Preparation and Properties of Polyacrylonitrile Fibers with Guanidine Groups

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Abstract: The polyacrylonitrile (PAN) fibers grafted with guanidine groups were prepared by hydrolyzing with sodium hydroxide solution followed by reacting with polyhexamethylene guanidine hydrochloride (PHGC). The grafting degree could be controlled by changing the treatment time of hydrolyzed PAN fibers with PHGC. The chemical composition and morphology of the modified PAN fibers were characterized by Fourier transform infrared spectroscopy (FTIR), Elemental analysis (EA), X-ray photoelectric spectroscopy (XPS) and scanning electron microscope (SEM). The results showed that the guanidine groups were effectively grafted on the fibers. The water contact angle of the surface modified PAN fibers was reduced and moisture regain was improved significantly with the immobilization of PHGC on the fibers. Furthermore, the modified PAN fibers exhibited favorable acid dyeability at low temperature (50 °C) over a wide pH range and good mechanical properties. The simple and applicable synthesis process provides a new avenue for modification of PAN fibers with improved hydrophilicity and acid dyeability.

Keywords: Surface modification, Polyacrylonitrile fiber, Polyhexamethylene Guanidine hydrochloride, Dyeability, Hydrophilicity

Introduction

Polyacrylonitrile fiber has been widely used in apparel, home furnishings and industrial fabrics because of its outstanding physical and chemical properties, such as good thermal stability, good abrasion resistance, and excellent property retention in environmental exposure, etc [1]. However, the highly polar nitrile groups of PAN also cause some disadvantages, such as low dye affinity, low moisture regain, and high static charge which limit its application [2].

In order to overcome these drawbacks, many efforts have been made to modify PAN fibers by various methods, including copolymerization of functional monomers, blending PAN with inorganic or organic functional materials and surface modification [3-6]. For copolymerization method, a variety of comonomers such as maleic anhydride [7,8], itaconic acid [9,10], ammonium itaconate [11], 2-acrylamido-2-methylpropane-sulfonic acid [12], N-vinylimidazol [13,14], *N*-vinyl-2-pyrollidone [15,16], vinylchloride [17], O,Odiethyl-O-allyl thiophosphate [18] and dialkyl-p-vinylbenzyl phosphonates [19] were used to endow PAN fibers with different functions like hydrophilicity, dyeability, antibacterial property, biocompatibility and flame-retardancy. Copolymerization has been proved as an effective method to obtain functional PAN fibers, but the complicated process, high cost of manufacture, and the requirement of special dissolving and spinning processes limit its practical application. Over the last decades, blending process, a simple and low production cost method, has been widely used to modify PAN fibers. Incorporation of carbon black [20,21], carbon nanotube [22,23], graphene oxide [24,25], zirconium dioxide [26], polyaniline [27], polyvinylidine fluoride [28,29],

polystyrene [30], poly(p-vinylphenol) [31], cellulose [32,33] and N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride [2,34] provide PAN fibers with various properties such as conductivity, thermal and tribological properties, hydrophilicity, ionic conductivity and electrochemical stability. However, the dispersion of inorganic particles in the high viscosity PAN spinning dope and compatibility between PAN and blended functional polymers become the key issues.

Recently, the surface modification has attracted much attention because of its simplicity, low production cost and easy for mass production. The nitrile groups of PAN can be converted into active groups (acid or amide) by chemical reaction. These active groups can further be used to prepare functional PAN fibers. These modifications limit to the surface so the original properties of PAN fibers could be preserved. There have been a large number of studies on surface modification of PAN fibers using hydrazine [35], hydroxylamine [36-38], chitosan [39], polyethyleneimine [40] polyetherimide [41], aqueous polyurethane [42] and enzymes [43]. These functionalized fibers were extensively used in the fields like water treatment, pervaporation, ion exchange materials, and biomedical applications.

