, a sample of the TA-C fiber was equilibrated in a solution containing ferrous ion. After the equilibration, the sample was taken out of the solution and washed repeatedly with deionized water. Then the distribution of ferrous ion across the hollow fiber was determined with an electron probe X-ray microanalyzer (XMA).

Adsorption and Elution of Iron

The equilibrium isotherm was measured for ferrous ion on the TA-C fiber by the batch method. Weighed quantities of the TA-C fiber were placed in an Erlenmeyer flask containing a ferrous ammonium sulfate solution, the initial pH of which was adjusted to 4 with sulfuric acid. The flask was tightly sealed and shaken by a mechanical shaker in a thermobath maintained at 303 K. The

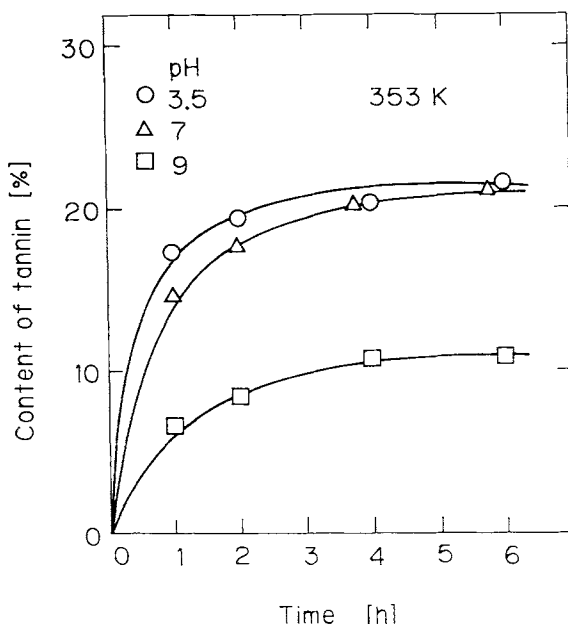


Fig. 4. Effect of initial pH on immobilization of tannin.

amount of iron adsorbed on the TA-C fiber was calculated by the decrease of iron in solution. The adsorption of ferrous ion was also measured as a function of time under the same conditions as in the equilibrium studies.

With the use of an iron-loaded TA-C fiber, the elution ratio was determined by different concentrations of hydrochloric acid ranging from 10^{-4} to 1 mol/L. Under the constant ratio of the hollow fiber/eluent volume, the elution of iron was achieved by 3 h of shaking at 303 K. To examine the durability of the TA-C fiber, adsorption–elution cycles were carried out with 4-day periods of contact with a ferrous ammonium sulfate solution followed by a 1-day elution period with 1 mol/L hydrochloric acid. The loading of iron at each cycle was determined. The iron concentration was determined by colorimetry using an *o*-phenanthroline reagent.

RESULTS AND DISCUSSION

Immobilization of Tannin onto Porous Polyethylene

A coupling reaction with the GMA-C fiber (d.g. 120%) and tannin was carried out at 353 K for initial pH levels of 3.5, 7, and 9. The results are shown in Figure 4. No significant differences in the conversion at the initial pH's of 3.5 and 7 were observed. The result of the initial pH 9 shows a lower tannin content. This is presumably due to the decrease in the effective tannin concentration by the decomposition in the alkaline medium. In fact, at alkaline pH, the color of the tannin aqueous solution gradually turned to brown under nitrogen bubbling. Figure 5 shows the tannin content as a function of the reaction time for the initial pH of 7. The tannin content reached a plateau within 4 h at 338 and 353 K. Figure 6 shows the dependence

