

STUDIES ON PAN MACROMOLECULAR SEMICONDUCTING FIBER

1. PREPARATION OF PAN CONDUCTING FIBER TREATED BY STANNIC CHLORIDE AND ITS SEMICONDUCTING BEHAVIOUR*

WANG Dexi (王德禧), CUI Dayuan (崔大源), LUO Boliang (罗伯良),
WANG Xiugang (王秀岗) and WU Renjie (吴人洁)

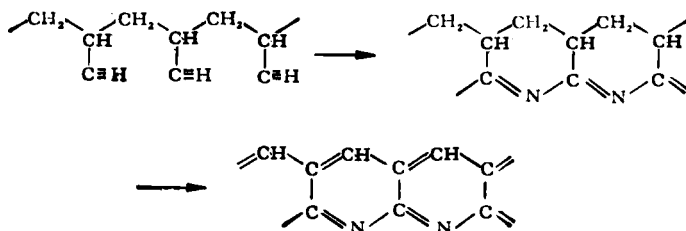
(Institute of Chemistry, Academia Sinica, Beijing)

ABSTRACT

The PAN fiber treated by Lewis acid (e.g. stannic chloride) could be transformed into a macromolecular conducting fiber by further thermal treatment. Depending on thermal treatment condition the resistance of the fiber varied from 10^3 to $10^{12} \Omega$ and kept stable after hydrolysis. The fiber has enough strength to be processed by various means. This is a new kind of macromolecular semiconducting fiber having some characteristics similar to those of organic semiconductors.

INTRODUCTION

It is well known that polyacrylonitrile (PAN) can be transformed into a kind of macromolecular semiconducting material after thermal or radiant treatment. There is a sharp contradiction between the mechanical and electrical behaviours of pyrolytic products. Although some studies dealing with this problem have been done^[1-4], but it has not been resolved. Usually, it is accepted that a linear chain of PAN molecule can be transformed into a ladder's chain owing to cyclization and dehydrogenation of cyanic groups during process of thermal treatment, which is shown as follows.



* Received May 6, 1984

The formation of conjugated system of bonds makes electrons moving freely along the chains. In general, the length of conjugated sequence is so short that the transition of free electrons between the conjugated sequences is prohibited. The resistivity of PAN material treated below 500°C is over $10^5 \Omega \cdot \text{CM}$. On further thermal treatment with nitrogen at temperature over 600°C, the reaction of deheterocyclic atoms between the ladder's sequences would happen and gradually form polymeric carbon having a resistivity of 10 to $10^8 \Omega \cdot \text{CM}$. In this case the properties of the pyrolytic products are too poor to be processed due to the products becoming a kind of hard, brittle materials and difficult to dissolve or melt.

During the study of the products of PAN fibers treated with Lewis acid, we have found that a stable polymeric conducting fiber with good electric and mechanical properties can be obtained after proper thermal treatment.

EXPERIMENTAL

1. Treatment condition of PAN fibers

(1) Treated by SnCl_4 : Liquid SnCl_4 - Ph_2O (Diphenyl oxide) system in which SnCl_4 is 0.3% by weight of Ph_2O ; Temperature: $220 \pm 2^\circ \text{C}$; Time: 28 min; Fiber tension: 0.025 gram / denier.

(2) Thermal treatment: The resistance of the fibers varies over a wide range depending on temperature chosen from 290 to 400°C; Fiber tension: 0.05 gram / denier; Time: 15 min.

2. Measurement of relative resistance of fiber

The measurements of relative resistance of fibers are carried out by using a pair of metal plate electrodes which are 1 cm apart and fixed by an insulator. The fibers are wound on the electrodes 20 turns and the ends are fixed. Relative resistance of the fibers can be measured by using high-resistor meter and universal meter for high resistance and low resistance respectively.

3. Semiconducting characteristic test of fiber

(1) Temperature dependence of resistance: PAN fibers treated by SnCl_4 - Ph_2O are annealed at temperature of 270, 290, 310, 350 and 400°C respectively. The relative resistance is then measured as a function of temperature from room temperature to 270°C. The activation energy E of charge carriers can be calculated with Arrhenius equation.

(2) Frequency dependence of conductivity and DC voltage-ampere character: A bunches of fibers with 10^4 and $10^7 \Omega$ are respectively buried into cured epoxy resin which is cut off with a sharp edge into thin sheets along the direction perpendicular to fiber axis. The thin sheet with a thickness of 2 mm is polished and plated with gold or silver for measuring the change of conductivity with frequency and DC voltage-ampere character.

RESULTS AND DISCUSSION

Temperature dependence and factor of effect on resistance of pyrolytic products of PAN fibers

The colour of PAN fiber treated by SnCl_4 - Ph_2O was apparently changed from white

to dark-brown. The results of IR, DTA and elemental analysis showed that about 50–70% $-\text{C}\equiv\text{N}$ groups were transformed into ladder's macromolecules due to cyclic reaction. But only cyclic reaction occurred and did not form $-\text{C}=\text{C}-\text{C}\equiv\text{N}-$ conjugated structure. The fiber had a resistance over $10^{14} \Omega$. On further thermal treatment the resistance of the fiber would undergo a great change.