PHGC is well-known for its wide spectrum of antimicrobial activity and low mammalian toxicity [44-47], which has been used as functional fillers in anti-bacterial materials such as cellulose, polypropylene, polyethylene and polyamide [48-50]. More recently, Wei *et al.* [51] prepared modified PAN fibers via copolymerization of acrylonitrile (AN) and M-PHGC (an oligomer prepared by the reaction of PHGC and glycidyl methacrylate). These fibers exhibited good antibacterial activity. Mei *et al.* [52] prepared electrospun PAN nanofibrous membranes functionalized with PHGC by a three-step reaction. These nanofibrous membranes possessed a combination of

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antibacterial and easy-cleaning properties.

Besides the antibacterial activity, the guanidine groups of PHGC can also provide fabric with cationic dyeing sites and improved hydrophilicity. In this paper, PAN fibers with guanidine groups were prepared through a two-step surface modification. The acid dyeability and hydrophilicity of the PHGC grafted PAN fibers were also investigated.

Experimental

Materials

The PAN fibers (a copolymer of acrylonitrile and vinyl acetate) were supplied from Zhongxin Acrylic Fibers Co., Ltd. (Ningbo, China). Polyhexamethylene guanidine hydrochloride (PHGC, M_η=2000 g/mol) was synthesized by polycondensation of guanidine hydrochloride and 1,6-hexamethylenediamine in two steps in our previous work [53]. Sodium hydroxide, guanidine hydrochloride and 1,6-hexamethylenediamine were of analytical grade and purchased from Sinopharm Chemical Reagent. Acid scarlet GR (C.I. Acid red 73) was obtained from Shanghai Jiaying Chemical Company.

Surface Modification of PAN Fibers

The process for the modification of PAN fibers is summarized in Scheme 1, including hydrolyzing of PAN fibers and grafting of PHGC. In the typical experiment, PAN fibers (4 g) were impregnated in 100 ml of 2 M NaOH aqueous solution. The reaction mixture was stirred continuously at 100 °C for 3 h (The mechanical properties of the modified fibers decreased significantly when reaction time lasted over 3 h). The fibers were then washed thoroughly with deionized water and dried in vacuum oven at 60 °C for 24 h. The modified fibers were marked as C-PAN fibers.

The C-PAN fibers were immersed in 15 wt% PHGC aqueous solution at 60 °C with occasional shaking. The fibers were then thoroughly washed with deionized water and extracted with ethanol for 12 h to remove any PHGC absorbed. Finally, the fibers were dried in a vacuum oven at 60 °C for 24 h and were marked as PHGC-g-PAN fibers. The degree of grafting can be controlled by the treatment time of
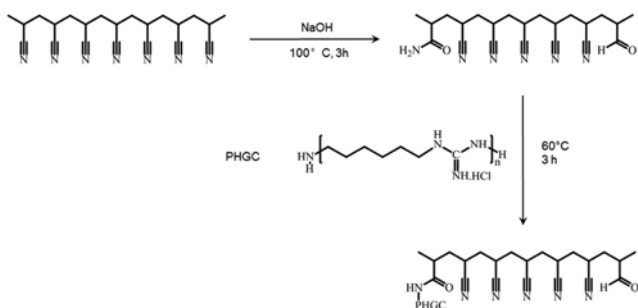
Scheme 1. Presentation of PAN fibers modification process.

C-PAN fibers with PHGC. Thus five samples were prepared by changing the treatment time from 1 h to 5 h, and these samples were marked as sample1 to sample 5.

Dyeing of PHGC-g-PAN Fibers

Dyeing was carried out using a beaker equipped with a reflux condenser in a HTF-24 laboratory dyeing-machine. The concentration of acid dye in the dye bath was fixed to 9.0 % and 18.0 % owf under a liquor ratio of 200:1. The pH of the dye bath was adjusted using sodium acetate-acetic acid buffer solution and hydrochloric acid. The PHGC-g-PAN fibers were introduced into the dyeing bath at initial dyeing temperature (40 °C) and the bath temperature was raised to 100 °C at 1 °C/min and kept for 30 min. The fibers were then thoroughly rinsed with distilled water several times and dried at 80 °C for 24 h.

