

Sorption Properties of the Composite Fibers Made of PAN and Chitosan

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ABSTRACT: A composite fiber of polyacrylonitrile (PAN) and chitosan was obtained by spinning the mixture of PAN/chitosan with a certain amount of diluted acetic acid as a plasticizer. Water plasticizes the PAN and acetic acid plasticizes the chitosan. The fiber showed a porous and fibrillar structure, which could be converted easily into pulplike short fiber by pulping. PAN/chitosan pulp showed a much higher amount of uptake for acid dye than that of either powdery chitosan or activated carbon. It is considered that this better sorption capacity of the composite fiber results from the relatively large surface area attributed to its pulplike shape. The adsorption behavior of the composite fiber was considerably affected by temperature and pH because the adsorption is exothermic and proceeds by an acid–base reaction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2505–2511, 2002

Key words: chitosan; polyacrylonitrile; melt spinning; dye; adsorption

INTRODUCTION

Small amounts of dyes contained in the wastewater of textile industries are highly detectable and have become a growing pollution concern. Recently, the adsorption process has been considered as a potential method to remove dyestuffs from wastewater discharged from industries.¹ The adsorption behavior of activated carbon particles and silica in granular form has been demonstrated.²

Chitosan, a derivative of chitin through deacetylation, is a kind of natural polymer that has various potential applications because of its functionality in antimicrobial and adsorptive

properties. Chitosan has been shown to have extremely high affinities for dyes, as well as heavy-metal ions and certain surfactants, which contribute to aquatic toxicity.³

An adsorbent is more effective if its material form has a large surface area. There are several ways to increase the surface area of a sorption material including methods to make it a porous bead¹ or fibrous structure. Yoshida et al.⁴ investigated the isothermal adsorption of chitosan fibers for several kinds of dyes. Chitosan is insoluble in water and most common solvents, although it is soluble without degradation in weak acids such as 5% formic and acetic acids and it is thermally stable up to 150°C. Therefore, chitosan fibers or membranes can be made by dissolving chitosan in a dilute acid solution, but it cannot be made by melt spinning because of its infusibility.

On the other hand, polyacrylonitrile (PAN) exhibits an unusually high melting point (T_m) of 320°C compared with that of other aliphatic poly-

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mers.⁵⁻⁷ The interactions between polar nitrile groups are responsible for the high T_m . PAN-based polymers containing acrylonitrile (AN) content higher than 85% do not produce a stable melt state because of exothermic reactions such as cyclization, crosslinking, and degradation before they reach the T_m . This thermal property allows PAN-based polymers to be used as the precursor of carbon fiber, although it is disadvantageous when applied to the melt-spinning process. Coxe⁸ first observed that high-pressure mixtures of PAN-based polymers and water could be melt extruded. After the pioneering work of Coxe, intensive research has been carried out to apply melt spinning to the production of acrylic fibers.⁹⁻¹⁵ The melt-spinning processes using water are less expensive and nonpolluting compared to the usual solution-spinning processes. Recently, it has been found that pulp-shape acrylic fibers can be obtained by extruding the melt of PAN-based polymers using water as a plasticizer followed by a pulping process.¹⁶⁻¹⁹

In this study, we have introduced a novel method to get pulp-shape composite fibers by extruding a mixture of PAN-based polymer, chitosan and water. We also investigated the effect of high surface area of chitosan caused by pulp shape on the sorption of dyes.

EXPERIMENTAL

Materials

The PAN-based polymer (denoted as PAN-88) was supplied by Tae Kwang Industrial Co. (Korea) in the form of a fine powder. It was reported that the copolymer consisted of 88 wt % of acrylonitrile (AN) and 12 wt % of methyl acrylate. Intrinsic viscosity was measured at 25°C from dilute dimethyl formamide solution. The average molecular weight (M_v) was then estimated to be 82,000 g/mol according to the Mark-Houwink-Sakurada equation.²⁰

$$[\eta] = 2.43 \times 10^{-4} M_v^{0.75}$$

Because the above parameters are corrected strictly for PAN at 25°C, the parameters for the sample in this study are expected to differ slightly from the parameters cited above. The polymer was dried under vacuum at 50°C for 24 h before use.