The dependence of resistance of fiber on thermal treatment temperature was shown in Fig. 1. The resistance of fiber decreased with increasing thermal treatment temperature and almost had a decrement of eight orders in a temperature range of 260 to 360°C. The fiber still exhibited a good appearance; smooth and soft with a tensile strength of 2000 kg/cm². That was strong enough for processing the fibers to form various types of cloths and tapes. As indicated by the results, the macromolecular semiconducting fibers having both certain resistance and good mechanical property could be obtained by means of simple thermal treatment.

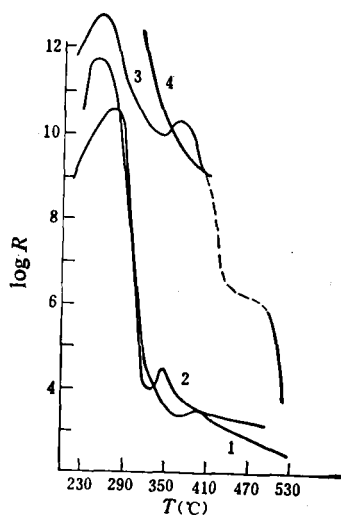


Fig. 1 Relationship of resistance of fiber and thermal treatment temperature under different treatment conditions

1. Copolymeric fiber (No. 2) treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$;
2. Copolymeric fiber (No. 3) treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$;
3. Homopolymeric fiber (No. 1) treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$;
4. Copolymeric fiber (No. 2) untreated by $\text{SnCl}_4\text{-Ph}_2\text{O}$.

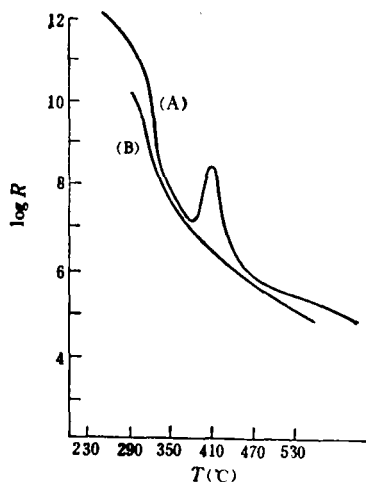


Fig. 2 Effect of thermal treatment atmosphere on resistance of fiber

A. In air; B. In argon.

Three kinds of PAN fibers were used in this study. The property and composition of those fibers were listed in Table 1. Those fibers were treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$ and then with further thermal treatment over a temperature range of 200 to 530°C under the same situation. As shown in Fig. 1, the resistance of fibers decreased with increasing temperature regardless of the composition of fibers. Comparing with copolymeric fiber, the change of resistance of homopolymeric fiber with temperature was slow and showed a scattering of data (see dotted line in Fig. 1). Obviously, copolymeric PAN fiber is much better than homopolymeric PAN fiber for making macromolecular semiconducting fiber. Curve 4 in Fig. 1 showed

Table 1 Composition and property of PAN fiber

Source of fiber samples No.	Composition (weight ratio)	Denier	Strength (gram / denier)	Breaking elongation (%)
1	AN	1.5	4.75	30
2	AN:MA:IA 91.95:6.75:1.48	1.3	5.0	15—25
3	AN:MA:IA 94:5:1	1.1	4.5	12

AN: Acrylonitrile; MA: Methyl acrylate; IA: Itaconic acid

the change of resistance of PAN copolymeric fiber with temperature, which was preoxidized fiber at temperature of 290°C without treatment by $\text{SnCl}_4\text{-Ph}_2\text{O}$. It could be seen that the resistance of same precursor treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$ dropped to $10^4\text{--}10^5\Omega$ at thermal treatment temperature of 350°C but the preoxidized fiber still had a high resistance of $10^9\Omega$ at thermal treatment temperature of 410°C. The strength of the latter was too low to be processed.

After treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$, PAN fibers were held in atmospheres of air and argon for thermal treatment. The change of resistance of fibers with thermal treatment temperature at different atmospheres was shown in Fig. 2. The tendency of change of resistance of fibers with temperature was almost the same and beared no appreciable difference.

Most of organic semiconducting materials have a strong ability of absorbing water. Fig. 3 showed the effect of water on resistance of PAN semiconducting fiber. At the beginning of heating the moisture of the system and fiber evaporated and condensed on the surface of electrode resulting in decrease in resistance. With increasing temperature the resistance of fiber went up due to evaporation of water from surface of electrode. When temperature reached a certain value, water exhausted and the fiber exhibited true resistance. It was necessary to adopt a proper glue for surface treatment of fiber in order to prevent absorbing moisture and improve the weaving property.

