Acid-Dye-Dyeable Polyacrylonitrile/Poly(*N,N*-dilkylaminoethylacrylate) Acrylic Blend Fiber

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ABSTRACT: An acid-dye-dyeable polyacrylonitrile/poly(*N,N*-dilkylaminoethylacrylate) blend fiber was prepared. On the basis of research for the dye uptake, color strength, tensile strength, and breaking elongation of the polyacrylonitrile/poly(*N,N*-dilkylaminoethylacrylate) blend fiber, it was found that the blend fiber and its fabrics for acid dyes possessed favorable dyeability and mechanical properties. The effect of the polyacrylonitrile ratio on the blend fiber was examined. The optimum dyeing-process parameters were determined. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 84–88, 2007

Key words: blends; fibers; functionalization of polymers

INTRODUCTION

Acid-dyeable polyacrylonitrile fibers (ADFs) were the main products of some manufacturers when the manufacturing industry began in the 1950s. However, they were soon replaced by cationic-dyeable polyacrylonitrile fibers (CDFs) because of their high production cost and the great improvement in cationic dyes. Polyacrylonitrile (PAN) fibers, to be dyed with acid dyes, were brought into industrial use through the copolymerization of vinyl comonomers containing pyridine rings.[1,2] Vinyl pyridines were then selected as the dyes of choice after a great number of studies on vinyl comonomers. In the 1960s, although most of the acrylic fiber manufacturers were focusing on producing CDFs, ADFs came back onto the market as specialty-type fibers for differential cross-dyeing.[3] In this new approach, the ADF component is used to complement the main product of CDFs to achieve improved style in textiles through more economical cross-dyeing of yarns or piece goods. Additionally, fibers and resins containing basic amino nitrogen have attracted great attention as antimicrobial materials.[4,5] Recently, we prepared an acid-dyeable PAN blend fiber by a copolymerization method.[6–9]

In this study, an acid-dye-dyeable PAN/poly(*N,N*-dilkylaminoethylacrylate) (PDA) blend fiber was subsequently prepared with different PAN/PDA ratios. In the blend fiber, PDA could provide dyeing sites for the acid dye to make the blend fiber possess acid-dye dyeability.

EXPERIMENTAL

Preparation of PDA

Liquid paraffin, *N,N*-dilkylaminoethylacrylate, and sodium dodecyl benzene sulfonate were charged into a 250-mL, three-necked flask equipped with a mechanical stirrer and a reflux condenser under nitrogen. After the mixture was stirred for 5 min, potassium persulfate was dissolved in 15 mL of distilled water and added dropwise to the three-necked flask. The polymerization was carried out at 55°C for 6–7 h. The polymer was washed with acetone and dried in a vacuum oven at 40–50°C for 2 h. In this case, PDA powders were obtained.

Preparation of the spinning solution

PAN and PDA powders were dissolved in a sodium thiocyanate (NaSCN) aqueous solution in different weight ratios. The blend powder was first put into an NaSCN aqueous solution and stirred at room temperature for 24 h; then, the blend polymer solution with a polymer concentration of 12 wt % and an NaSCN concentration of 45 wt % was prepared. The solutions were stirred at 60°C for 5 h. Before the spinning, the blend polymer solution was filtered to meet the requirements of spinning.

Spinning of the blend fiber

Under a pressure of 300 kPa, the blend polymer was spun by a spinneret with a diameter of 100 μm and a length/diameter ratio of 1.0. The primary fiber was formed in a coagulation bath, and then the fiber was drawn 1.5 times in a warming bath at a temperature

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of 95°C. Finally, the obtained filament was washed with distilled water and dried in a vacuum oven at 50°C for 24 h.

Dyeing experiments

The fabrics made of the blend fibers were dyed. All dyeing, including the blend fiber and its fabrics, was carried out in sealed stainless dye tubes at a liquor ratio of 100 : 1 with a little high temperature (LHD) dyeing machine. The pH of the mixture was adjusted to 2–7. The mixture was heated to 100°C for an hour. The sample was filtered, washed, and dried.