The degree of deacetylation of the chitosan was estimated to be 90%, which was measured by titrating chitosan solution in 0.3M HCl with 0.1M aqueous NaOH solution.²¹ The intrinsic viscosity of chitosan was obtained from the solution of chitosan and the mixture of 0.2M NaOH and 0.1M acetic acid. The M_v of chitosan was then estimated to be 8300 g/mol, according to the following equation²²:

$$[\eta] = 1.81 \times 10^{-3} M_v^{0.93}$$

DSC Measurement

The T_m and crystallization temperature (T_c) of wet polymers were measured by using a DuPont 910 DSC (DuPont, Wilmington, DE) and large-volume stainless-steel capsules (Perkin-Elmer, Part 319-0218; Perkin Elmer Cetus Instruments, Norwalk, CT), which can withstand steam pressure up to 220°C because a rubber O-ring is fitted into the top of the capsule. Polymers (PAN-88 and/or chitosan) and water at a given ratio were uniformly mixed in a high-speed mixer before DSC measurements. Approximately 50 mg of the mixture was packed into the capsule. In the measurements, both heating and cooling rates were 20°C/min.

Preparation of Composite Fibers

Melt extrusion of the mixture was performed with an apparatus constructed in our laboratory. Fibers of PAN-88 or composite fibers of chitosan/PAN were obtained by extruding the wet polymers through a circular hole of 1-mm diameter by the pressure of nitrogen gas, to avoid escaping steam during the experiment at 170°C. The pulp-shape composite fiber was easily made by beating the porous and fibril structure of the fibers in water.

Adsorption Test for Dyes

An acid dye was used for measuring the equilibrium isotherms for the adsorption of the dye on the composite fibers, chitosan powder, and activated carbon. The amount of adsorption was estimated using a calibration curve prepared by measuring the different concentrations of the dye with a UV-Vis spectrophotometer. The experiments were carried out at 30, 50, and 70°C, respectively.

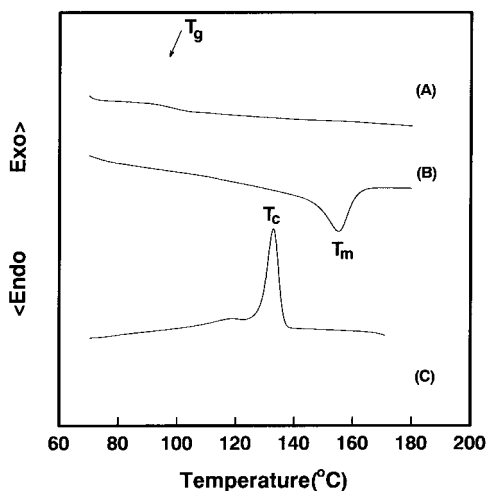


Figure 1 Effect of water on the melting behavior of PAN-88. (A) Heating of dry PAN; (B and C): heating and cooling of wet PAN containing 23 wt % of water (B).

RESULTS AND DISCUSSION

Melting Behavior of the Materials

The DSC curves in Figure 1 show T_m depression of PAN-88 caused by water acting as a plasticizer. As is well known, the T_m of anhydrous (dry) PAN-88 could not be observed because of exothermic side reactions below melting, although the glass-transition temperature (T_g) is observed in the vicinity of 90°C (curve A). However, it is noted that addition of water lowers the T_m of PAN-88 to 156°C (curve B), and further a distinct T_c is observed at 129°C during the cooling stage (curve C). The high T_m of PAN is mainly attributed to the chain rigidity resulting from strong interactions of neighboring nitrile groups. It has been suggested that T_m depression of PAN is caused by the reduced interactions by hydration of nitrile groups.⁹

