Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yu, Chengbing and Chen, Yanmo(2006) 'Study on Dyeing Properties of Functional Acrylic Fiber', Journal of Macromolecular Science, Part A, 43: 11, 1695 — 1702
To link to this Article: DOI: 10.1080/10601320600938983
URL: http://dx.doi.org/10.1080/10601320600938983

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1695–1702, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600938983

Study on Dyeing Properties of Functional Acrylic Fiber

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Anti-mite acrylic fiber is a new type of functional fiber which incorporates a small amount of anti-mite agent. Basic dye can be used in the dyeing of the functional acrylic fiber. Compared with the dyeing properties of conventional fibers, the dyeing properties of the functional acrylic fiber have new characteristics such as different dyeing temperature, time, amount of leveling agent and pH level due to the rough surface and larger size of micro-channels in the functional fiber structure that helps basic dye molecules to diffuse into the fiber.

Keywords anti-mite acrylic fiber, dyeing, equilibrium dye uptake, diffusion, basic dye, functional fiber

Introduction

With the rapid improvement of people's living level, higher demand on dress including various functional fibers has occurred. Various inventions have provided acrylic fibers with the properties of anti-microbial, anti-fungal and anti-yeast (1), anti-pilling (2), anti-snag (3), high luster and anti-soiling (4), anti-crease (5), anti-odor (6) and other special functions, all based on inorganic/organic additives. The harm of mites to humans has been recognized and numerous anti-mite measures have been taken. Development of anti-mite fiber occurred in the 1980s and several anti-mite products (7–9) have been put into the market.

It is known that basic dye can be used in acrylic fiber in conventional dyeing processes. Some articles have described the chemical composition of basic dyes and their properties, and the dyeing behavior and kinetics with basic dyes in the exhaustion dyeing of acrylic fiber (10–12). Factors affecting the dyeing of acrylic fiber, the fundamentals of dyeing and the problems of dyestuff migration were discussed by Agnihotri (13). The equilibrium sorption of two basic dyes by acrylic fibers at different pH levels and sodium chloride concentrations was studied by Alberghina et al. (14) In this article, the dye distribution coefficients were discussed in relation to the structures of the dyes

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and the fibers and the effect of sodium chloride. The equilibrium sorption at different pH levels indicates to some extent the strength of the strongly and weakly acidic groups in the acrylic fibers not immediately accessible by experiment. The effect of a range of dyebath additives on the thermal behavior, swellability and second-order glass transition temperature of an acrylic fiber (Leacril) was studied to correlate fiber properties with dyebath conditions by Achi et al. (15). In all these works, they studied conventional acrylic fibers. However, there exist many difficulties in applying these dyeing theories to the dyeing of functional acrylic fibers, because there are different sizes of micro-channels in the fiber structure.

A new kind of functional acrylic fiber with self-made anti-mite additive has been developed by Shanghai Petrochemicals Co., Ltd. The structure of the functional acrylic fiber, which is modified with the anti-mite agent, changes and the dyeing properties of these anti-mite acrylic fibers have many new characteristics. In this paper, the dyeing properties of these anti-mite acrylic fiber were analyzed, with the dye uptake of these functional fibers compared with that of conventional acrylic fibers under normal dyeing conditions.

Experimental

Material

Commercial acrylic fiber (0.89dtex) and anti-mite acrylic fiber (0.89dtex), provided by Shanghai Petrochemicals Company Ltd., were purified by extracting the spinning oil with dimethyl ether for 4 h in a Soxhlet extractor.

Commercial cationic yellow 7GL (C.I. Basic Yellow 24) was used in the present study. Purification of the basic dye was carried out according to the method suggested by Balmforth et al. (16). The dye was extracted with 10 volumes of boiling absolute alcohol. Easily filterable crystals were recovered after chilling the solution overnight. This procedure was repeated three times to insure good purity of about 99.9%.

