Adsorption of Surfactant and Ammonium Ion to Chemically Modified Cellulose Fiber

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Abstract

Cellulose fibers, cotton and rayon were grafted with a monomer or monomer mixtures, and the adsorption of linear alkylbenzenesulfonic acid sodium salt (LAS) and ammonium ion in water on the grafted fibers was investigated.

An effective adsorption of LAS was observed in the cotton grafted with a mixture of *N,N*-dimethylaminopropyl acrylamide and methyl methacrylate. Acrylic acid was grafted effectively to rayon (40 grafting %) and the grafted rayon showed high adsorption property for ammonium ion.

1. Introduction

Recently, the influence of contaminations such as alcohols, trihalomethanes, ammonia, surfactants, fats, and proteins, etc. included in water on our life environment is regarded as one of the important problems.

On the other hand, a lot of fiber materials are used and finally disposed in our life. Incineration of the used fiber materials causes the waste of the wealth and the energy. Much attention is paid for the reuse of the fiber materials.

We have studied the adsorption of small molecules to polymeric materials.[1-7] In addition, the separation of basic amino acids such as L-lysine and L-arginine from a mixture of various amino acids was investigated and the patents were applied in the research of the COE project of the National Institute of Agrobiological Sciences in Japan.[8,9] We investigated the possibility of the removal of organic compounds in waste water by using usual untreated fibers.[10] In the present article, we would describe the preparation of cellulose derivatives which can adsorb linear alkylbenzenesulfonic acid sodium salt (LAS) and ammonium ion in water.

2. Experimental

2.1 Materials

Fibers

Cotton (average diameter (d.) 25-30 μm), silk fibroin (d. 15-25 μm), wool (d. 10-30 μm), rayon (d. 25 μm), polyester (PET : d. 15 μm), polypropylene (PP) (d. 15 μm) were washed with methanol and water and dried at 60℃ under reduced pressure. Fibers were cut in average length of 1 - 2 mm.

Monomers

Methyl methacrylate (MMA : product of Wako Pure Chemical Indusries Co. Ltd.), *N,N*-dimethylaminoethyl acrylate (DMAEA : product of Kojin Co. Ltd.), *N,N*-dimethylaminopropyl acrylamide (DMAPAA : product of Kojin Co.

Ltd.), methacrylic acid (MA) and acrylic acid (AA) (reagent-grade products of Wako Pure Chemical Industries Co. Ltd.) were passed through a column containing activated alumina in order to remove polymerization inhibitors and were used without any other purifications.

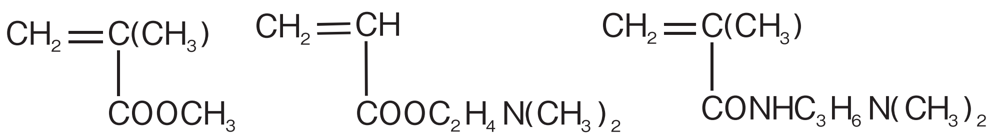

Figure 1. Structural formula of MMA, DMAEA and DMAPAA from the left.

2.2 Grafting of monomers

MMA, DMAEA, MA, AA or a mixture of monomers (MMA and DMAEA, or MMA and DMAPAA) were dissolved in water. Weighed cotton fiber was mixed with the monomer solution. An aqueous solution of hydrogen peroxide (conc. 0.3 w/w%) was added to the reaction mixture, and UV light of a Toshiba high-pressure mercury lamp H400P was irradiated to the reaction mixture from the distance of 10 cm. After the irradiation for 2 h, the reaction mixture was poured into methanol, and the precipitated product was filtered off. The obtained product was washed with water and chloroform successively to remove homopolymers. The resulting product was dried and weighed. The apparent grafting % was estimated from the weight increase in the product to the original fiber.

Similarly, the grafting reactions were carried out without hydrogen peroxide in the case of rayon.

