Investigation on the Effect of Activators and Polysulfide on Durability of Electrically Conductive PAN Fibers

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ABSTRACT: A method to improve the durability of electrically conductive polyacrylonitrile (PAN) fibers treated with the Cu_xS method was developed in this article. The influence of pretreatment with activators and posttreatment with polysulfide on the durability was studied, and the mechanism was proposed. The results showed that, combining activation with acetic acid with posttreatment with polysulfide, the durability of the electrically conductive fiber increased. This is attributed to the swelling and etching effects of the activator as well as the formation of uniform, thick, and compact conductive layers obtained from polysulfide treatment. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1039–1045, 1999

Key words: durability of conductivity; electrically conductive PAN fiber; specific resistance; activating agent; polysulfide; electrically conductive crystal layer; Cu_9S_5 crystalline

INTRODUCTION

Electrically conductive polyacrylonitrile (PAN) fiber has been well accepted, and was rapidly developed as soon as it made its appearance, because the procedure for making conductive PAN with the Cu_xS method is simple, and the electric conductivity is good, with specific resistance as low as 10^{-2} – $10^{-1} \Omega \cdot \text{cm.}^{1-4}$ Furthermore, this procedure does not influence the hand of the fiber and dyeing and finishing of fibers.¹⁻⁴ The conductive PAN fiber, which reduces static charge, can be blended with normal PAN fiber at a blending ratio 2–5% to produce variety of antistatic materials, such as safety cloth, trolleybus shroud, shield cloth for precision instruments, life jackets, etc.¹⁻⁴ However, this kind of electrically conductive produce variety of antistatic states.

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Journal of Applied Polymer Science, Vol. 72, 1039–1045 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081039-07 tive PAN fiber has a fatal weakness. The conductive layer will partly or even entirely disconnect from the fiber during its storage in a wet and hot climate or with strong alkaline treatment at a high temperature.⁵ As a result, the conductivity will greatly decrease. This can be attributed to the following factors: there exist crystal defects in the electrically conductive crystal layer⁶; free CuS in the crystal layer may easily be oxidized into soluble substance by oxygen in the air⁷; and the PAN fiber itself is not resistant to alkali. The present effort focuses on enhancing the durability of conductive PAN fiber to resist weathering and alkaline as well as preparation processes.

EXPERIMENTAL

Materials

PAN fiber samples (3.3d) were provided by Jinshan Petroleum & Chemical Science General Co.,

Shanghai, China. Chemicals used in this article including copper sulfate (Cu₂SO₄ \cdot 5H₂O), sodium thionate (Na₂S₂O₃ \cdot 5H₂O), phosphoric acid (H₃PO₄), sulfuric acid, acetic acid, sodium carbonate, were AR grade. *N,N*-Dimethylformamide (DMF) and ammonium polysulfide were industry grade.

Fiber Treatment Process

Preparation of the Electrically Conductive PAN Fiber

The PAN fiber (or yarn) was immersed in a solution of 30% copper sulfate. The temperature was raised to 55°C, with appropriate agitation. Thirty percent sulfur-contained reducing agent $(Na_2S_2O_3)$ was added in batches. The solution was then heated to 95–100°C and maintained at that temperature for 50 min with stirring. A greenish-black electrically conductive PAN fiber was then obtained.⁴

Activation of the PAN Fiber

The PAN fiber was added in a solution of 5% activating agents at 90°C for 30 min, and then rinsed and dried.

Posttreatment of the Conductive PAN Fiber

The electrically conductive PAN fiber was immersed in a solution of 5% (w/w) ammonium polysulfide at 60°C. The solution was kept stirring for approximate 30 min. The fiber was then taken out, washed, and dried.

Treatment Processes for Evaluating the Durability of Electrically Conductive Fibers

Durability to 5% NaOH Solution

Conductive PAN fibers were immersed in an aqueous solution containing 5% (w/w) of sodium hydroxide for a specified time, then washed and dried.⁸

Durability to Steaming

The above procedure was repeated except that the fiber was steamed in a saturated vapor of water for a specified time instead of treatment with a 5% NaOH solution.

Durability to Preparation Processes

The electrically conductive fiber was treated in the same conditions as the preparation process for polyester/cotton blend fabrics in dyeing and finishing plants, i.e., desizing (fibers were saturated with a 8% NaOH solution, and steamed for 60 min), scouring, and bleaching (fibers were steamed for 60 min at 100°C in a solution containing 5 g/L $\rm H_2O_2$ and 3 g/L NaOH), mercerizing (fibers were immersed in 280 g/L NaOH for 60 s) and then washing and drying.