Characterization

The FTIR spectra were recorded on a Nicolet 6700 FTIR spectrophotometer (USA) with a resolution of 2 cm^{-1} and scanning times of 32. The elements C, H, N were measured by a Vario el3 Elemental Analyzer (Italy). The XPS spectra were obtained by means of a PH1500C X-ray photoelectron spectrometer (Japan) in the FAT mode (using Mg Ka X-radiation). The test temperature was 25 °C and the sample chamber was pumped to about 10^{-7} Pa. The C1s spectra were deconvoluted with software XPS PEAK using a sum of Lorentzian-Gaussian functions. SEM images were recorded on a Quanta-250 instrument (Czech).

The Dye uptake (D) was determined with the following equation:

$$D = (C_0 - C_1)/C_0 \times 100\% \qquad (1)$$

where C_0 and C_1 are the dye concentrations in the dye bath before and after dyeing, respectively. A LambdaA35 UV/Vis Spectrophotometer (USA) was used to measure the dye concentration. The color parameters of fibers after dyeing were tested by a Data-Color 650 Spectrophotometer (USA). The color strength (K/S) of dyed fibers was calculated with the following Kubelka-Munk equation [54]:

$$(K/S)_\lambda = \frac{(1-R_\lambda)^2}{2R_\lambda} \qquad (2)$$

where R is the observed reflectance of dyed fiber at λ_{max}, S is the scattering coefficient at λ_{max}, and K is the absorption coefficient of the dye at λ_{max}.

Moisture regain (M) was defined as:

$$M = (W_1 - W_0)/W_0 \times 100\% \qquad (3)$$

where W_0 is the weight of dry fibers and W_1 is the weight of fibers balanced at 20 °C, 65 % R. H. for 24 h. The reported values were the mean of at least 5 experimental results.

Water contact angle was measured at room temperature on an automatic single fiber contact angle measuring instrument

OCA40Micro (Germany). The mechanical properties of various PAN fibers were measured by a XQ-1 tensile-testing machine (Shanghai New Fiber Instrument Co., Ltd., China) at a crosshead speed of 0.5 mm/min with a testing length of 20 mm and initial load of 0.1 cN. In each case, at least 30 filaments were tested, and the average was taken for each experiment.

Results and Discussion

Chemical Composition and Morphology of Fibers

The grafting degree of as-prepared PHGC-g-PAN fibers was determined by the weight gain method. Figure 1 shows the effects of treatment time of C-PAN fibers with PHGC on the grafting degree and guanidine groups content on PHGC-g-PAN fibers. The grafting degree reached 7.0 % after 3 h treatment. As the treatment time was further prolonged, the degree increased slightly. Guanidine group content on the fibers varies directly with the degree of grafting, and the value was calculated to be 410 mmol/kg after 3 h of treatment. Elemental analysis was also applied to determine the grafting degree [55]. The results are shown in Table 1. The degree of grafting of PHGC-g-PAN fibers (sample 3) was about 7.29 % which was close to the weight gain of the modified fibers (7.0 %).