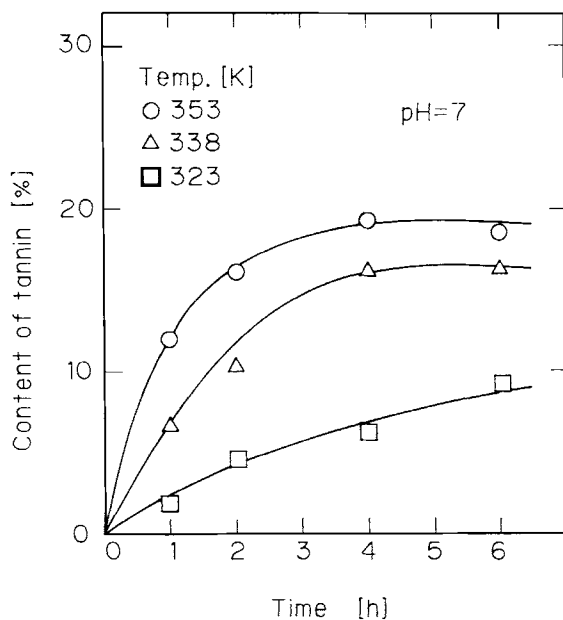


Fig. 5. Effect of reaction temperature.

of the tannin content on the initial molar ratio. Similar results were obtained at initial molar ratios higher than 10. The nitrogen bubbling did not have any considerable effects on the tannin content; however, the presence of nitrogen was required to prevent oxidation of tannin by dissolved oxygen.

In the case of the TA-C fiber with a tannin content of 20% which was prepared from the GMA-C fiber (d.g. 120%), the conversion in the coupling reaction amounts to about 4% using eq. (3). This low conversion can be

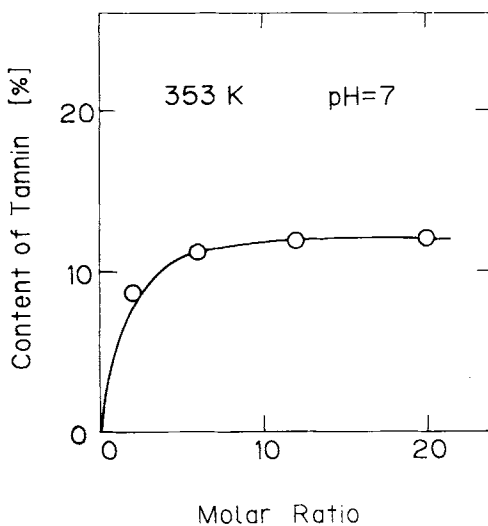


Fig. 6. Tannin content as a function of molar ratio.

explained by either the steric interference between the graft chains and tannin or the occurrence of the side reaction. Svec et al.¹⁰ reported that, at neutral pH, the hydrolytic reaction of the epoxide group does not take place easily. Therefore, the tannin content may be limited mainly by the steric effect. The tannin content, 20%, of the porous polyethylene-based immobilized tannin obtained in this study is approximately equivalent to that of the cellulose-based immobilized tannin produced by Watanbe et al.²

Our approach has the advantage that suitable backbone polymers can be employed in order to obtain desirable mechanical and physicochemical properties in the derived tannin-containing polymers, and that many synthetic steps used to interpose the space arm, which makes it possible to introduce relatively large molecules such as tannin, can be omitted.

Properties of the TA-C Fiber

After functionalization, the inner and outer diameters of the TA-C fiber (d.g. 120% and tannin content 20%) in the wet state were 0.74 and 1.39 mm. Thus, the TA-C fiber swelled in thickness by 5% compared with the PE-C fiber.

Figure 7 shows a line profile of iron across the fully iron-loaded TA-C fiber along with a SEM picture. The uniform iron distribution corresponds to the uniform immobilization of tannin throughout the hollow fiber membrane. Uniform introduction of tannin to the hollow fiber membrane is due to high porosity of the porous polyethylene hollow fiber used as the base polymer.

