

Note

REDUCING NONSELECTIVE PROTEIN ADSORPTION AND CELL ADHESION ON POLYACRYLONITRILE FILMS BY COPOLYMERIZATION OF ACRYLONITRILE WITH α -ALLYL GLUCOSIDE*Rui-qiang Kou^a, Chao Qu^b, Zhi-kang Xu^{a**}, You-yi Xu^a and Ke Yao^b^a Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China^b Medical College, Zhejiang University, Hangzhou 310027, China

Abstract In this work, the surface properties of novel sugar-containing polymers, α -allyl glucoside (AG)/acrylonitrile (AN) copolymers, were studied by contact angle, protein adsorption and cell adhesion measurements. It was found that the contact angle of the copolymer films decreased from 68° to 30° with the increase of AG content in the copolymer. The adsorption amount of bovine serum albumin (BSA) and the adhesive macrophage onto the film surface also decreased significantly with increasing α -allyl glucoside content from 0 to 42 wt% in the copolymer. These preliminary results reveal that both the hydrophilicity and the biocompatibility of polyacrylonitrile-based membranes could be improved by copolymerizing acrylonitrile with vinyl carbohydrates.

Keywords α -Allyl glucoside/acrylonitrile copolymer, Surface properties, Contact angle, BSA adsorption, Macrophage adhesion

INTRODUCTION

Polyacrylonitrile and acrylonitrile-based copolymers have been widely applied as membrane materials in the realms of dialysis, pervaporation, and ultra-filtration. However, their relatively poor hydrophilicity and biocompatibility limit their further applications for aqueous solution and biomedical usage. Therefore, considerable attention has been paid to the improvement of these characteristics of polyacrylonitrile^[1]. Carbohydrates or sugars exist in many forms and they play important roles in living systems. Synthetic carbohydrate-containing polymers have received much interest in recent years^[2–4]. One can envisage that copolymerizing vinyl carbohydrates with acrylonitrile should offer some inherent functions of the carbohydrates to the copolymer, and improve the hydrophilicity and biocompatibility of polyacrylonitrile^[5]. In our previous papers, acrylonitrile/ α -allyl glucoside copolymers were synthesized by solution^[6] and water phase precipitation^[7] copolymerizations. In this note, the surface properties of the films fabricated from these copolymers are tentatively reported.

EXPERIMENTAL

α -Allyl glucoside was synthesized by the method reported by Talley *et al.*^[8]. Copolymerization of AG and AN was conducted in water by the method described in our previous paper^[7]. 100 mL of distilled and de-ionized water, AG and AN were introduced into a four-necked round bottomed flask equipped with mechanical stirrer, thermometer, and nitrogen inlet tube. 0.0456 g K₂S₂O₈ and 0.0212 g Na₂SO₃ were added to the stirred solution

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while maintaining the reaction temperature at 60°C under a nitrogen atmosphere. The copolymerization was continued for 3 h and the formed copolymer precipitate was filtered, washed with excess distilled and de-ionized water and ethanol to remove residual monomers. The obtained copolymer was dried under vacuum at 60°C to constant weight. The composition of the copolymers was determined by elemental analysis (EA1110). The films were prepared by casting the DMSO solution of the copolymers (7 wt%) onto a glass plate. The films were dried at 60°C for 24 h and then at 150°C under vacuum for a week to remove the residual solvent completely. The final thickness of the dried films was approximately 100 μm . The sessile contact angle of the copolymer films was determined on a Kruss DSA10-MK instrument. Bovine serum albumin (BSA) adsorption was carried out by the following method. BSA was dissolved in a tris-HCl buffer (pH 8) that can facilitate the hydrophobic interaction and inversely depress the electrostatic binding between the protein and the polymer surface. A certain amount of the copolymer film was immersed in the BSA solution. The mixture was incubated at 30°C for 24 h to reach an adsorption-elution equilibrium. The amount of protein adsorbed on the film was calculated from the decreased concentration of BSA solution. The concentration of BSA solution was determined by UV spectroscopy. The macrophage adhesion was measured by the procedure reported by Li *et al.*^[9].