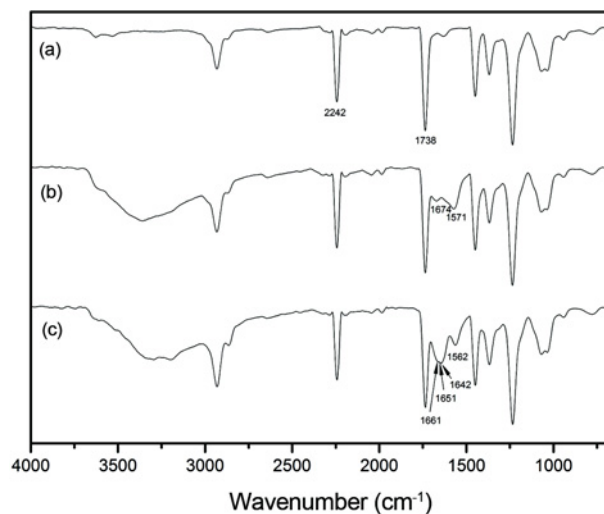Figure 2 shows the FTIR spectra of raw PAN fibers, C-
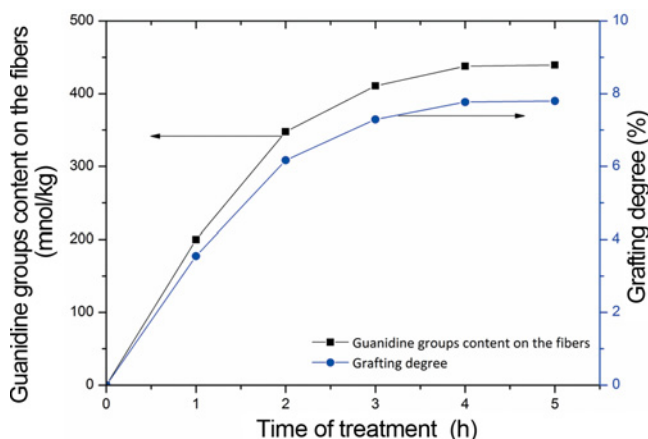
Figure 1. Effects of treatment time of C-PAN fibers with PHGC on the grafting degree and guanidine groups content on PHGC-g-PAN fibers.

Table 1. Elemental analysis results for raw PAN, C-PAN and PHGC-g-PAN fibers (sample 3)

| Sample	C (wt %)	N (wt %)	C/N[a]
PAN	65.76	24.52	2.682
C-PAN	64.85	23.44	2.766
PHGC-g-PAN	63.66	23.46	2.713

[a]C and N represent the carbon and nitrogen contents, respectively.

Figure 2. FTIR spectra of (a) raw PAN fibers, (b) C-PAN fibers, and (c) PHGC-g-PAN fibers (sample 3).

PAN fibers and PHGC-g-PAN fibers (sample 3). As demonstrated in Figure 2, the typical absorption peaks of raw PAN fibers at 2946, 2242, 1738, 1454, 1360, 1242, and 1075 cm^{-1}, correspond to the stretching of CH_2, C≡N, C=O, bending deformation of CH_2, rocking of CH_2, and CH and C-O vibration, respectively. These peaks also existed in the spectra of C-PAN fibers and PHGC-g-PAN fibers, which implies that the modification was limited to the fiber surface. After hydrolysis of raw PAN fibers, two new peaks appeared at 1571 cm^{-1} and 1674 cm^{-1} which could be assigned to carboxylate and amide group. After grafting PHGC on C-PAN fibers, the peak at 1674 cm^{-1} disappeared, and two peaks at 1642 cm^{-1} and 1661 cm^{-1} assigned to the amine in-plane bending vibration and imine stretching vibration were observed, which indicated that PHGC were grafted on PAN fibers. The peak at 1571 cm^{-1} shifted to 1562 cm^{-1}, resulting from the electrostatic interaction between carboxylate and guanidine groups. The FTIR results imply that carboxylate group does not take part in guanidine grafting. It could be attributed to the fact that the reactions between carboxylate groups and amine groups are much more difficult and usually need condensing agents [56].

