Polymer Bulletin 59, 13–23 (2007)
DOI 10.1007/s00289-007-0739-z

Polymer Bulletin

Surface modification of polyacrylonitrile (PAN) fibers by grafting of natural polymer-soybean protein (SP)

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Received: 21 September 2006 / Revised version: 18 January 2007 / Accepted: 19 January 2007

Summary

A novel method of modifying polyacrylonitrile (PAN) fibers by grafting of soybean protein (SP) onto it was studied. The reactant of PAN-g-SP fiber was prepared based on chlorination of the hydrolyzed PAN fiber. The effects of chlorination and grafting conditions on the grafting efficiency were investigated. The grafting efficiency first increases with the increase of the addition of thionyl chloride ($SOCl_2$), chlorination time and temperature and then levels off. In grafting reaction, grafting efficiency increases at first and then declines significantly with increasing addition of sodium hydroxide (NaOH), grafting temperature and time. The grafted polymer was characterized by FT-IR spectroscopy, X-ray diffraction and SEM images. The results indicated that SP was grafted onto the PAN fiber. PAN-g-SP also exhibits good hygroscopicty and proper mechanical properties.

Introduction

From the textile point of view, almost all synthetic fibers have many superior characteristics such as high durability, heat-settable and good wash-and-wear properties, etc. But they also exhibit low moisture-absorbency, electrostatic tendency and inadequate heat resistance. Natural polymers always possess excellent tensile, handle and moisture absorption, though they suffer from some inferior performances too. In the last decades, chemical modification of the synthetic and natural polymers has been a subject of both academic as well as industrial interest [1-6].

PAN fiber, for its relatively cheap price and other important characteristics, such as soft, wool-like hand, good antibacterial property and excellent resistance to sunlight, is widely used not only in the textile industry, but also as the precursor for carbon fibers and reinforcement fibers. But compared with natural fiber, PAN fiber has very low moisture absorption and high collection of static electricity, which greatly limits its further applications. In recent years, a lot of studies have been found in the literature concerning the combination of AN-based polymers and natural polymers.

Most of the work, to our knowledge, has been focused on graft copolymerization of acrylonitrile (AN) and natural polymers, such as silk fibroin [7-11], casein [12-14], and wool keratin [15-20] etc. Sun Y.Y. et al. have studied the acrylic polymer-silk fibroin blend fibers [21-23] in detail. However, little research has been done on the grafting of SP onto PAN fiber directly. This kind of SP grafted PAN fiber is healthy and nutritional to people's skin and such kind of "naturalized synthetic fiber" combines the merits of natural polymer and synthetic polymer. In addition, soybean is massive in quantity and inexpensive in price. So, this new method is presumed to bring a relatively low production cost for the chemical modification of PAN fiber.

This paper investigated the preparation of PAN-g-SP fiber on the basis of the chlorination of the hydrolyzed PAN fiber at first and the following grafting of SP onto it. The effects of the chlorination and grafting conditions on the grafting efficiency were studied. The structure of PAN-g-SP fiber was investigated through FTIR and XRD analyses. The morphologies of PAN-g-SP fiber before and after graft modification were examined through SEM images. The moisture absorption and mechanical properties were also measured.

Experimental

Materials

PAN fiber, an acrylonitrile- methyl methacrylate- sodium styrene sulfonic terpolymer, was kindly provided by Sinopec Qilu Company Ltd. SP was prepared as described in literature [24].The other chemicals used in the study were analytically pure.

Graft modification

Samples of the original PAN fiber were hydrolyzed in aqueous alkali as reported in our previous work [25-26]. 30 gram of PAN fiber was dispersed in 400mL of 10 wt % NaOH aqueous solution at 80°C for 10 min. After hydrolysis, the samples were separated from the solution, thoroughly washed with distilled water, dried at 50°C to a constant weight. Then, ten gram of the hydrolyzed PAN fiber was put into a hermetically sealed vessel which was filled with $SOCl_2$ for a period of time. Required amount of chlorinated PAN fiber (10g) was put into the SP-H_2O mixture (pH 9-10, adjusted by NaOH aqueous solution) directly for some time. After completion of the grafting reaction, PAN-g-SP fiber was taken out and washed thoroughly with boiling distilled water, then dried under vacuum at 50°C to get the modified PAN fiber.