Measurements of the dye uptake and color strength

The absorbance was tested with a spectral photometer made in Exactitude Instrument Company of Shanghai (China) according to the following formula: $A = \log(I_0/I) = \varepsilon bC$, where A is the absorbance; C is the dye concentration; I_0 and I are the strengths of the incident light and transmission light, respectively; ε is the absorption coefficient; and b is the light path length of the solution. The absorbance and concentration of the staining solution had a quantitative relationship. First, a series of absorbances for different dye concentrations of the staining solution was measured. A concentration–absorbance standard curve diagram was drawn. The absorbance of the residual dye in the solutions, after the removal of the dyed copolymer, was tested. Through a comparison with the concentration–absorbance standard curve, the concentration of the staining solution could be obtained. Thus, the dye uptake (R) of the specimens was determined with the following equation:

$$R(\%)'(1 - C/C_0) \times 100\% \qquad (1)$$

where C is the concentration of the staining solution and C_0 is the original concentration of the staining solution.

The relative color strength (K/S, where S is the scattering coefficient and K is the absorption coefficient) of the dyed fabrics made from the blend fiber was measured by a light reflectance technique with the Kubelka–Munk equation [eq. (2)]. In the process, the undyed fabrics were using as corresponding substrates. The reflectance (R) of the dyed fabrics was measured with a model Ics-3000 reflectance spectrophotometer (Dione, USA):

$$K/S = (1 - R)^2/2R \qquad (2)$$

Measurement of the thermal properties of the blend fibers

A differential scanning calorimetry (DSC) analysis was carried out on a Netzsch 204 F1 (Kerkin Klmer,

Germany) differential scanning calorimeter operating from 20 to 250°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Measurement of the tensile strength and breaking elongation of the blend fibers

The mechanical properties of the blend fibers were measured with an XQ-1 fiber analysis instrument made in Donghua University of Shanghai (China), at a temperature of 25°C and a relative humidity of 65%, respectively. The gauge length and crosshead speed were 20 mm and 20 mm/min, respectively.

RESULTS AND DISCUSSION

Effect of the PDA ratio on the dye uptake and K/S values

Figures 1 and 2 show that with an increase in the content of PDA, the dye uptake and K/S values of the PAN/PDA blend fiber increase. Because of the basic groups in the PDA chains, they offer branches that can combine with dye molecules, and they are helpful to acid-dye dyeing. Therefore, the addition of PDA can effectively improve the dye function of the blend fiber and its fabrics.

However, this tendency levels off after a PDA concentration of 10 wt %. When the concentration of PDA exceeds 10 wt %, the inhomogeneity of the blend fiber will increase, and this will influence the spinnability of the PAN/PDA blend fiber remarkably. It is highly effective to fix the amount of N,N-dilkylaminoethylacrylate added at about 5 wt % for the fabrication of an acid-dyeable blend fiber.
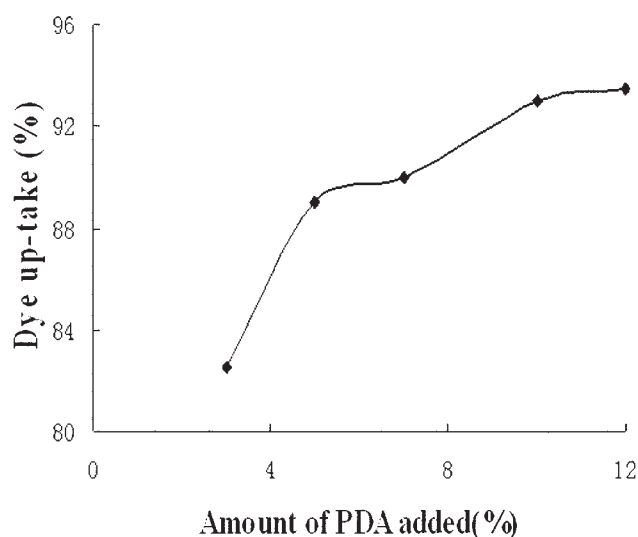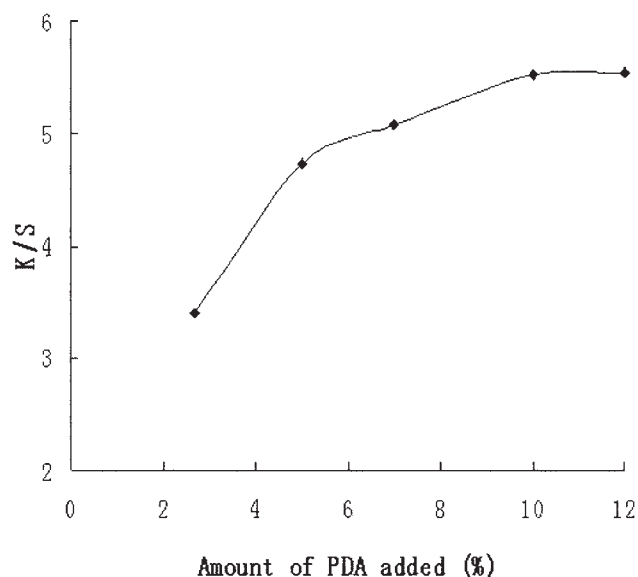