XPS was employed to study the chemical composition and confirm the grafted functional groups on fibers. High resolution (HR) scans of the C1s curves were shown in Figure 3(a). After grafting PHGC on PAN fibers, the major peak at the binding energy (B.E.) of 284.7 eV shifted to 285.9 eV, which indicated distinct changes of the chemical composition on the fiber surface. Deconvolution of the C1s peaks of raw PAN, C-PAN and PHGC-g-PAN fibers (sample 3) were shown in Figure 3(b), 3(c) and 3(d), respectively. The C1s peak of raw PAN fibers was composed of four components assigned to carbon atoms of the main polymer chain (B.E.=284.6 eV), the carbon bonded to the nitrile
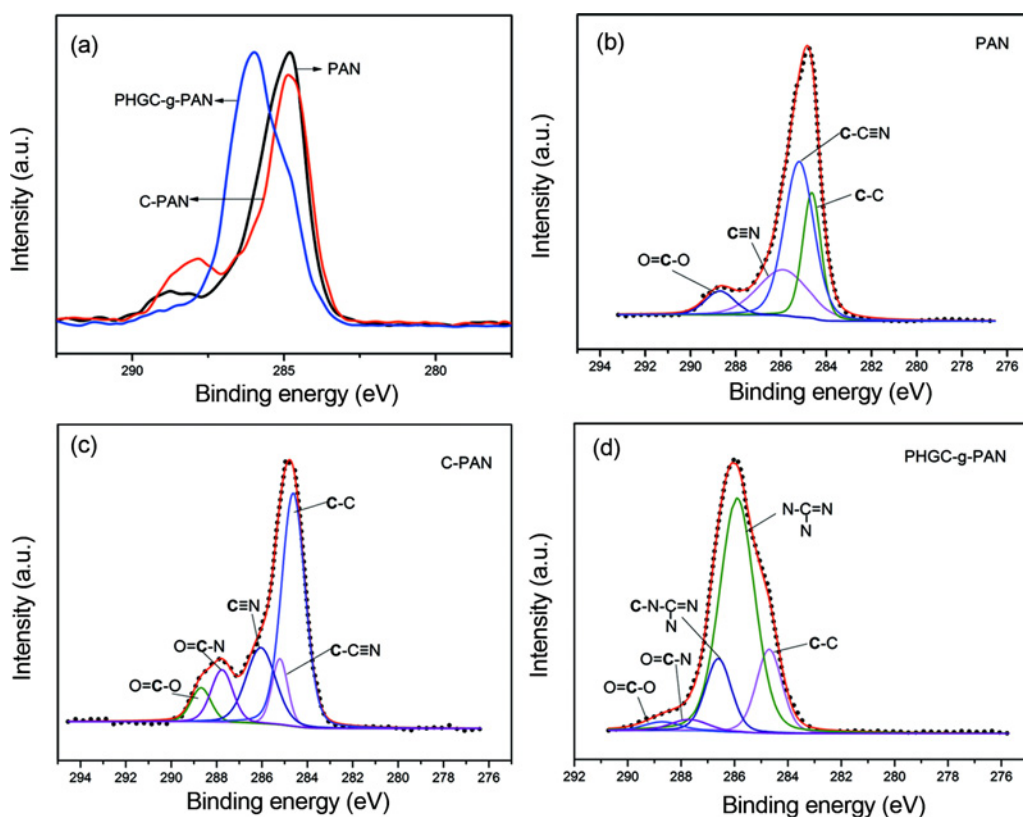
Figure 3. (a) C1s spectra of raw PAN, C-PAN fibers and PHGC-g-PAN fibers (sample 3) C1s spectra resolving results of (b) raw PAN fibers, (c) C-PAN fibers, and (d) PHGC-g-PAN fibers (sample 3).
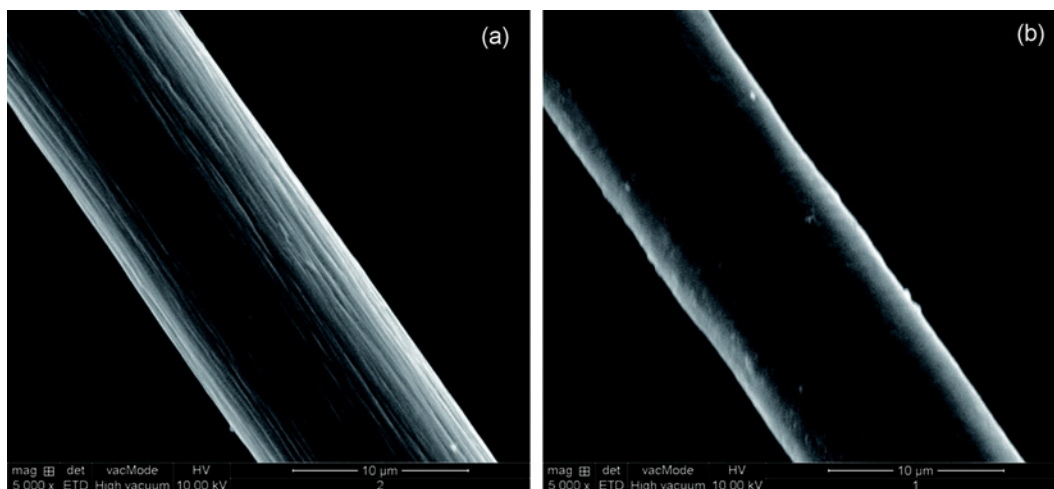
Figure 4. SEM images of (a) raw PAN fibers and (b) PHGC-g-PAN fibers (sample 3).