Measurements

Grafting efficiency

The grafting efficiency can be calculated as follows:

$$\text{Grafting efficiency (\%)} = \frac{W_2\text{-}W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of the original PAN fiber and the PAN-g-SP fiber respectively.

FTIR spectroscopy

The samples of both original PAN and PAN-g-SP fibers were cut into about 1-mm pieces, blended with KBr and pressed into discs. The FTIR spectra of samples were measured using Nicolet 5700 spectrometer.

X-ray diffraction

The X-ray analyses of the PAN fibers before and after grafting were carried out at room temperature on a Powder X-ray Diffractometer (D8 ADVANCE, Bruker AXS, Germany).

SEM

Gold was sprayed on sample in vacuum. Both external surface and cross section of the original and grafted fibers were investigated by Scanning Electron Microscope (Sirion 200, FEI, Holland).

Mechanical properties

Mechanical properties of both fibers were determined by using YG-003 fiber tensile machine, length between two holding jigs was 10 mm, and drop rate was 20 mm/min at room temperature.

Moisture absorption

The moisture absorption experiments were performed as follows: Fibers were balanced at 25°C for 48 h, 65% RH, then it is weighed (W_1/g). After balancing at 60°C for 60 h in vacuum baking oven, it was weighed again (W_2/g). The moisture absorption (%) of the fibers was calculated by the following formula:

$$\text{Moisture absorption (\%)} = \frac{W_1 - W_2}{W_1} \times 100$$

Antistatic property

Specific electric resistance of the blend fiber was determined by using YG321 Specific Resistance Indicator.

Results and discussion

Discussion of graft modification mechanism

SP contains many solar groups [24] on its macromolecular, such as amino group $-NH_2$ and hydroxyl group $–OH$ which contribute to the excellent hydrophilicity as well as the reactivity of the SP molecules.

The graft modification consists of three parts: (a) hydrolysis of the original PAN fiber [Fig.1 (a)]; (b) chlorination of the hydrolyzed PAN fiber [Fig.1 (b)]; (c) grafting of SP onto the chlorinated PAN fiber as depicted in Figure 1(c) and (d).

After these three reactions, SP is grafted onto the PAN fibers, which provides the synthetic fiber with physiological properties similar to those of natural fibers without greatly disturbing the mechanical behavior of them.

Effect of addition of $SOCl_2$ on grafting efficiency

Keeping all other variables unchanged, the effect of the addition of $SOCl_2$ on grafting efficiency is shown in Figure 2 (a). The grafting efficiency increases with the augment