Dyeing and Characterization

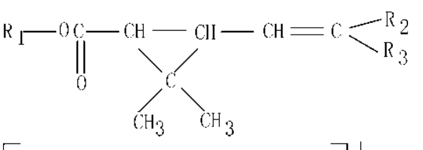
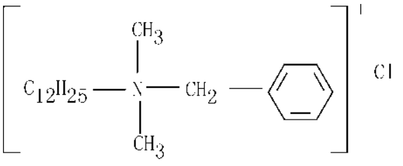
The commercial dyeing formula for 50 mg acrylic fiber was used in terms of dyeing time, temperature, concentration of dye, amount of anhydrous sodium sulfate and leveling agent 1227 (Table 1), sodium acetate and acetic acid was added to a selected pH value. The H_2O/fiber ratio was 100:1. After the dyeing, the fibers were taken out immediately and washed with cold water. Absorbed dye concentration in the fibers was determined by extraction in a mixed solvent of dimethylformamide/$H_2O = 88:1$ at 90°C, followed by colorimetry, which was recorded on a Hitachi U-3210 Spectrophotometer. The scanning electron micrographs (SEM) were obtained by means of a JSM-5600LV microscope.

Results and Discussion

SEM Micrographs of Anti-Mite Acrylic Fiber

Figure 1 shows SEM micrographs of conventional acrylic fiber and anti-mite acrylic fiber. Both fibers show a large amount of defects and crackle in the surface. This confirms that acrylic fibers are formed by violent coagulation in the wet-spun process. The

Table 1
The structure and amount of chemicals

Chemicals	Chemical ingredients	Chemical structure	Amount used
Anti-mite additive	Special dimethrin		4–8% of weight fiber
Leveling agent 1227	Alkyl aryl quaternary ammonium salt		0–2% of weight fiber

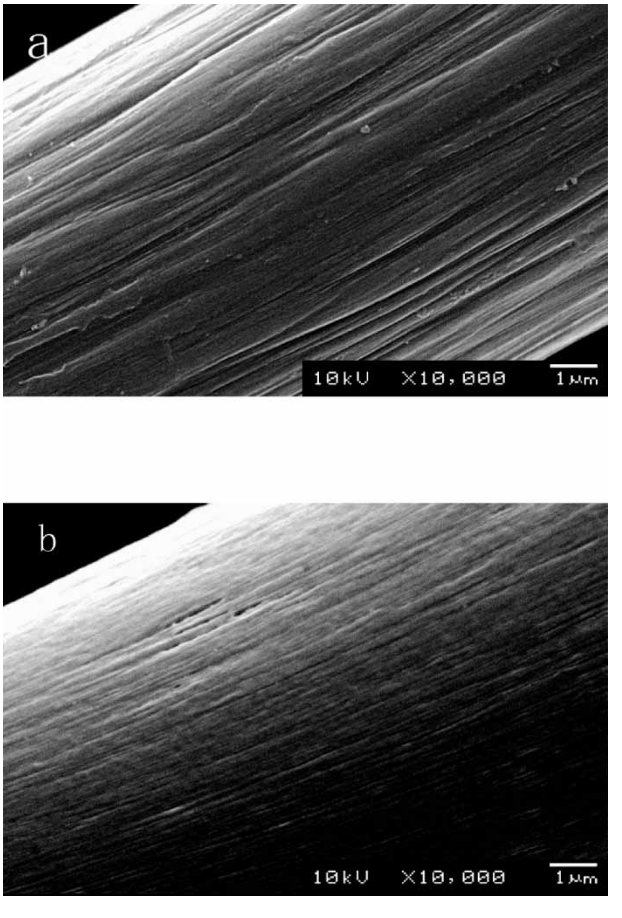


Figure 1. SEM image of acrylic fiber: (a) functional acrylic fiber, (b) conventional acrylic fiber.

micro-channels with sizes bigger than ten micron are formed by penetration of precipitant and water into the fiber; they are difficult to eliminate in the following procedures of drawing, drying and heater treatment (17). The acrylic fiber used in the present experiment was spun with the wet spinning method, the polymer having been blended with a small amount of anti-mite agent in the spinning solution. A rough surface and larger micro-channels were observed in the functional acrylic fibers, which makes dye easily diffuse into the fiber (Figures 1a and b).