group (B.E.=285.2 eV), the nitrile group (B.E.=285.9 eV) and the carbon of the ester (B.E.=288.7 eV), respectively. For C-PAN fibers, the C1s component peak at 287.7 eV appeared, which demonstrated that the nitrile group on the fiber surface partially converted to amide. For PHGC-g-PAN fibers, a new C1s component peak at B.E. of 286.5 eV which was attributed to the carbon bonded to the guanidine

group was observed. Furthermore, the C1s component peak at 285.9 ev was obviously enhanced owing to the carbon of guanidine group. The XPS results reconfirmed that PHGC was successfully grafted on the fibers. Figure 4 presents the SEM images of raw PAN fibers and PHGC-g-PAN fibers (sample 3). After modification, most of the grooves on the surface of raw PAN fibers disappeared, which also indicated
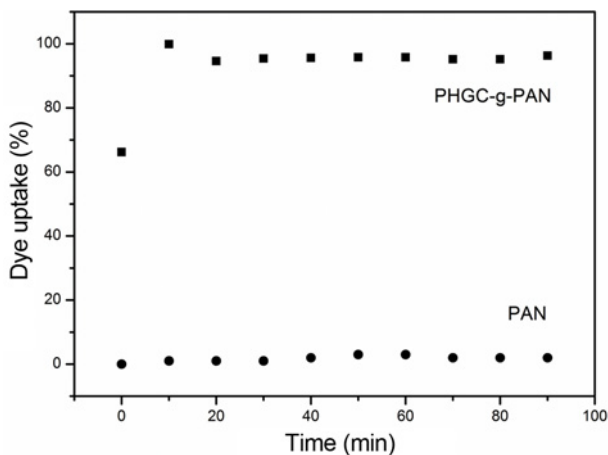
that PHGC was grafted on the fibers.
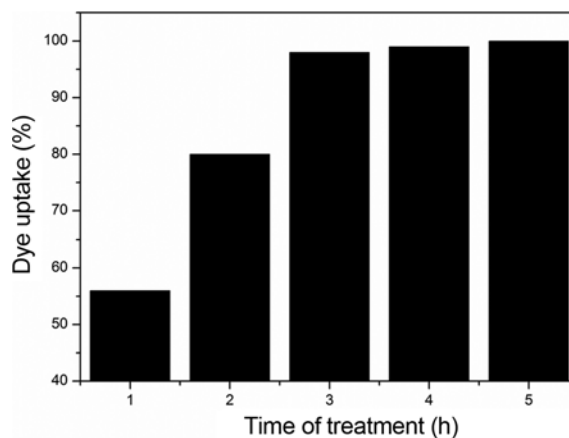
Dyeing Properties

The dyeing rate curves of PAN fibers and PHGC-g-PAN fibers (sample 3) with Acid scarlet GR are shown in Figure 5. The dye uptake of PAN fibers remained zero during the whole dyeing process, because there were none of cationic dyeing sites inside or outside fibers. However, for PHGC-g-PAN fibers, the dyeing equilibrium was reached very fast and it took only 10 min (50 $^{\circ}$C) to achieve a dye uptake of 95%. After the dyeing process, the weight of PHGC-g-PAN fibers increased 8.0 % from 0.10 g to 0.108 g. The dyeability of PHGC-g-PAN fibers with acid dye was attributed to the interaction of the cationic guanidine groups and acid dye molecules. The rapid dyeing speed was due to the fact that the acid dye molecules were fastened on the PHGC-g-PAN fibers very easily without additional diffusion inside the fibers.