RESULTS AND DISCUSSION

It is well known that the hydrophobic interaction between biomaterial surfaces and proteins plays a very important role for non-selective adsorption of protein onto biomaterials. Usually, materials possessing a hydrophilic surface show relatively low non-selective adsorption for proteins or cells. Therefore, improving the hydrophilic surfaces is normally favored for biomaterials. Figure 1 shows the contact angle curve of pure water for the films fabricated from the acrylonitrile/ α -allyl glucoside copolymers. It was found that the contact angle decreased from 68.5° to 29.7° on increasing the AG content in the copolymers from 0 to 42 wt%. This is due to the contribution of the hydroxyl groups in AG moieties. The decreased contact angle indicated that a kind of highly hydrophilic copolymer was obtained.

Figure 2 illustrates the results of BSA adsorption on the copolymer surface. It can be seen that the adsorbed amount of BSA decreased with the increase of AG content in the copolymers, and the high BSA concentration could lead to an increase in the amount of BSA absorbed onto the copolymer films. The decreasing of the BSA adsorption could be mainly ascribed to the improvement of the hydrophilicity of the copolymer surface.

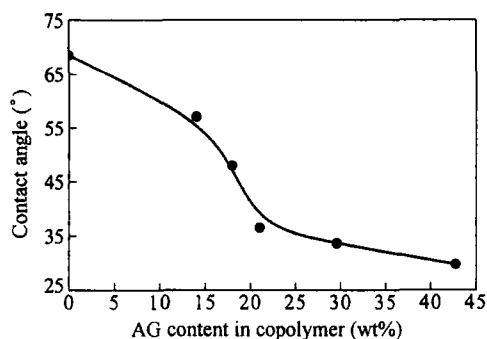


Fig. 1 Pure water contact angle of the acrylonitrile/ α -allyl glucoside copolymer films

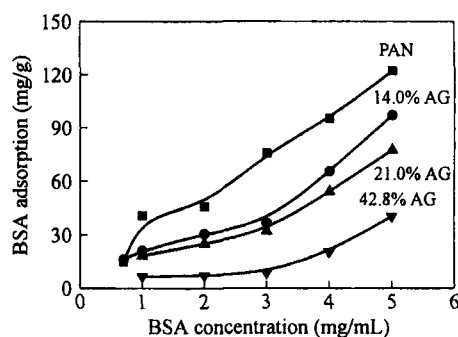


Fig. 2 Adsorption of BSA onto the acrylonitrile/ α -allyl glucoside copolymer films

Macrophages are a kind of immune cell and perform various functions, such as migration, phagocytosis, secretion, antigen presentation and survival through precisely modulated adhesion, in living bodies. However, the molecular mechanism in macrophage adhesion is complex, and its dynamics is not yet fully understood. Generally speaking, lower amounts of macrophages adhering to the material's surface indicates better blood compatibility for the material. In other words, the immunological reaction or immunological rejection will decrease after the materials are implanted into the living body. The results of macrophages adhesion tests on the

acrylonitrile/ α -allyl glucoside copolymer surface are shown in Fig. 3. It was clearly demonstrated that the number of macrophages adhering to the acrylonitrile/ α -allyl glucoside copolymer was significantly decreased as compared with that on the polyacrylonitrile film. That is, the incorporation of α -allyl glucoside into polyacrylonitrile could induce the reduction of macrophage adhesion.

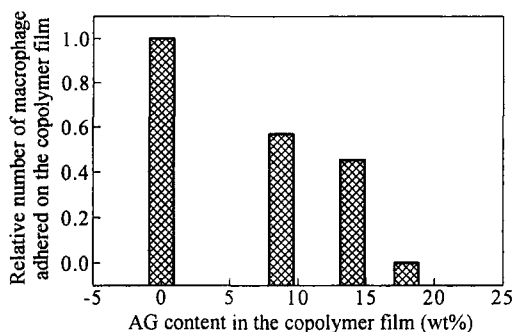


Fig. 3 Relative macrophage number versus α -allyl glucoside content in the copolymer film

The above results indicate that both the hydrophilicity and the biocompatibility of polyacrylonitrile could be improved by copolymerizing vinyl carbohydrates with acrylonitrile. It is expected that this kind of copolymer will be useful as membrane materials in the fields of fouling control and blood dialysis. Further work concerning the preparation, structure characterization and separation properties for the asymmetric acrylonitrile/ α -allyl glucoside copolymer membranes is in progress.

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