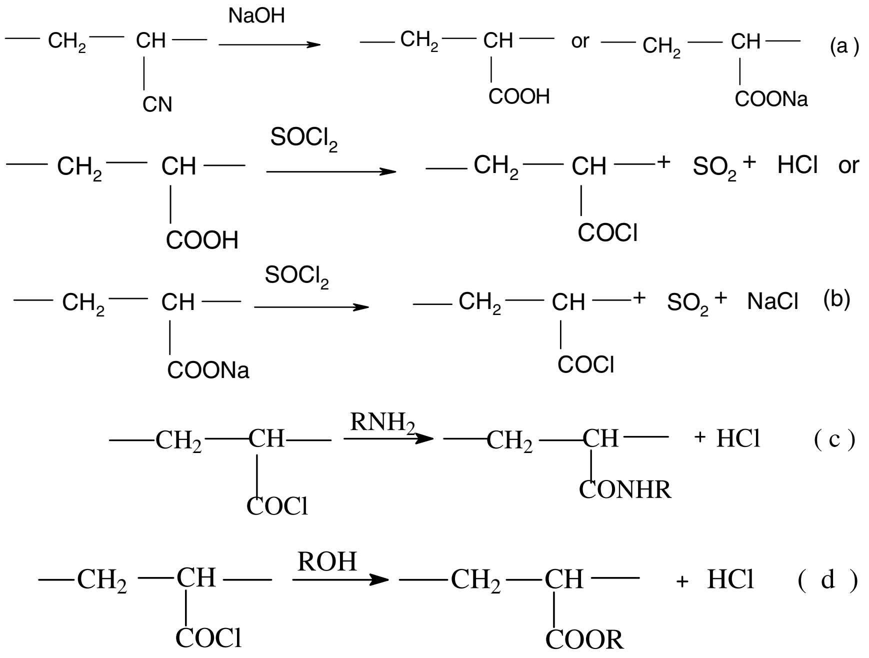


Figure 1. Graft modification of PAN fiber.

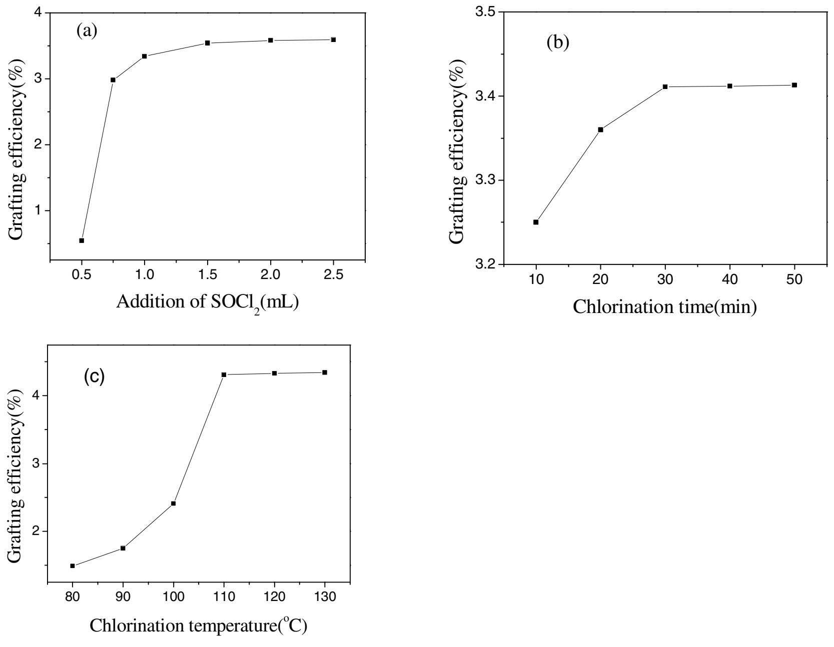


Figure 2. Effect of (a) Addition of SOCl2 (chlorination temperature: 110°C; chlorination time: 30min); (b) Chlorination time (SOCl2=1.0mL; chlorination temperature: 110°C);
(c) Chlorination temperature (SOCl2=1.0mL; chlorination time: 30min).

of $SOCl_2$ first and then levels off. It can be explained as follows: a large number of –COOH and –COONa groups are formed after the hydrolysis of PAN fiber, which can react with $SOCl_2$ easily. Insufficient $SOCl_2$ may result in an incompleteness of chlorination reaction, while excessive $SOCl_2$ may lead to a waste of $SOCl_2$ and unnecessary side reactions. The optimum addition of $SOCl_2$ in this study was 1.0mL which resulted in 3.42wt % of grafting efficiency.

Effect of chlorination time on grafting efficiency

The relationship between chlorination time and grafting efficiency under the conditions of 1.0mL of $SOCl_2$ at 110°C is shown in Figure 2 (b). As can be seen, the grafting efficiency presents a steady increase initially in the first 30min and then changes little after that. With increasing time, more $SOCl_2$ reacted with –COOH and –COONa and more –COCl is obtained. As a result, the grafting sites for SP to be grafted onto the PAN fiber were increased accordingly, so increased the grafting efficiency. As the chlorination reaction only occurs on the surface of the fiber and after a period of time, the chlorination reaction is nearly complete, so the increasing tendency of the grafting efficiency becomes unobvious. Considering prolonged reaction time may aggravate the properties of the fiber [27], the proper chlorination reaction time is about 30 min.