Influence of Dyeing Temperature on Dye Uptake

Dyeing temperature has a large influence on the dye uptake of anti-mite acrylic fiber. Figure 2 shows equilibrium dye uptake of acrylic fiber and anti-mite acrylic fiber at different dyeing temperatures, 24 h and pH 4.5, without anhydrous sodium sulfate and leveling agent 1227. It is seen that the tendency of these curves is very similar. With the increasing of dyeing temperature, equilibrium dye uptake of these acrylic fibers increases very slowly below 65°C, but rapidly at temperatures from 65°C to 95°C and slowly again above 95°C. The size of the basic dye molecule used is nearly the same as the size of the space between acrylic molecules in the static state and thus the dye molecule is very difficult to diffuse into fiber at least up to the glass transition temperature (18).

Figure 2 also shows that equilibrium dye uptake of the functional acrylic fiber is always higher than that of conventional fibers at temperatures below 80°C. After being incorporated with 4% anti-mite agent, the size of micro-channels in the structure of functional fiber becomes larger, helping the dye molecule to diffuse into the fiber (19, 20). Therefore, the initial heating-up time stage for anti-mite acrylic fiber should be 5°C below that of the conventional dyeing process of acrylic fiber. In the meantime, with rising dyeing temperature, the mobility of molecule chain segments in the acrylic fibers becomes faster and faster, and equilibrium dye uptake depends mainly on the amount of sulfonic acid group in the fiber. The equilibrium dye uptake of anti-mite acrylic fiber is less than that of conventional acrylic fiber at above 80°C was found.

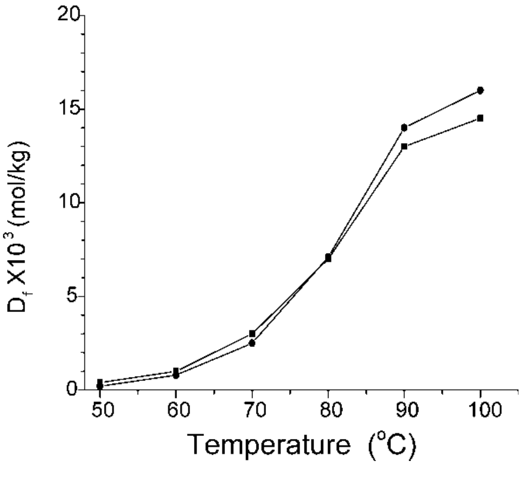


Figure 2. Influence of dyeing temperature on dye uptake: (■) Anti-mite acrylic fiber, (●) Conventional acrylic fiber.

Influence of Dyeing Time on Dye Uptake

Figure 3 shows the dye uptake of conventional acrylic fiber and anti-mite acrylic fiber as a function of time, at 100°C and pH 4.5, without anhydrous sodium sulfate and leveling agent 1227. The rate of dyeing is very fast in the initial stage. A convenient experimental apparatus was developed by Yoichiro et al. (21) for analyzing the initial stage of several seconds at the start of the dyeing process under rapid adsorption conditions. They found the initial stage adsorption one second after the start of the dyeing process is 6% and three seconds after the start, 9.6% is already adsorbed in the fiber. Compared with the dyeing curve of conventional acrylic fiber, higher dye uptake occurs in the first half-stage and lower dye uptake in the second half-stage of anti-mite acrylic fiber, resulting from the rough surface and larger micro-channels in the structure of anti-mite acrylic fiber. Equilibrium dye uptake is achieved within two hours of dyeing time, and prolonging the dyeing time is unnecessary.

Influence of Leveling Agent on Dye Uptake

The dyeing rate is high at temperatures above the glass transition temperature due to a strong affinity between basic dyes and acrylic fiber, and the migration of basic dye molecules becomes very difficult after being adsorbed on the fiber. Therefore, a leveling agent is necessary in the dyeing bath for even color.

Sodium sulfate is usually used as a leveling agent in a dyeing bath. In order to verify the leveling effect of the salt, we made measurements at different concentrations of sodium sulfate. The salt effect is clearly shown in Figure 4. The increase of ionic strength decreases the amount of equilibrium sorption of the dye due to the competitive sorption of sodium cation on the negatively charged fixed sites in the fiber.