2.3 Adsorption of LAS

Untreated or grafted fibers were packed in a stainless column with a size of 150 mm length and 4 mm inner diameter (i.d.). The column packed with grafted fibers was connected to the LC pump, Shimadzu LC-10 AS and rinsed with an aqueous HCl solution (concentration, 0.1 M). Consequently, an aqueous solution of LAS (typical concentration, 0.1wt.%) was passed through the column with a flow rate of 0.2-0.4 ml/min at 20 ℃. The solution passed through the column was collected in a glass tube at a given time by a fraction collector, Advantec SE-2120. The concentration of LAS in the collected solution (eluent) was estimated from the absorbance at 223 nm in the UV spectroscopy using a Shimadzu UV-2200 spectrophotometer or a JASCO V-530UV/VIS spectrophotometer.

2.4 Adsorption of ammonium ion

Experiments on adsorption of ammonium ion to fibers were carried out by two methods. The first method was similar to that for LAS as described above. An aqueous ammonium ion solution was prepared from ammonium chloride and water. The solution was passed through the column packed with fibers. The concentration of ammonium ion in the original ammonium ion solution and the eluent was measured by an ammonia meter, Ti-900KA of Tokyo Kagaku Kenkyusho Co. Ltd.

The second one is a batch system method as follows. Untreated or grafted rayon fabrics were immersed in an aqueous ammonium ion solution and the time change of the concentration of ammonium ion of the solution was measured by the ammonia meter.

3. Results and discussion

3.1 Adsorption of LAS

An aqueous solution of LAS was passed through a column containing various kinds of untreated fibers. Figure 2 gives the result of the adsorption of LAS. Fibroin gave the most adsorption amount among the examined fibers. On the other hand, wool gave the least amount although it is protein fiber similar to fibroin. This fact suggests that protein molecules should adsorb LAS preferably because of the amphoteric property. Nevertheless, the cuticle structure of wool would prevent the adsorption of LAS.

Rayon adsorbed LAS much in the second rank in the examined fibers. However, cotton did not adsorb LAS well. As the thickness of cotton and rayon is similar to each other, the difference in the adsorption is considered to be caused by the difference in their fiber structures.

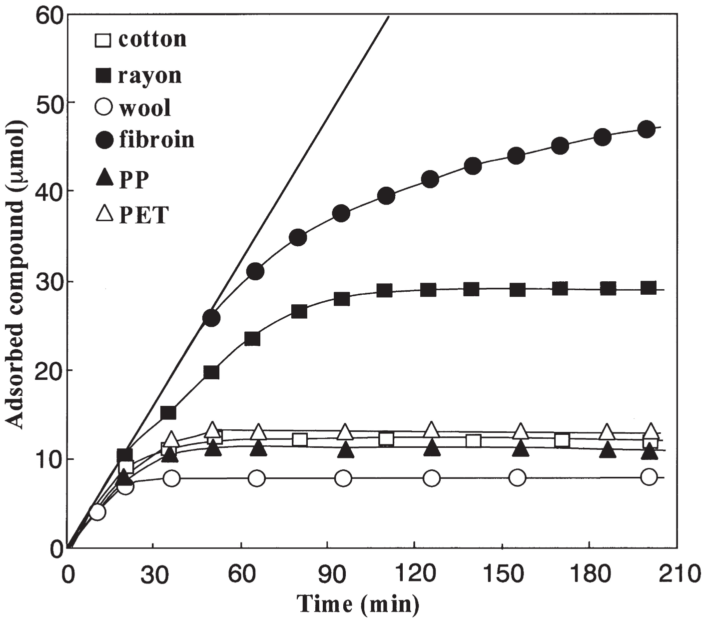

Figure 2. Adsorption of LAS to various untreated fibers.
Flow rate 0.4 ml/min; [LAS] 1.37 μmol/ml.

If cellulose fiber is chemically modified to make a similar property to proteins, the modified materials are expected to have a high adsorption property for LAS.