Effect of chlorination temperature on grafting efficiency

The influence of chlorination temperature on grafting efficiency when all the other conditions are made invariable is illustrated in Figure 2(c). The boiling point and decomposition temperature of $SOCl_2$ are 78.8 and 140°C respectively. So the reaction temperature range was from 80 to 130°C.As is shown from the figure, when the chlorination temperature is lower than 100°C, the grafting efficiency increases slowly with the rising of temperature. Then the grafting efficiency presents a significant increase with the continuous increase of chlorination temperature and the maximum grafting efficiency of 4.31wt % was obtained at 110°C.The grafting efficiency then levels off with further increase of chlorination temperature, which indicates an almost completion of the grafting reaction.

Effect of addition of NaOH on grafting efficiency

The influence of the addition of NaOH on the grafting efficiency is shown in Figure 3 (a). It is obvious that the grafting efficiency increases at first and reaches its maximum with 1.0mL of NaOH aqueous solution. Then the grafting efficiency decreases rapidly with the continuous increase of the amount of NaOH and presents a negative value beyond 2.0 mL. In the grafting of SP onto PAN fiber, besides neutralizing hydrochloric acid HCl which is produced in the nitrogen acylation and esterification reactions as depicted in Figure1(c) and (d), NaOH also has an effect on the hydrolysis of the PAN fiber and the degradation of the SP. With increasing addition of NaOH, the hydrolysis of PAN fiber is performed excessively which results in the constant decrease of the weight of the fiber itself. In addition, more SP degrades with the increase of the amount of NaOH, which leads to a decrease of the molecular weight of the protein grafted onto the fiber too. As a result, the weight of the grafted PAN fiber declines which brings the negative increase of the grafting efficiency.

Effect of grafting temperature on grafting efficiency

The effect of grafting temperature on grafting efficiency is depicted in Figure 3(b) when the chlorinated fiber was treated with 1.0mLof NaOH aqueous solution for 5 min. With the increase of the grafting temperature, the grafting efficiency increases continually, up to a maximum of 2.24wt %. Then the grafting efficiency declines dramatically which is attributed to both denaturation of SP and excessive hydrolysis of the PAN fiber after 80°C. So, the suitable grafting temperature in this work was 80°C.

Effect of grafting time on grafting efficiency

The relationship between grafting efficiency and grafting time is illustrated in Figure 3(c) under the conditions of 1.0mL of NaOH aqueous solution at 80°C. The grafting efficiency has a drastic increase at the beginning and then decreases obviously when the grafting time was beyond the optimum point of 5 min. It can be explained as follows: because of its high active property, the chloroformyl group –COCl reacts with the protein rapidly at the first 3~5 min. The later gradual decline on the grafting efficiency could be partly due to both the over-hydrolysis of PAN fiber and degradation of SP with increasing grafting time.