Durability to Weathering

The electrically conductive fiber was stored in a natural environment for 8 months (from December to October) to expose it to typical weathering conditions, i.e., high temperature in summer and high humidity in a rainy season.

Evaluation of the Conductivity of PAN Fibers

The specific resistance of electrically conductive fibers was measured on a Four Electrodes Specific Resistance Instrument, which was specially made for this purpose.⁹ The lower the value of specific resistance, the higher the conductivity of the fibers; the less the specific resistance increases after the fiber suffering from various treatments, the better the durability of the conductive fiber.

The IR spectra were collected on an IR-408 Infrared Spectrophotometer (Japan). The photography by a scanning electron microscope was obtained using Com Scan-4 Scanning Electron Microscope (UK). The elemental analysis was analyzed on a Varian AA-475-ABD Atomic-Adsorption Spectrometry (China).

Table IThe Specific Resistance of ConductivePAN Fibers Activated with 5% Phosphoric AcidAfter Immersing in a 5% NaOH SolutionFor a Specified Time

	Specific F $(\Omega \cdot cm)$	Resistance $ imes$ 10 ⁻¹)
Immersion Time (day)	Without Pretreatment	With Pretreatment
0	0.88	0.69
2	2.00	1.33
4	3.73	2.00
6	4.96	2.88
8	6.37	3.92
12	13.60	4.30
16	43.40	15.7



Figure 1 The specific resistance of electrically conductive PAN fibers activated with different acids or an alkali after immersing in a 5% NaOH solution for a specified time.



Figure 2 SEM photographs of PAN fibers before and after activation with different acids.



Figure 3 Infrared spectra of PAN fibers before and after activation with acetic acid: (a) unactivated; (b) activated.

RESULTS AND DISCUSSION

Influence of Pretreatment with Activating Agents

The uniformity and durability of the electrically conductive crystal layer will increase greatly if a PAN fiber is treated with concentrated phosphoric acid (H_3PO_4) at room temperature.¹⁰ In this article, the PAN fiber was first treated with 5% phosphoric acid, and then treated with the Cu_xS method described in the Experimental section to obtain a conductive property. The conductive fibers were subjected to immersion in a 5% NaOH solution for different times. Their specific resistances are presented in Table I.

It can be seen from the data in Table I that the initial specific resistance of the electrically conductive PAN fiber pretreated with phosphoric acid is lower than that of the untreated fiber, and the increment of specific resistance for the PAN fiber with pretreatment is less than that for the untreated PAN fiber after immersing in a 5% NaOH solution for a specified time, indicating that the conductivity of the fiber and its resistance to 5% NaOH solution is indeed improved by pretreatment. This pretreatment process is called "activation," and the fiber is called an "activated" fiber.

In our research, some other acidic and basic compounds such as sulfuric acid, phosphoric acid, acetic acid, and sodium carbonate were selected to activate the PAN fiber so as to achieve the desired durability. The results are illustrated in Figure 1.

Figure 1 shows that the specific resistance of PAN fibers increases with the increase of immersion time no matter what kind of acid or alkaline applied in pretreatment. There is the least increment of specific resistance for the pretreated fibers with acetic acid, indicating that acetic acid has the best activating ability.

The scanning electron microscope photographs of the PAN fiber with and without pretreatment show that surface coarseness of the fiber greatly increases after pretreatment, especially for the fiber pretreated with acetic acid (Fig. 2).

Infrared spectra of unactivated PAN fibers and fibers activated with acetic acid are shown in Figure 3. The peaks near 1700 cm^{-1} and 1450 cm^{-1} are due to vibration mode of -C=0, and $-(CH_2)$, respectively. The only difference between the two infrared spectra is that the peak near 3400 cm^{-1} (the stretch vibration of hydroxyl in carboxyl group) for the activated fiber is wider and sharper than that for the original fiber. The characteristic peak of the cyano group (CN) at around 2240 cm^{-1} does not change, and no new peaks appear. The reason that the amount of carboxyl groups increases is likely due to the hydrolysis of cyano and ester groups in PAN molecules under an acidic or alkaline condition at a high temperature¹¹:

Table IIThe Specific Resistance of Conductive PAN Fibers Activated with5% DMF Before and After Immersing in a 5% NaOH Solution for 10 Days

	Specific Resistance ($\Omega \cdot cm \times 10^{-1}$)	
Treatment Process for Samples	Before Immersing in a 5% NaOH Solution	After Immersing in a 5% NaOH Solution
Unactivated	1.81	4.88
Activated with 5% acetic acid	1.63	3.81
Activated with 5% DMF	1.41	3.44

Immersion Time (day)	Specific Resistance $(\Omega \cdot \text{cm} \times 10^{-1})$	
	Without Posttreatment	With Posttreatment
0	0.987	1.07
4	2.83	1.87
7	7.12	2.45
11	11.2	5.07
13	17.4	10.4
16	63.6	21.1