Figure 2 represents the dependency of T_m and T_c of hydrated PAN-88 on water content. With increasing water content, T_m was rapidly decreased, but the rate of decreasing T_m was gradually reduced and finally leveled off above a critical water content, about 23 wt %, over the range of water contents observed. This critical water content is equivalent to the theoretically predicted value calculated on the assumption that one nitrile group of PAN-88 is combined with one water molecule.¹³ The excess water above this content does not contribute to the depression of

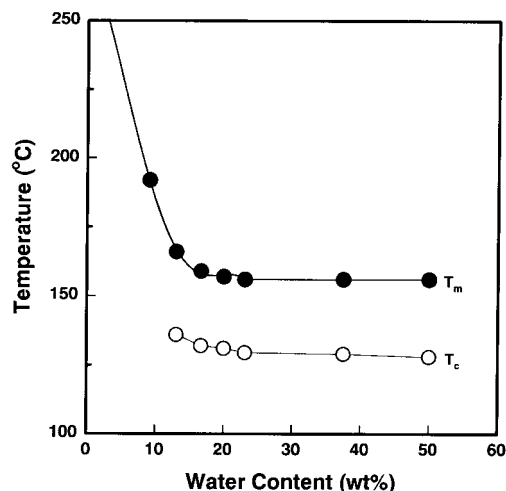


Figure 2 Variation of T_m and T_c of PAN-88 with water content.

T_m of PAN but seems to be helpful for the extrudability of the mixture.

On the other hand, chitosan itself is known as infusible similar to PAN. Moreover, wet chitosan having 50% of water also did not show any melting trace until 200°C, as seen in the DSC thermogram of Figure 3(A). This means that water does not plasticize chitosan like it does PAN. The mixture of chitosan and 1% aqueous acetic acid, which is a solvent for chitosan, was tested to understand whether it performs as a plasticizer, although it resulted in no endothermic peak, as shown in Figure 3(B). The melting behaviors of the mixtures of PAN/chitosan/water and PAN/chitosan/aqueous acetic acid were subsequently

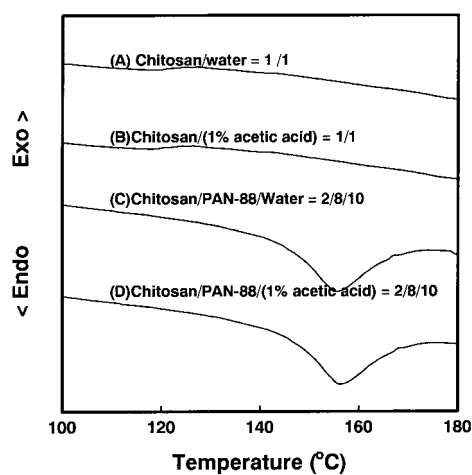


Figure 3 DSC thermograms of the mixtures.

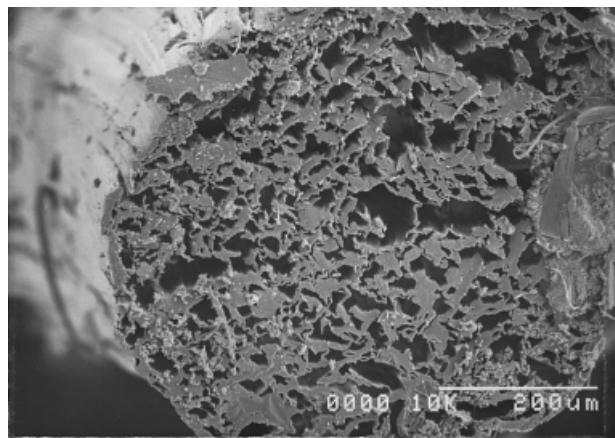


Figure 4 SEM micrograph of porous and fibrillar structure of PAN extruded from the melt formed by hydration.

investigated. They exhibited the same endothermic peak as that of PAN/water, as noted in Figure 3(C).