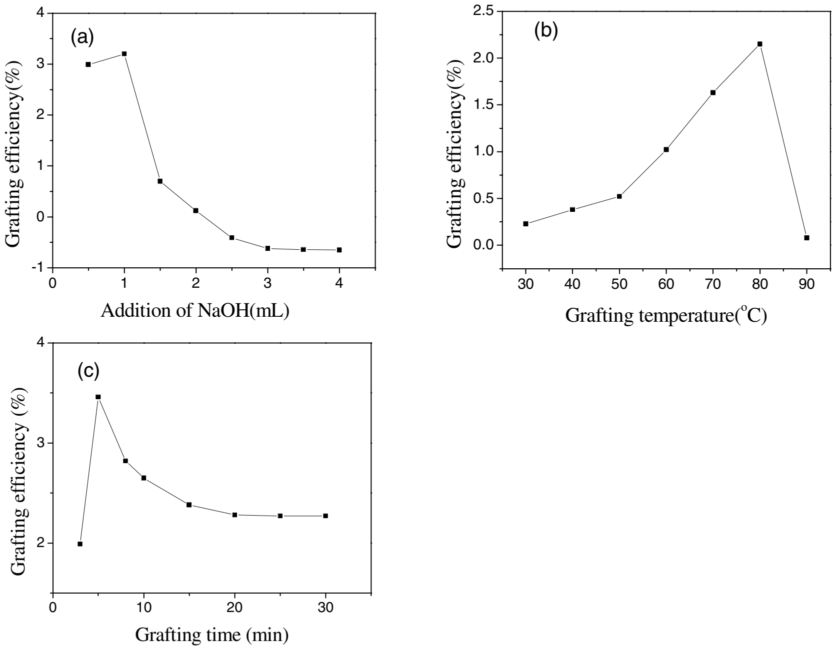


Figure 3. Effect of (a) Addition of NaOH (grafting temperature: 80°C; grafting time: 5min); (b) Grafting temperature (NaOH=0.1g; grafting time: 5min); (c) Grafting time (NaOH=0.1g; grafting temperature: 80°C) on Grafting efficiency.

FT-IR spectra

Figure 4 shows the FTIR absorption spectra of SP, [Fig.4 (a)] the original PAN fiber [Fig.4 (b)] and PAN-g-SP fiber [Fig.4(c)]. The IR spectrum of the original PAN fiber shows the characteristic peaks at 2243(γ C≡N), 1732(γ C=O), and 1451(δCH_2) cm^{-1},

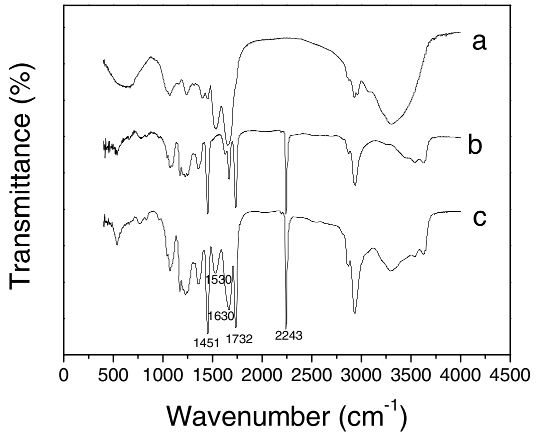


Figure 4. FTIR spectra of (a) pure SP; (b) original PAN fiber; (c) PAN-g-SP fiber.

where γ represents a stretching vibration and δ a bending vibration. SP shows absorption at 1630(γ C=O, amide I) and 1530(δ N-H, amide II).The grafted fiber displays the absorption bands typical of the two pure components, which was attributed to the introduction of SP on the surface of the fiber by graft modification. From above analysis, we can say that grafting of SP onto PAN fiber was obtained.

X-ray diffraction

Figure 5 shows the XRD spectra of the ordinary PAN fiber [Fig.5 (a)] and grafted PAN fiber [Fig.5 (b)]. The diffraction peaks of the original PAN fiber present at 2θ=16.8° and 22.5° respectively and the spectrum presents a platform in the range of scattering angles of 17°~23° which corresponds to the coexistence of high orientation and low amorphous order of PAN. The diffraction image of PAN-g-SP fiber was almost the same with the ungrafted PAN fiber and no additional diffraction peak appears which indicate that there is no significant change on the crystal structure of the modified fiber after the grafting of SP.