A larger decrease in dye absorption was obtained with leveling agent 1227 (Figure 5). Leveling agent 1227 appears to be a strong competitor for dye cation sorption. The

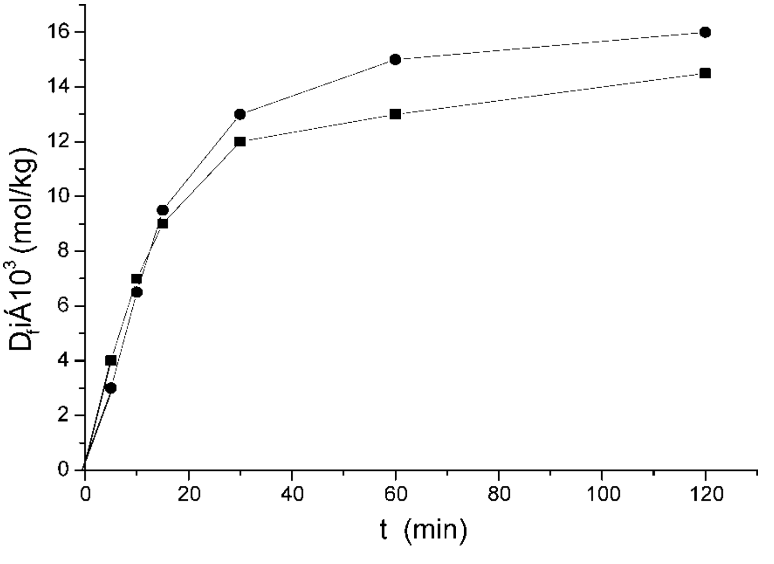


Figure 3. Influence of dyeing time on dye uptake: (■) Anti-mite acrylic fiber, (●) Conventional acrylic fiber.

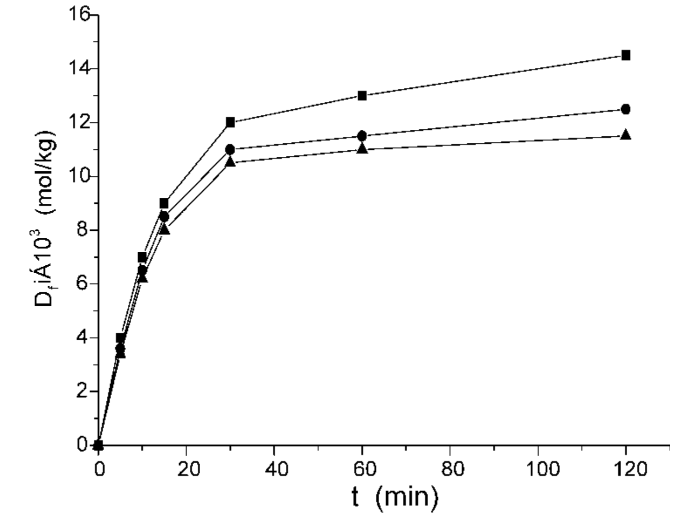


Figure 4. Influence of sodium sulfate on dye uptake: (■) 0% of weight fiber, (●) 1% of weight fiber, (▲) 2% of weight fiber.

leveling mechanism of leveling agent 1227 is that the leveling agent forms electrovalent bonds with sulfonic acid groups in the fiber at the beginning of dyeing and the basic dye gradually substitutes for leveling agent with increase of dyeing temperature because the electrovalent bond between basic dye and sulfonic acid group is more stable than that between leveling agent 1227 and sulfonic acid group (22). The amount of the dye uptake is markedly influenced by the dye cation, decreasing with increasing size of the ion (23). Notwithstanding obtaining even color of dyed fiber, it is suggested that the