To further investigate the dyeing properties, the dye uptake and *K/S* values for the samples with different grafting degree were tested. Figure 6 and 7 shows the relationship between the treatment time of C-PAN fibers with PHGC and its dyeability with Acid scarlet GR. The dye uptake and *K/S* values of the obtained fibers after treatment increased with the treatment time which indicated that the grafting of PHGC can effectively improve the dyeability of the PHGC-g-PAN fibers. Because each PHGC molecule grafted on the PAN fiber can provide more than 10 cationic dye sites, the *K/S* values of dyed PHGC-g-PAN fibers were much higher than that of the reported acid-dyeable PAN fibers [54,57].

Figure 8 shows the relationship between the pH of the dye bath and dye uptake for PAN and PHGC-g-PAN fibers (sample 3). There were almost no acid dyes absorbed by PAN fibers over the pH ranges from 2 to 6. For PHGC-g-PAN fibers sample, the dye uptake decreased with the

Figure 6. Effect of treatment time of C-PAN fibers with PHGC on the dyeability with acid scarlet GR (conc. of dye, 18 % owf; pH of dyebath, 3; liquor ratio, 200:1).
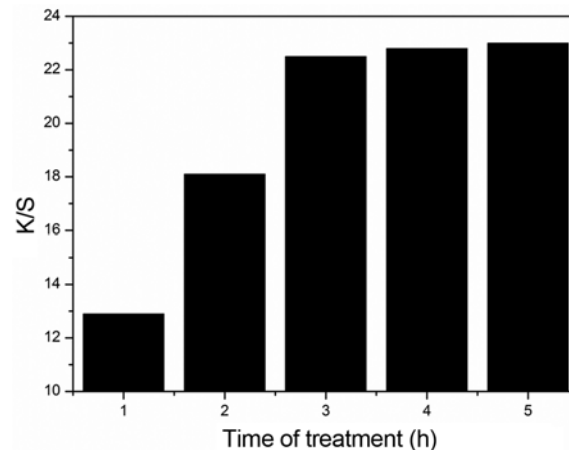
Figure 7. Effect of treatment time of C-PAN fibers with PHGC on the color strength with acid scarlet GR (conc. of dye, 18 % owf; pH of dyebath, 3; liquor ratio, 200:1).
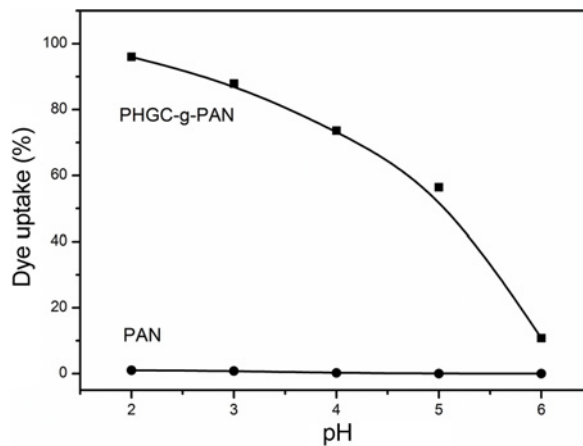

Figure 5. The dyeing rate curve of raw PAN and PHGC-g-PAN fibers (sample 3) with acid scarlet GR (conc. of dye, 9 % owf; pH of dyebath, 3; liquor ratio, 200:1).