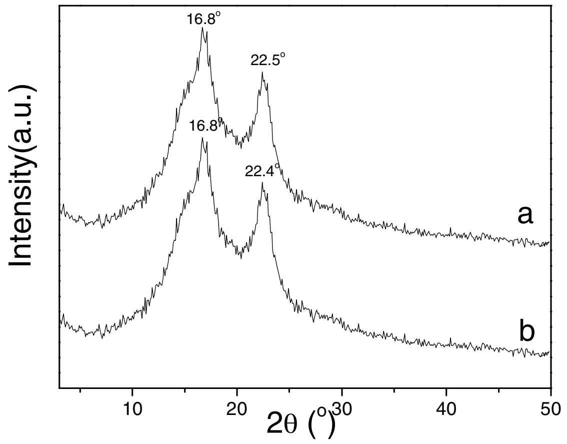
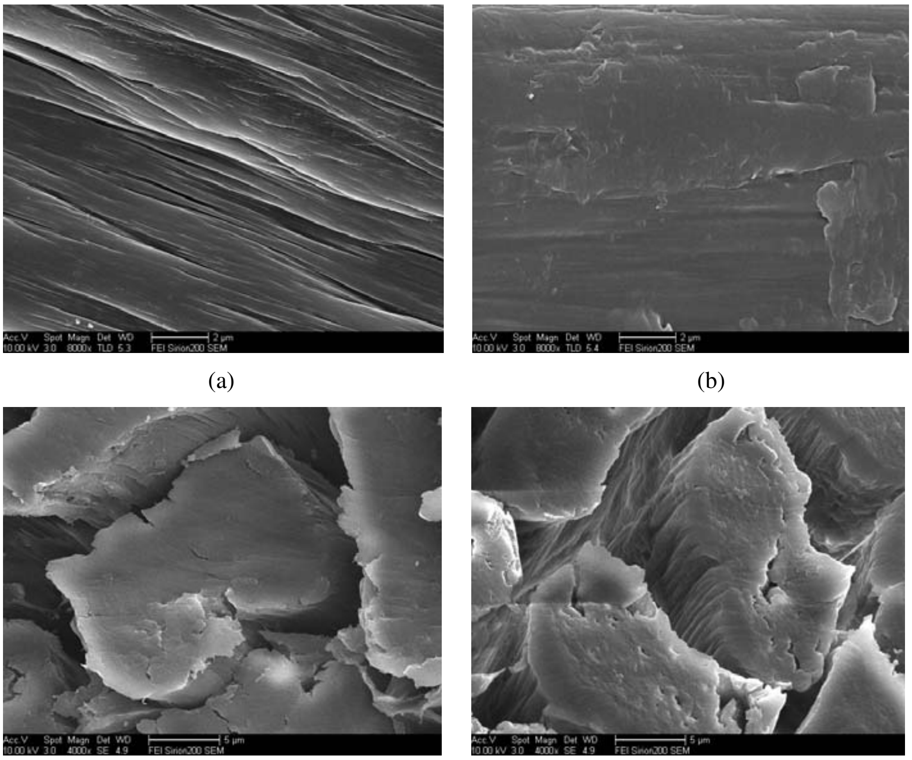


Figure 5. X-ray diffraction of (a) ordinary PAN and (b) PAN-g-SP fiber.

Scanning electron microscopy

The external and cross section SEM images of the PAN fiber before and after grafting are shown in Figure 6 respectively. As can be seen, the internal structure of original PAN fiber is quite integrated and compact and there are a lot of microcracks along the axis on its external surface which has been produced in the procedure of high-ratio stretching in spinning. After grafting, the external surface of the fiber becomes rougher and there is obvious deposition after grafting, which indicated that a SP film was formed on the surface. Some micropores appear on the cross section of the PAN-g-SP fiber due to the hydrolysis in the modification. As a result, we presume that the strength of modified fiber is lower than the original one, which is verified by the test of mechanical properties.



(a) (b)

(c) (d)

Figure 6. SEM photographs of (a) external surface of original PAN fiber; (b) external surface of PAN-g-SP fiber; (c) cross section of original PAN fiber; (d) cross section of PAN-g-SP fiber.

Mechanical properties

The mechanical properties of both ungrafted PAN and grafted PAN fibers are recorded in Table 1. It shows that, with the increase of the graft efficiency, the elongation of the PAN-g-SP fiber does not change much while the breaking strength decreases compared with the original fiber. Alkaline treatment of the fiber leads to the surface erosion of the PAN fiber and loosening of the structure. Similar observations have also been reported by a number of authors [28-30] and it is believed this lack of original structural integrity decreased the intermolecular interaction between the PAN macromolecular chains. In spite of all these factors, the grafted polymer still meets the requirement for wearing fiber.