With these results we tried to adopt melt processing to obtain chitosan/PAN composite fibers having a potential application as a material for wastewater treatment by combining the easy and ecofriendly processibility of the PAN/water system and the adsorption functionality of chitosan.

Melt Processibility of the PAN/Chitosan Compounds

The mixture of PAN-88 and water could be extruded easily at 160°C, resulting in a porous and well-oriented fibril structure, depicted in Figure



Figure 5 SEM micrograph of pulp-shape PAN fiber obtained by pulping the porous PAN fiber.

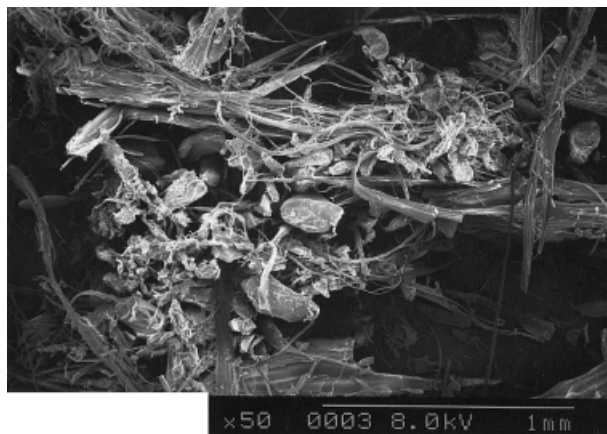


Figure 6 SEM micrograph of composite fibers obtained from the mixture of PAN/chitosan/water by the weight ratio of 80/20/100.

4, obtained by SEM. This structure was obtained from 50 wt % of water, which is higher than the critical water content of 23 wt % mentioned above. The porous structure has been reported to result from the phase separation between excess water and hydrated melt during processing.²³ The porous and fibrillar structure could be converted easily into pulplike short fibers, as shown in Figure 5.

However, wet chitosan containing either neat water or diluted acetic acid was not extrudable. Therefore, the extrudability of the mixture of PAN-88/chitosan/water with a ratio of 80/20/100 by weight was tested. As shown in Figure 6, chitosan particles still remained without melting,

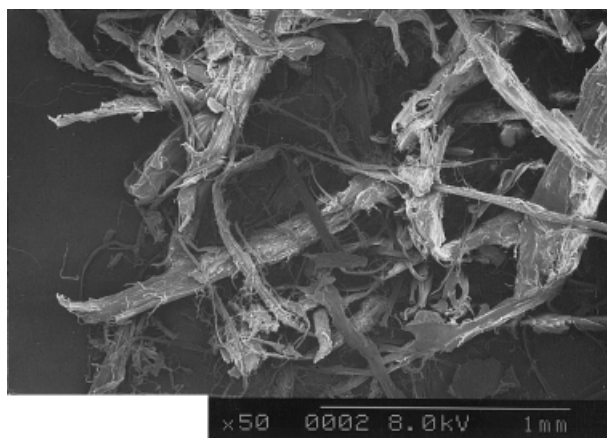
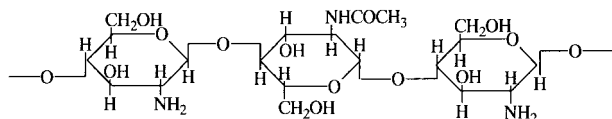


Figure 7 SEM micrograph of composite fibers obtained from the mixture of PAN/chitosan/diluted acetic acid by the weight ratio of 80/20/100.