Thus, we carried out photografting cationic monomers to cellulose fiber. When a single monomer was not grafted so much to cellulose, an addition of MMA to the reaction mixture improved the yield. Thus, the grafting of a mixture of DMAEA and MMA or that of DMAPAA and MMA was carried out to obtain high grafting %.

Figure 3 gives the adsorption of LAS to cotton cellulose grafted with DMAPAA, a mixture of DMAPAA and MMA or a mixture of DMAEA and MMA. MMA grafted cotton did not give any adsorption of LAS. Although the grafting of DMAPAA to cotton was 18.0 %, the grafting of a mixture of DMAPAA with MMA (DMAPAA 80.0 v/v %) was 54.1 %. When it was postulated that DMAPAA and MMA were grafted to the cotton according to the monomer mixing ratio, the grafting wt % of DMAPAA in the polymer was estimated to be 49.3 %. Thus, the monomer mixed with MMA seems available to get high grafting % in the reaction of inactive monomers. DMAPAA grafted cotton and the cotton grafted with a mixture of DMAPAA and MMA gave relatively high adsorption of LAS. The adsorption mechanism should be due to the ionic interaction between the functional group, $-CO-NH-C_3H_6-[N(CH_3)_2H]^+$ and LAS anion.

As DMAEA was not grafted well to cotton fiber, the mixture of DMAEA and MMA was grafted to it. However, the DMAEA–MMA grafted cotton did not give high adsorption property for LAS. Thus, DMAPAA seems available for the adsorption of LAS.

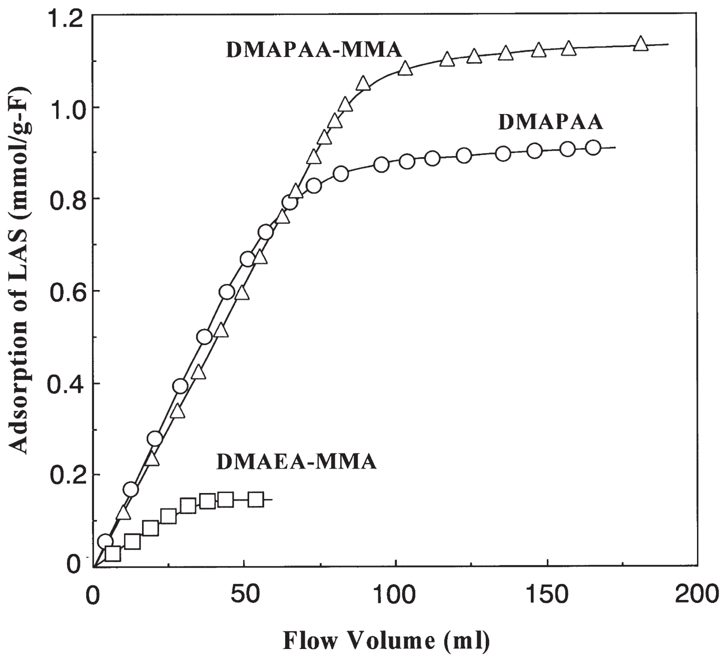

Figure 3. Adsorption of LAS to cotton cellulose grafted with DMAEA–MMA mixture (DMAEA 80 v/v%, 16.4 grafting %), DMAPAA (16.0 grafting % and DMAPAA–MMA mixture (DMAEA 80 v/v%, 54.1 grafting %). LAS concentration 0.1 w/w% (2.87 mM); flow rate 0.2 ml/min.

3.2 Adsorption of ammonium ion

MA grafted cotton was prepared and the adsorption of ammonium ion to the grafted cotton was examined. Figure 4 gives the adsorption of ammonium ion to the MA grafted cotton (9.50 grafting %). The saturated adsorbed amount of LAS was estimated as 4.28 mg/g-fiber.