Table 1. Mechanical properties of PAN-g-SP fiber.

Sample	Grafting efficiency (%)	Breaking strength (CN/dtex)	Breaking Elongation (%)
Original PAN	0	2.42	25.2
PAN-g-SP	1.21	1.95	24.5
PAN-g-SP	1.93	2.05	26.6
PAN-g-SP	3.27	1.89	26.5
PAN-g-SP	3.90	1.84	25.2
PAN-g-SP	4.40	1.86	26.6

Moisture absorption

Hygroscopicities of the PAN-g-SP fiber and the original PAN fiber were determined in this study. The moisture absorption of ordinary PAN fiber is 2wt % and that of the modified fiber with the increasing grafting efficiency is shown in Figure 7. With the increase of grafting efficiency the moisture absorption of the PAN-g-SP fiber increases accordingly which is attributed to the presence of SP deposited on the surface of the fiber as confirmed by the SEM of PAN-g-SP fiber.

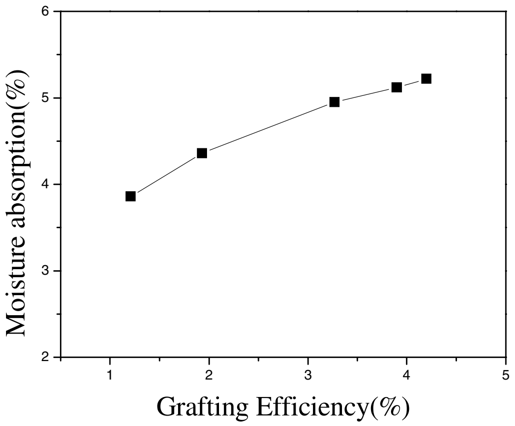


Figure 7. Effect of Grafting Efficiency on Moisture absorption.

Antistatic property

The specific electric resistances of ungrafted and grafted PAN fiber were measured and the results are recorded in Table 2. The data for the specific electric resistance of original PAN fiber was $1.9 \times 10^9 \Omega \cdot g/cm^2$ and the values of the grafted fibers were obviously lower. Besides, the specific electric resistance values of the grafted fibers were in decreasing order with augment in the grafting efficiency. The decreased specific electric resistance indicated that the antistatic property of the grafted fibers was improved. The improved hydrophilicity of the fibers contributed to the enhancing antistatic property, which was due to the combination of natural protein and synthetic PAN fiber.

Table 2. Specific electric resistances of ungrafted and grafted PAN fibers.

Sample	Grafting efficiency (%)	Specific Electric resistance ($\Omega\cdot g/cm^2$)
ungrafted	0	$(1.9\pm0.1)\times10^9$
grafted	1.6±0.1	$(3.5\pm0.2)\times10^8$
grafted	2.4±0.3	$(1.7\pm0.3)\times10^8$
grafted	3.4±0.2	$(9.2\pm0.5)\times10^7$
grafted	4.3±0.4	$(4.6\pm0.3)\times10^7$

Conclusions

SP can be grafted onto PAN fiber after hydrolysis, chlorination and grafting reactions in sequence. FT-IR spectra have proved the presence of protein on the surface of the PAN-g-SP fiber. X-ray diffraction shows that the crystal structure of the protein-modified PAN fiber has not been greatly changed. SEM micrographs have confirmed that the surface of PAN-g-SP fiber was covered by integrated and compact protein film. The resulting PAN-g-SP fiber still exhibits good mechanical properties which can meet the requirement of wearing fiber. PAN-g-SP fiber also has good moisture absorption and antistatic property which resulted from the protein coverage on its surface.

Acknowledgements. The authors gratefully acknowledge the financial support of the Nature Science Foundation of Shandong Province (No.9001104020), China.

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