Semiconducting characteristics of pyrolytic product of PAN fiber

The semiconducting characteristics of pyrolytic product of PAN fiber treated by $\text{SnCl}_4\text{-Ph}_2\text{O}$ have been demonstrated by results of measurements of resistance-temperature, body conductivity-frequency and DC voltage-ampere as shown in Figs. 4, 5 and 6 respectively.

$\log R$ vs. $1/T$ exhibited linear relation in the range of measurements but not a straight line. There was a reflexive point in the temperature range of 180 to 200°C. It might be related to migration of charge carriers and molecular structure of polymeric aggregate state. The change of activation energy E with measuring temperature was in good agreement with that of the resistance of fiber with thermal treatment temperature. The higher the treatment temperature, the lower the activation energy. Fig. 5 showed that the body conductivity increased with increasing frequency and also had a reflexive point. The result of DC voltage-ampere experiment indicated that this kind of semiconducting fiber exhibited typical characteristics of organic semiconductors.

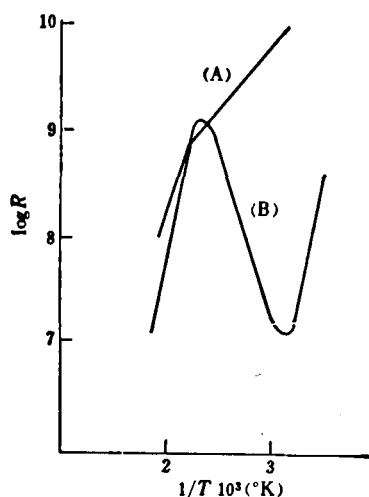


Fig. 3 Effect of water on resistance of fiber
A. Dried fiber;
B. Undried fiber.

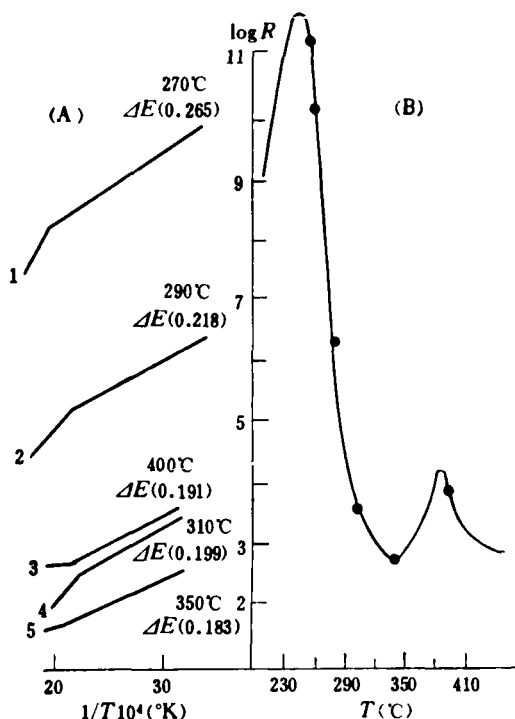


Fig. 4 A. Relationship of resistance of fiber and measurement temperature;
B. Relationship of resistance of fiber and thermal treatment temperature.

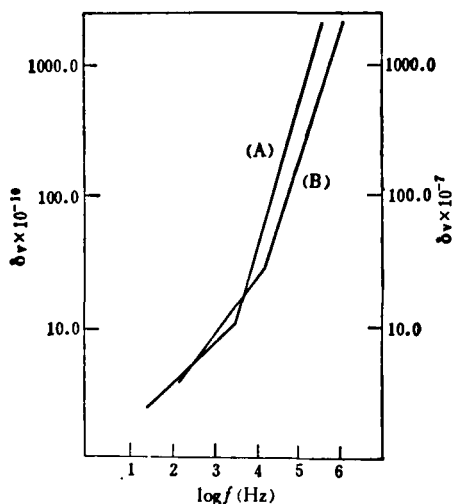


Fig. 5 Dependence of body conductivity of pyrolytic fibers on frequency
A. High resistance fiber ($10^7 \Omega$);
B. Low resistance fiber ($10^4 \Omega$).

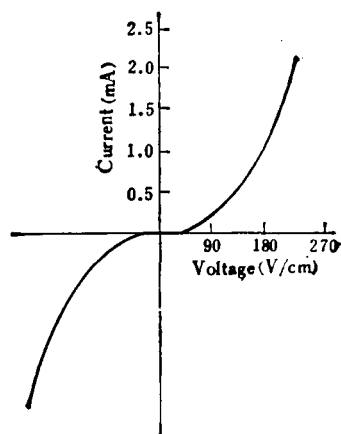


Fig. 6 DC voltage-ampere characteristic curve of pyrolytic fiber
* The place of both words of current and voltage in Fig 6 was put upside down

Acknowledgement The authors are grateful to You Shaoshen for mechanical work; Liu Shuquan for body conductivity measurement of sample; Ying Xinfang for plating film of sample; Wu Meiyun for providing glue of surface treatment of fiber; Prof. Qi Zongneng for valuable comments.

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