Figure 1 Dyeing curve of the blend fiber.

Figure 2 K/S curve of the dyed fabrics (pH 4, 90°C).

Figure 4 K/S values of the dyed fabrics at various temperatures (pH 4): (a) 5% PDA and (b) 10% PDA.

Effect of the dyeing-process variables on the color strength

The color strengths of the dyed fabrics at various dye-bath pHs are given in Figure 3. K/S is maintained at a high level at pHs of 2–4. The color strength of the dyed fabrics is not affected by pH changes over a wide range because the basic amido groups of the PDA chains remain ionized even in a weakly acidic dye bath.[10,11] K/S decreases as the pH increases beyond 4.0. Thus, the dyed fabrics have a stable and high level of dyeability in a wide weakly acidic range because of the basicity.

Figure 4 shows the dyeability behavior for the dyed fabrics at different temperatures. The color strength
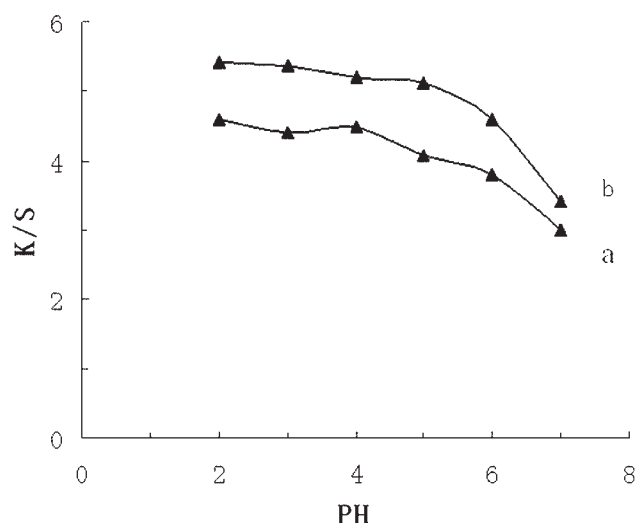
of the dyed fabrics increases rapidly above 70°C and reaches a maximum level at about 80–85°C, which is around the glass-transition temperature (T_g) of the acrylic fiber. Above T_g of the fiber, at which the polymer chain segmental movement occurs, the free volume within the polymer chain increases, and this allows more dye molecules to migrate into the inner fiber easily and results in a higher color strength for the dyed fabrics. Although the dyeing is faster above T_g, the optimal temperature of 90°C has been selected to avoid any potentially undesirable side reactions in the fiber.