Scheme 1 Chemical structure of chitosan.

even though the PAN was transformed to fibers. Most of the chitosan powder was separated from the fibrils of PAN while the extruded bundle was beaten to transform to pulp shape. This is evidence that neat water cannot play a role to plasticize chitosan. This problem was solved by using diluted acetic acid as a plasticizer instead of neat water. It was found that homogeneous composite fiber can be obtained from the mixture of PAN-88/chitosan containing acid water. As depicted in Figure 7, no chitosan powder was found after extrusion by using 1% acetic acid instead of pure water. This result implies that chitosan was plasticized, resulting in coextrusion with PAN; however, by comparing the results of Figures 5 and 7, it is noted that with the addition of chitosan the degree of fibrillation was reduced. An amount of chitosan of more than 20% of the solid made it difficult to extrude the mixture.

Conclusively, the composite fiber of PAN and chitosan could be made by extrusion of the mixture containing diluted acetic acid as a plasticizer.

Sorption Properties of the Composite Fibers

Chitosan, containing many amine groups (Scheme 1), is known as a good sorptive material for heavy metals or dyes.¹ Chitosan has been known to show an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, vat, sulfur, and naphthol dyes.² The only class for which chitosan has low affinity is basic dyes.

Sorption is influenced by many physicochemical factors, including sorbate/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. Many common sorbents have ionic interactions or a highly porous structure, as found in activated carbon, with extremely high specific surface area, which is ideal for sorption. From this viewpoint, PAN/chitosan composite fiber is expected to exhibit better sorption properties than those of powdery chitosan because of its higher surface area compared to the same amount of chitosan.

From the isothermal adsorption of an acid dye at 35°C by the three kinds of sorbents shown in Figure 8, it is noted that PAN/chitosan pulp showed a much higher rate of acid dye uptake than that of either powdery chitosan or activated carbon, which is used for color removal from the wastewater of the dyeing industry. This uptake was normalized on the basis of the same amount of chitosan. Given that PAN-88, which has no

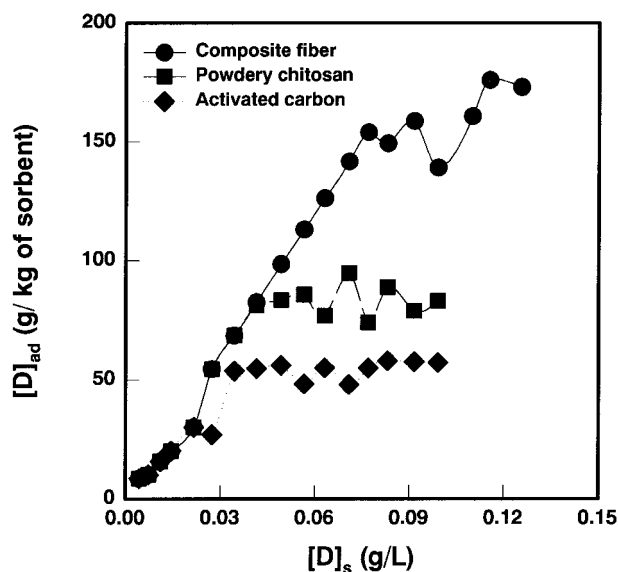


Figure 8 Sorption isotherm of an acid dye by the sorbents at 35°C.

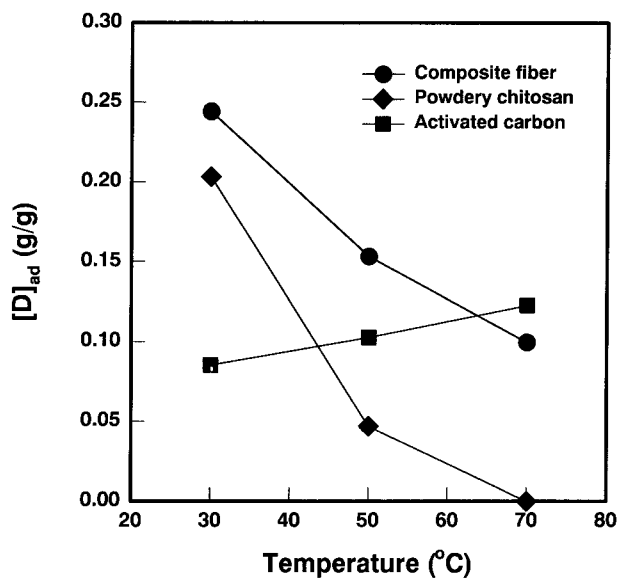


Figure 9 Effect of temperature on the adsorption of an acid dye by the sorbents.