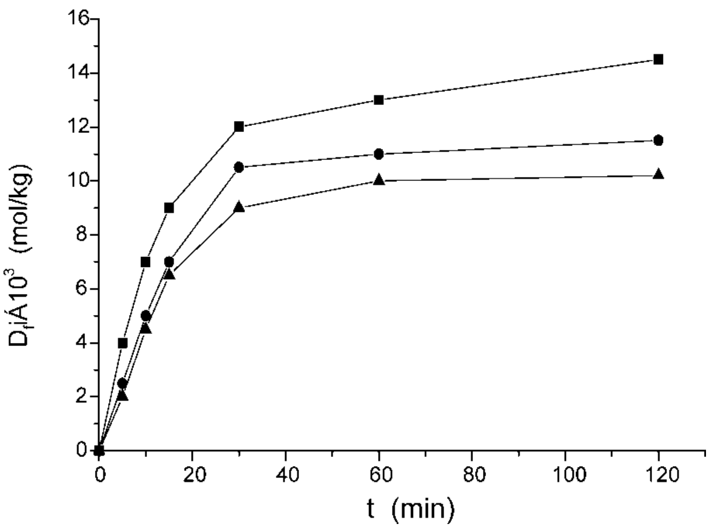


Figure 5. Influence of leveling agent 1227 on dye uptake: (■) 0% of weight fiber, (●)1% of weight fiber, (▲) 2% of weight fiber.

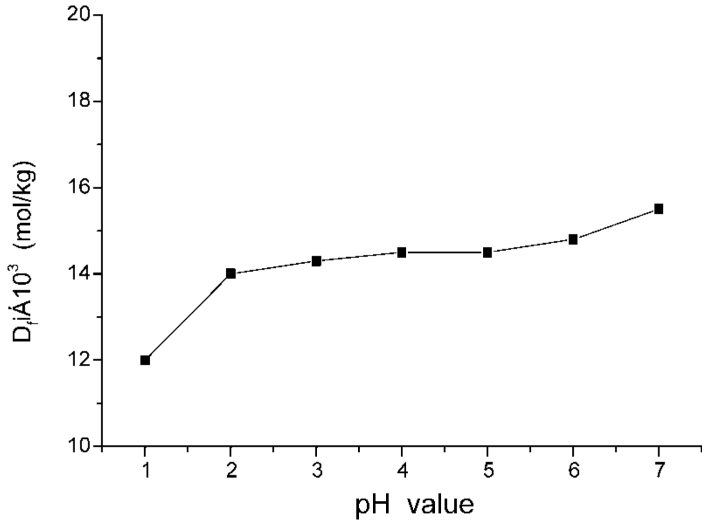


Figure 6. Influence of pH on dye uptake of anti-mite acrylic fiber.

amount of leveling agent should be minimized due to decreasing the equilibrium concentration of dye cation.

Influence of pH Value on Dye Uptake

In studying the change in dye sorption at different pH, it is very important to understand the dyeing mechanism of acrylic fibers with basic dyes. The changes in dye sorption resulting from changes in pH are as dependent on the number and strength of acidic groups present on the fiber (24).

The sorption isotherms of cationic yellow 7GL in the pH range of 2–6 are quite similar (Figure 6), indicating that in this range the strongly acidic groups are completely ionized or present as a mixture of the ionized and sodium forms. The dye uptake at pH below 2 is low, indicating that the strongly acidic groups at this pH are not completely ionized. On the other hand, some types of dye molecules are prone to color degradation, precipitation and destruction. Therefore, pH in the range 4–5.5 is recommended as the dye pH for functional acrylic fiber.

Conclusions

Basic dye can be used in the dyeing of anti-mite acrylic fiber. Dyeing conditions, including dyeing temperature, dyeing time, and pH value and dyeing auxiliaries, all have influence on dye uptake. The temperature at the initial heating-up stage of anti-mite acrylic fiber dyeing should be 5°C lower than that of the conventional dyeing process due to larger size of micro-channels of the fiber to help dye molecules to diffuse into the fiber after blending with anti-mite agent. The rate of dyeing is very fast in the initial stage. Equilibrium dye uptake is achieved within two hours of dyeing time. PH in the range 4–5.5 is suitable for the dyeing of anti-mite acrylic fiber. Leveling agent in the dyeing bath should be used for even color. But sodium sulfate and leveling agent 1227 should be minimized to have even dyeing, due to decreasing the equilibrium dye uptake.

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