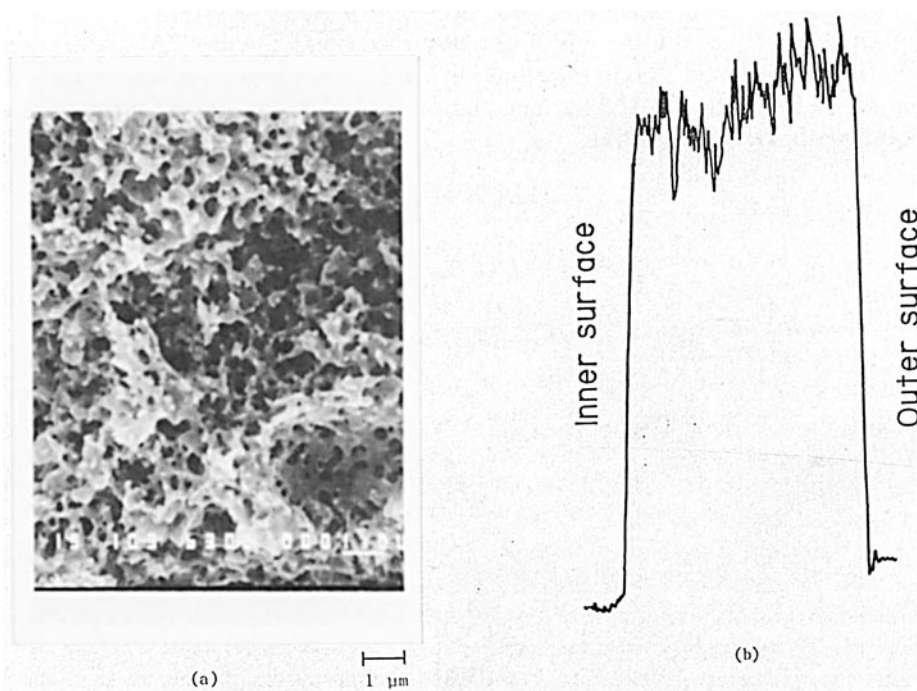


Fig. 7. Distribution of ferrous ion across the TA-C fiber: (a) SEM picture; (b) line profile.

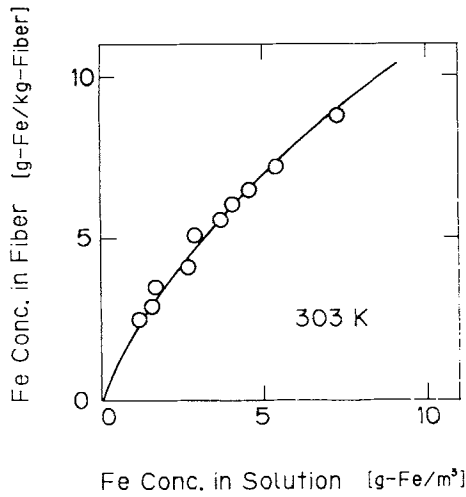


Fig. 8. Adsorption isotherm for the TA-C fiber.

Adsorption and Elution of Iron

To attain the adsorption equilibrium by the batch method, about 10-day periods of contact with the iron solution were required. The results for the equilibrium adsorption of iron from the ferrous ammonium sulfate solution onto the TA-C fiber are plotted in Figure 8. The data were well represented by the Freundlich isotherm

$$q = 2.1C^{1/1.4} \quad (4)$$

where q and C are the amount of iron absorbed (mg Fe/g dry TA-C fiber) and the concentration of iron in solution (mg Fe/L), respectively. After a sufficient length of time, the TA-C fiber has a uniform black color, indicating complete equilibration of iron loading.

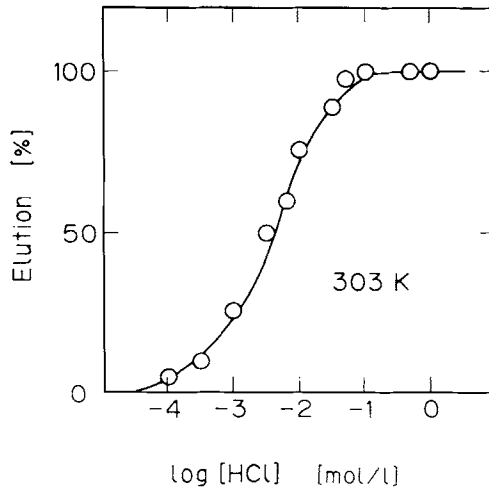


Fig. 9. Elution efficiency as a function of HCl concentration.

Elution of the iron adsorbed onto the TA-C fiber was carried out with hydrochloric acid under the same ratio of fiber to elution volume. Almost all the iron adsorbed is easily removed by stripping with 0.1 mol/L hydrochloric acid, as shown in Figure 9. No appreciable deterioration of the iron loading was observed after 10 adsorption–elution cycles.

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