The color strength/time curves of the dyed fabrics are shown in Figure 5. At 90°C, K/S increases as the dyeing time increases. The rate of the color yield is

Figure 3 K/S values of the dyed fabrics at various dye-bath pHs (90°C, 100 : 1 liquor ratio): (a) 5% PDA and (b) 10% PDA.
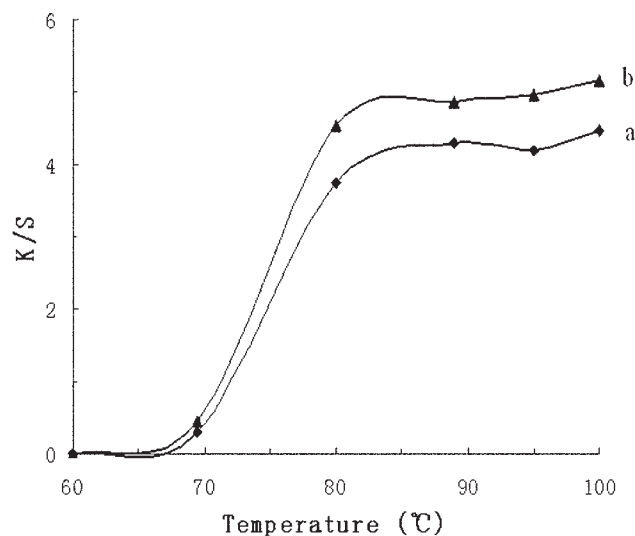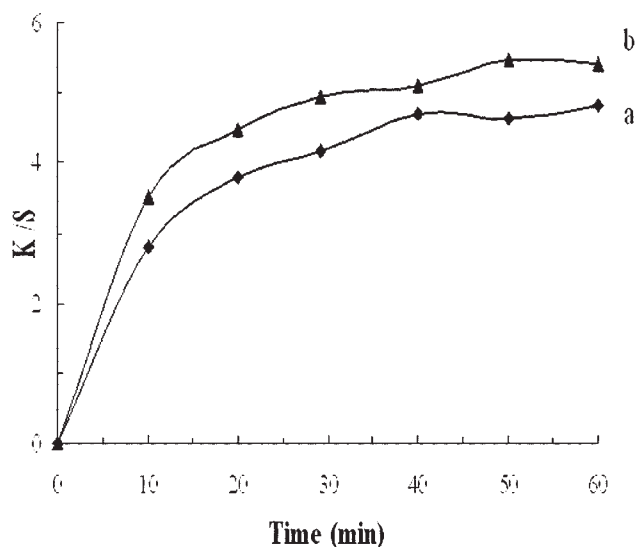

Figure 5 Effect of the dyeing time on the K/S values of the dyed fabrics (pH 4, 90°C): (a) 5% PDA and (b) 10% PDA.
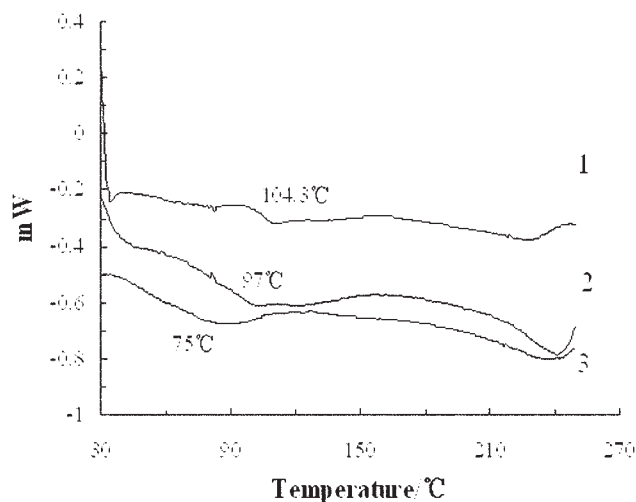
Figure 6 Comparison of DSC curves for the PAN/PDA blend fiber and reference PAN fiber: (1) PAN, (2) 5% PDA, and (3) 10% PDA.

much faster, with the color strength of the dyed fabrics reaching a plateau after only 20 min. The color strength increases slowly from 20 to 40 min.

Thermal properties of the blend fiber

To express the thermal properties of the blend fiber, DSC curves for the blend fiber were recorded, as shown in Figure 6. The curves show that T_g for the blend fiber is visibly reduced versus that of the PAN fiber.