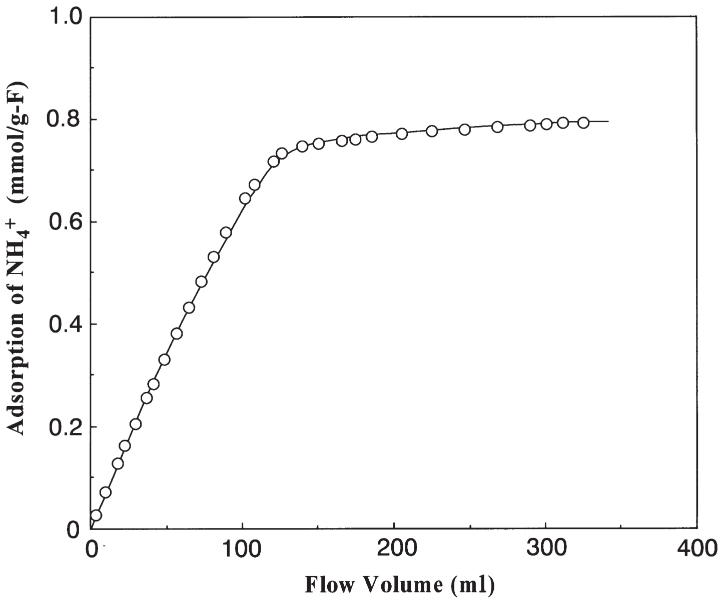

Figure 4. Adsorption of ammonium ion to cotton grafted with MA (9.50 grafting %). [NH_4^+] 0.01 w/w%; flow rate 0.2 ml/min.

AA grafted rayon was prepared and the adsorption of ammonium ion to the grafted cotton was examined. Figure 5 gives the adsorption of ammonium ion to AA grafted rayon. The method of the adsorption was carried out in a batch system as described in the Experimental. The saturated adsorbed amount of LAS was estimated as 1.04 g/g-fiber. As the fibers, monomers and adsorption method are different between Figure 4 and Figure 5, the direct comparison of them is impossible. However, the adsorbed amount of ammonium ion in AA grafted rayon was extremely more than that in MA grafted cotton. The functional group, -COOH in AA grafts is very effective for the adsorption of ammonium ion.

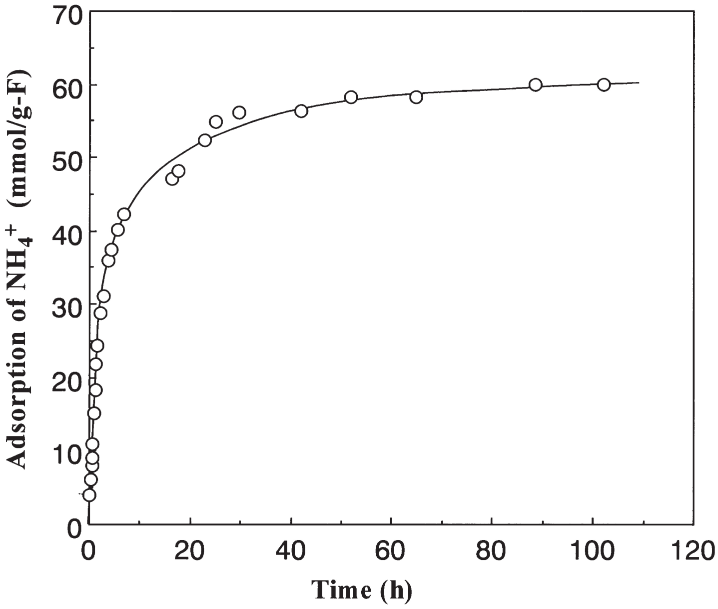

Figure 5. Adsorption of ammonium ion to rayon grafted with AA (40 grafting %) $[NH_4^+]_{t=0}$ = 371 mg/l ; temp. = 20 ℃.

4. Conclusions

The grafting of a mixture of DMAPAA and MMA to cellulose fiber was effective for the preparation of materials which adsorb LAS in water. AA grafted rayon gave a high adsorption property for ammonium ion in water. These adsorption mechanisms are considered to be due to the ionic interaction. The experimental conditions to prepare modified fibers with more effective adsorption ability will be investigated in the future.

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