Figure 8. Dyeability of raw PAN and PHGC-g-PAN fibers (sample 3) with acid scarlet GR at various dyebath pH (conc. of dye, 9 % owf; liquor ratio, 200:1).

increasing of pH values, but it still kept a high level of dye uptake in the pH ranges from 2 to 5. When PHGC-g-PAN fibers are blended with wool and nylon which are commonly dyed with acid dyes under weak acidic conditions (pH ranging from 3 to 5), the blended yarns can be dyed with the same dye via one-step process. The dyeing process is more convenient and economic than using two kinds of dyes [3].

Mechanical Properties

The mechanical properties of the PAN and PHGC-g-PAN fibers (sample 3) are summarized in Table 2. When the PAN fibers were grafted with of PHGC, the breaking strength and elongation decreased by 17.8 % and 14.6 %, respectively, but the initial modulus increased by 2.0 %. Because the modification process limited to the surface, the mechanical properties of the PHGC-g-PAN fibers (sample 3) were still favorable for the post-procedure of yarn spinning and dyeing.

Hydrophilic Properties

Water contact angle and moisture regain had been usually

Table 2. Mechanical performance of raw PAN and PHGC-g-PAN fibers (sample 3)

Sample	Breaking strength (cN/dtex)	Elongation at break (%)	Initial modulus (cN/dtex)
PAN	2.8±0.1	22.6±0.5	39.8±0.8
PHGC-g-PAN	2.3±0.1	19.3±0.4	40.6±0.8
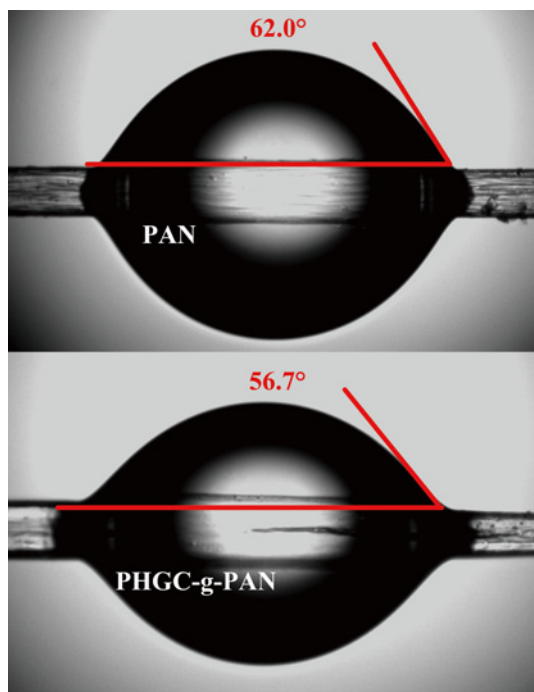
Figure 9. Photographs of static water contact angle of raw PAN and PHGC-g-PAN fibers (sample 3).

Table 3. Moisture regain and water contact angle of raw PAN and PHGC-g-PAN fibers (sample 3)

Sample	Moisture regain (%)	Contact angle (deg)
PAN	0.8±0.1	62.0±0.9
PHGC-g-PAN	4.9±0.3	56.7±0.8

used to characterize the relative hydrophilic properties of PAN fibers. Due to the introduction of hydrophilic guanidine groups, the contact angle of PHGC-g-PAN fibers (sample 3) was 56.7 $^\circ$ lower than that of the raw PAN fibers (Figure 9). The moisture regains of PAN and PHGC-g-PAN fibers (sample 3) are summarized in Table 3. Because of the hydrophilic properties of guanidine groups, the moisture regain of PHGC-g-PAN fibers (sample 3) reached 4.9 %, nearly 5 times higher than that of the raw PAN fibers (0.8 %).

Conclusion

PAN fibers containing guanidine groups were prepared by surface modification using PHGC as the functional material. The FTIR and XPS spectra indicated that PHGC was successfully grafted on the PAN fiber. Dyeing results showed that PHGC-g-PAN fibers possessed good acid-dyeable properties over a wide pH range. The dyeing process was very fast and can be carried out at much lower temperature. The mechanical properties of PHGC-g-PAN fibers decreased slightly whereas the hydrophilicity was improved significantly. The moisture regain was 5 times more than that of the commercial type.

Acknowledgements

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