Table III The Specific Resistance of
Conductive PAN Fibers Posttreated with 5%
Polysulfide After Immersing in a 5% NaOH
Solution for a Specified Time



Therefore, the proportion of carboxyl groups in the PAN fiber increases, which in turn, increases the fiber's solubility in water. The low molecular weight PAN molecules on the surface of the fiber maybe dissolve away, which is called "etching." As a result, the fiber surfaces are more rough, and ditches and hollows appear that are advantageous for an electrically conductive crystal layer to inlay into the fiber firmly. In addition, the cyano groups (CN) in the inner fiber are exposed, increasing the possibility of forming coordinate bond between cuprous ions (Cu^+) and cyano groups.

If etching is believed to be the only activating mechanism, sulfuric acid and phosphoric acid with higher acidity should bring about more severe etching effect than acetic acid. However, acetic acid produces a better etching effect. So it is not enough to explain why acetic acid has the best activating ability only using the "etching theory." Considering that acetic acid has a similar structure to the PAN fiber, we assume that acetic acid not only has an etching effect but also produces a certain degree of swelling on PAN fibers. To verify the above assumption, we employed 5% organic solvent DMF to pretreat the PAN fiber and then prepared an electrically conductive PAN fiber. The comparative results are shown in Table II.

From Table II, we can see that the initial conductivity and the durability of the PAN fiber pretreated with DMF is better than that with acetic acid. Swelling and etching did influence conductivity of conductive PAN fibers.

Swelling and then etching led to the structure change of PAN fibers: gaps between individual fibers enlarge, surface areas expand, accessibility and adsorbing capacity to curpric and cuprous ions increases, thus laying a good foundation to form large and firm conductive crystal layers in the fiber. The amount of copper-contained in the PAN fiber pretreated with DMF increased by 11.4% according to a quantitative analysis with atomic-adsorption spectrometry (AAS), confirm-

	Specific Resistance $(\Omega \cdot cm \times 10^{-1})$		
Electrically Conductive PAN Fiber Samples	Before Steaming	Dry Steaming ^a	Wet Streaming ^b
Without activation and posttreatment	2.22	4.49	26.8
Activated with 5% DMF	1.17	2.37	24.3
Activated with 5% DMF and post-treated with 5% polysulfide	1.45	1.77	15.1

Table IVThe Specific Resistance of Conductive PAN Fibers Treated withDifferent Procedures After Dry Streaming and Wet Steaming for 30 h

^a Fiber samples were steamed in a saturated aqueous vapor.

^b Fiber samples were sealed in a dry beaker, and the beaker was steamed in a saturated aqueous vapor.

Table VThe Specific Resistance of ConductivePAN Fibers Treated with Different ProceduresAfter Storing in a Natural Environmentfor 8 Months

	Specific Resistance $(\Omega \cdot cm \times 10^{-1})$	
Electrically Conductive PAN Fiber Samples	Before Storing	After Storing
Without activation and posttreatment	0.800	10.5
Activated with 5% acetic acid	0.613	5.40
Activated with 5% acetic acid and posttreated with 5% polysulfide	0.907	2.10

ing that the swelling and etching effect is the essence of activation.

The Influence of Posttreatment with Polysulfide

It has been reported that the conductivity of electrically conductive PAN will be raised if the fiber is treated with an organic solvent of brimstone or an aqueous solution of the compound that releases sulfur, and that the adhesive strength of the electrically conductive layer to the PAN fiber will not be affected.¹² In this article, a 5% aqueous solution of ammonium polysulfide was used to treat the electrically conductive PAN fiber to improve the durability. Presented in Tables III– VI is the conductivity of PAN fibers treated with different processes and their specific resistance to 5% NaOH solution, dry and wet steaming, weathering, and preparation.

The results show that the initial specific resistance of the electrically conductive PAN fiber goes up due to polysulfide posttreatment, while its durability increases, specifically for its resistance to weathering and preparation. Furthermore, when combining activation with a posttreatment process, the specific resistance of conductive PAN fibers is lowered, which means that its conductivity and durability is superior to other PAN samples after exposure to various conditions.