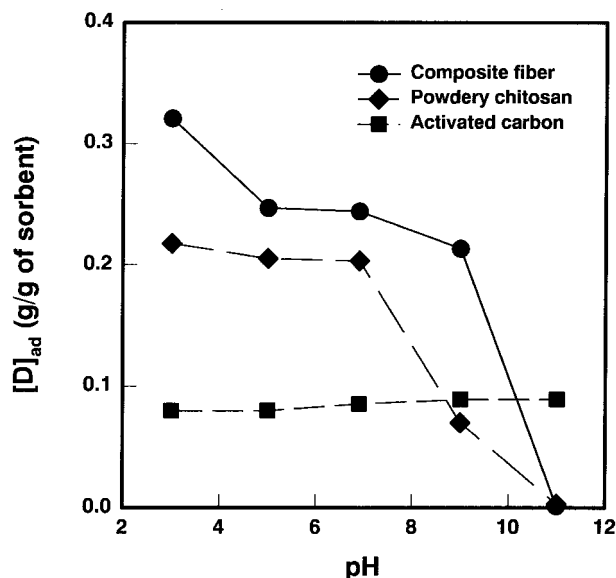


Figure 10 Effect of pH on the adsorption of an acid dye by the sorbents.

basic groups, does not adsorb acid dye, this better sorption for the composite fiber is considered to result from the relatively large surface area of chitosan in the composite than that of the powder.

Although the powdery chitosan and activated carbon exhibited Langmuir adsorption behavior, showing an equilibrium after the sorption sites were exhausted, the composite fiber did not show a clear leveling off in the range of concentrations tested. This result seems to imply that pulp-shape chitosan has a greater number of effective sorption sites than that of powdery chitosan. It is also noted that the powdery chitosan still showed a higher amount of dye adsorption than that of activated carbon.

Figure 9 shows the effect of temperature on the dye adsorption of the sorbents. Because adsorption of dyes by chitosan is exothermic,² an increase in temperature leads to an increase in dye sorption rate, but diminishes total sorption capacity. The amounts of dye adsorbed by both the composite fiber and powdery chitosan decreased rapidly with increase in temperature. On the other hand, activated carbon showed increasing adsorption with increase of temperature.

Moreover, wastewater pH may be an important factor in the sorption of certain dyes onto chitosan because the sorption mechanism of chitosan to acid dye is an acid–base reaction between amine groups in chitosan and sulfonated anions of acid dyes.⁴ At low pH, chitosan's free amines are pro-

tonated, causing them to attract anionic dyes (i.e., acid dyes). As depicted in Figure 10, the adsorption of both types of chitosan decreased with increase of pH. Above a pH of 10, they showed no adsorption to acid dyes. In comparison, there is no effect of pH on the activated carbon.

CONCLUSIONS

The mixture of PAN-88/chitosan/water can be extruded from the hydrated melt state, resulting in a porous and fibrillar structure. However, wet chitosan containing neat water or diluted acetic acid was not extrudable. Moreover, diluted acetic acid was more effective than neat water in plasticizing chitosan, resulting in a homogeneous composite fiber of PAN and chitosan. This implies that water plasticizes the PAN and acetic acid plasticizes the chitosan. However, the addition of chitosan reduced the degree of fibrillation of PAN after extrusion from the hydrated melt. From the adsorption of acid dye by the composite fiber, it is noted that the pulp-shape fiber showed a much higher rate of uptake of acid dye than that of powdery chitosan because of its higher surface area. We hope that this material can be applied to the treatment of industrial wastewater containing dyes.

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