Meanwhile, for the PAN/PDA blend fiber, with an increasing PDA ratio, the laterally ordered distribution of the PAN/PDA blend fiber changes to such an extent that its amorphous region becomes predominant. The unfolding temperature of the segments
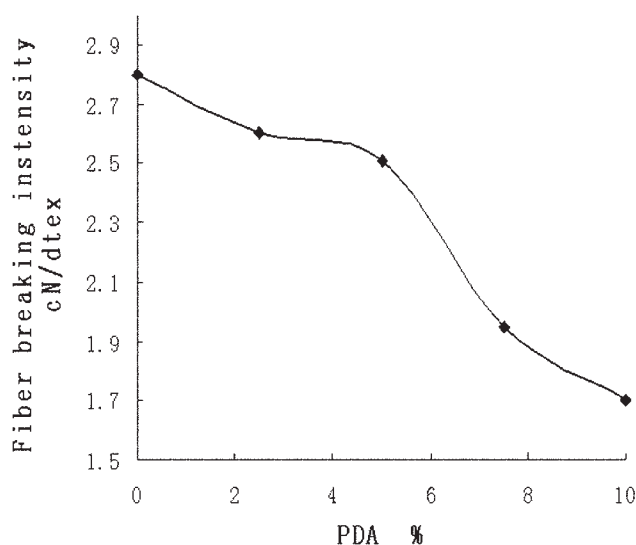

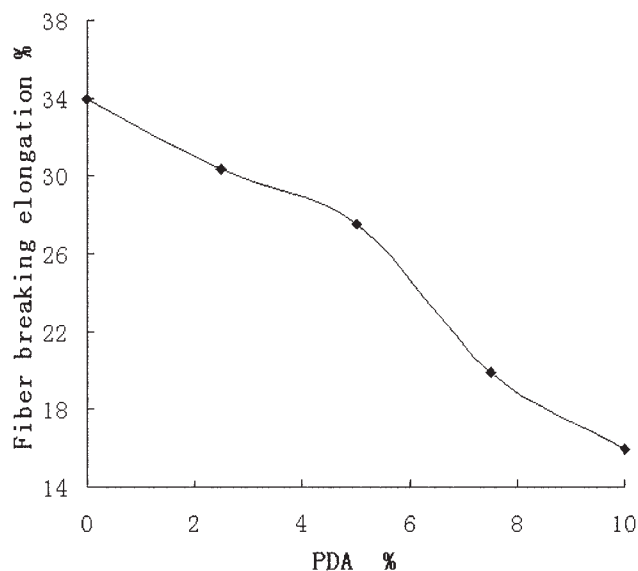**Figure 7** Effect of the PDA ratio on the tensile strength of the blend fiber.

Figure 8 Effect of the PDA ratio on the breaking elongation of the blend fiber.

between PAN chains decreases, the endothermic peak becomes broader, and the homogeneity of its structure gets worse.

Mechanical properties

The mechanical properties of the PAN/PDA blend fiber are shown in Figures 7 and 8. The strength of the PAN/PDA blend fiber is lower than that of the pure PAN fiber. When the amount of PDA increases, the tensile strength of the PAN/PDA blend fiber drops. The reason is that the PDA molecules have long side chains, which result in the distance between the molecules increasing and the interaction force of the molecules decreasing. In addition, increasing amounts of PDA destroy the regularity of the PAN chains, and thus the tensile strength and the breaking elongation drop.

To prepare the acid-dye-dyeable PAN/PDA blend fiber, the added amount of PDA is expected to be high to make a good acid-dye-dyeable fiber. However, a high added amount causes the mechanical properties of the blend fiber to become poor. An added concentration of 5 wt % PDA is appropriate for the mechanical properties and dyeability of the PAN/PDA blend fibers.

CONCLUSIONS

With an increase in the content of PDA, the dye uptake of an PAN/PDA blend fiber for acid dyes increases; the tensile strength and breaking elongation of the PAN/PDA blend fiber decrease. pH values of 2–4, a temperature of 90°C, a dyeing time of 40 min are optimum for the dyeing process. On the basis of

dye uptake (%), color strength, and mechanical properties of the blend fiber, a PDA concentration of 5 wt % is optimum for the blend fiber.

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