Chemical reactions listed below may take place if polysulfide is added to the system containing cupric sulfide, cuprous sulfide, cupric ion, and sulfur-contained reductive agent.

$$2M_2S_2 + 3O_2 = 2M_2S_2O_3 \tag{1}$$

$$\mathbf{M}_2 \mathbf{S}_2 = \mathbf{M}_2 \mathbf{S} + \mathbf{S} \tag{2}$$

$$2CuS + 2M_2S_2 = Cu_2S + 2M_2S + 3S \quad (3)$$

Polysulfide can be oxidized to thiosulfate $(S_2O_3^{2^-})$ (reaction 1); the latter then partially reduces CuS to Cu₂S; polysulfide can directly turn CuS into Cu₂S in reaction 3. The sulfion (S^{2^-}) provided by reaction 2 would promote extra Cu⁺ and Cu²⁺ ions absorbed on the fiber to produce Cu₂S and CuS, resulting in thickening the electrically conductive crystal layer.

In addition, another physical and chemical phenomenon should be noticed. CuS does not dissolve in water, and only slightly dissolves in a solution of ammonium polysulfide or alkali metal polysulfide.¹³ In the case of our posttreatment system, some cupric sulfide existing in a monomolecular or loose state in the crystal layers may dissolve in the solution of polysulfide, and then be reduced to cuprous sulfide by polysulfide, thus increasing the relative proportion of Cu₂S in the electrically conductive crystal layer.

The increase in amount of Cu_2S brings about two results. The initial specific resistance of elec-

Electrically Conductive PAN Fiber Samples	Specific Resistance ($\Omega \cdot cm \times 10^{-1}$)		
	Before Preparation Processes	After Preparation Processes	
Without activation and posttreatment	1.48	18.6	
Activated with 5% acetic acid	0.73	15.1	
Posttreated with 5% polysulfide	1.56	8.97	
Activated with 5% acetic acid and posttreated with 5% polysulfide	0.889	3.97	

 Table VI
 The Specific Resistance of Conductive PAN Fibers Treated with Different Procedures After

 Preparation Processes (Desizing, Scouring, Bleaching, and Mercerizing)



(a) before polysulfide treatment

(b) after polysulfide treatment

Figure 4 SEM photographs of the electrically conductive crystalline layer with and without posttreatment with polysulfide.

trically conductive fiber will rise a little because the specific conductance of CuS is at least 10 times higher than that of Cu₂S.¹² The crystal structure of electrically conductive crystal layer will change a great deal because an extremely stable Cu₉S₅ crystalline will be formed when the proportion of Cu_2S to CuS is up to $4:1^{14,15}$ due to the considerably high lattice energy of Cu₉S₅ crystalline. Thus, its fastness to climate is much higher than that of other copper sulfide. The durability of the electrically conductive PAN fiber, therefore, improves considerably. From the SEM photographs shown in Figure 4 one can recognize the difference in uniformity and density of the crystal layer before and after polysulfide treatment. Obviously, the conductive layer is uniform, thick, and of high density after polysulfide treatment.

CONCLUSION

The compactness, uniformity of the Cu_9S_5 crystalline layer, the density of the conductive crystal layers as well as the proportion of Cu_2S play an important role in achieving the durable electrically conductive PAN fiber. Combining activation with acetic acid or an organic solvent (DMF) with a posttreatment with polysulfide, an electrically conductive PAN fiber durable to weathering and alkaline would be produced. The product can be used or stored in a natural environment for a long time without losing its conductivity, and can

withstand preparation processes such as desizing, scouring, bleaching, and mercerizing.

REFERENCES

- 1. Fuchiraizou, G. JP55-51873, 1980.
- Tomibe, S.; Gornibuchi, R.; Takahashi, K. USP 4378226, 1983.
- 3. Kitamura, T.; Ohash, T. Eur P 160406 A2, 1984.
- 4. Hou, Q. CN87 104346A, 1987.
- Zhao, Z.; Zou, L.; Lu, D. J Textile Res 1991, May, 204.
- Qian, Y. Crystal Chemistry; Publishing House of China Science and Technology University: Hefei, 1988, p. 8.
- Sherwood Taylor, F. Inorganic and Theoretical Chemistry; William Heinemaan Ltd: London, 1960, p. 307, 10th ed.
- 8. Masatoshi, F.; Hiroshi, T. JP61-2549, 1986.
- 9. Wang, L. J Textile Res 1992, Feb., 28.
- 10. Takitomo, S.; Tsumeaki, D. JP60-198004, 1984.
- Wang, J.; Sun, K. Principles of Dyeing and Finishing Technology; Textile Industry Publishing House: Beijing, 1982, p. 253.
- Zhao, Z. Antistatic Technology for Polymers; Textile Industry Publishing House: Beijing, 1991, p. 33, 253.
- Chen, S. Important Inorganic Chemical Reactions; Shanghai Publishing House of Science and Technology: Shanghai, 1982, p. 81.
- Tomibe, S.; Gornibuchi, R.; Takahashi, K. Eur Pat Appl 35406 1981.
- 15. American Society for Testing Materials (ASTM) CARD, 1965.