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Structure and property of electrospinning PAN nanofibers by different preoxidation temperature

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Abstract In this work, PAN fibers web was fabricated by Electrospinning, and then was pre-oxidated. Effect of the temperature on the structure and property of pre-oxidation web was discussed. The results showed that better level of pre-oxidation nanofibers web can be obtained when the pre-oxidation temperature is 250 °C. At this temperature, Infrared Spectroscopy showed that cyclization and dehydrogenation reaction have occurred and DSC curves showed that cyclization was basically complete, as well as moisture content can be appropriately controlled. Moreover, the preoxidated web with better breaking strength, elongation at break, and the initial modulus could be obtained.

Keywords Cyclization index (CI) · Differential scanning calorimetry (DSC) · Electrospinning · Pre-oxidation · Polyacrylonitrile (PAN)

Introduction

The carbon nanofibers not only have a low-density, high modulus, high strength and high electrical conductivity and thermal stability, and other characteristics, but also have a very small number of defects, aspect ratio, large surface area, and other advantages [1, 2]. The application is of great value in the field of the catalyst, catalyst support, lithium-ion rechargeable battery anode materials, double-layer capacitor electrode, high efficient absorbent, structural reinforcement materials. Preparation of carbon nanofibers have a variety of ways, but mostly in the laboratory stage. Faced with endless market value of carbon nanofibers, the industrial production of carbon nanofibers becomes necessary.

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Electro-spinning is the only way of preparing polymer nanofiber directly and continuously at present. With the craft and equipment moving towards industrialization gradually, electrospinning method of producing carbon nanofibers web will become a research hotspot in the future.

In the preparation of carbon nanofiber web by electrospinning, the degree of pre-oxidation determined the structure and performance of carbon nanofiber to a large extent. The pre-oxidation process of PAN fiber is more complicated, mainly in 4 chemical reaction, that is, cyclization, dehydrogenation, cracking and oxidation. Among that, cyclization and dehydrogenation form heat stability structure, which is the key of pre-oxidation process [3]. It is easy to produce hollow fibers if pre-oxidation is lack. However the over of pre-oxidation will effects structure rearrangement of fiber [4]. Fibers which have heat stability structure can make sure that the fibers do not melt incombustible in the high-temperature carbonization, and maintain stable in thermodynamics.

Pre-oxidation of PAN fiber is not only depend on the structure of the fiber itself, but also closely related to pre-oxidation temperature, the speed of temperature rising and other factors in the process of oxidation. Till now, there are a lot of research on the process of pre-oxidation of PAN fiber [5–8], but published literature about that of electrospinning PAN nanofibers is limited. This article focused on effect of pre-oxidation temperature on the structure and property of electrospinning PAN nanofibers web.

Experimental

Materials

Polyacrylonitrile (PAN) with a molecular weight of 75,000 was purchased from Shanghai Chemical Fibers Institute. N,N-Dimethylacetamide (DMAC) was purchased from Shanghai Chemical Co., and LiCl was purchased from Pinjiang Chemical Co.

Electrospinning setup

Experimental set-up device used for electrospinning process is shown in Fig. 1. Variable high voltage power supply was used for the electrospinning. It was used to produce voltages ranging from 0 to 50 kV, the voltage used in the experiment was 40 kV, and the current was adjusted to be constant. PAN solution was poured in a syringe attached with a capillary tip of 0.5 mm diameter, and the flow rate was uniform, 0.5 ml/h. In addition, the glass fiber fabric was fixed in the steel plate as a receiver. Then, we got uniform area of 30 × 30 cm^2 of the nanofiber web.

Pre-oxidation equipment

101A-1E-blast electric oven which is from Shanghai test instrument factory was used as pre-oxidation device, the temperature rated 300 °C.

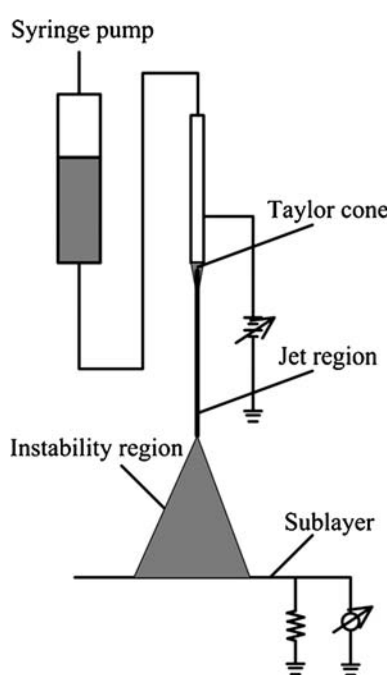


Fig. 1 Experimental set-up device

Measurements

METTLER TOLEDO DSC822e was used to measure heat output of PAN nanofibers and pre-oxidized PAN nanofibers. The microstructure of pre-oxidized PAN nanofibers webs by different pre-oxidation temperature was performed by infrared spectrum. LLY-06 single-fiber tensile strength instrument was used to measure breaking strength and breaking elongation and modulus of different pre-oxidized PAN nanofibers web. Scanning electron microscope (SEM, JSM-5600LV) is used to investigate the morphology of carbon nanofibers web.

METTLER TOLEDO DSC822e thermal analyzer is used to test cyclization degree. Test conditions: scan in the rangeof 50–450 °C, heating rate to 10 °C/min, for the atmosphere of nitrogen. Cyclization of –CN is exothermic reaction. The higher the cyclization degree, the better the pre-oxidation effect. Quantity of heat release is related with cyclization degree of –CN. DSC curve is measured according to Eq. 1:

$$\textit{Cyclization degree}\ (\%) = \frac{H_u - H_o}{H_u} \quad (1)$$

H_μ is quantity of heat release of PAN nanofibers; H_o is quantity of heat release of PAN pre-oxidated nanofibers

Results and discussion

Infrared spectroscopy analysis

As Fig. 2 shows, with the pre-oxidation temperature increasing, –C ≡ N characteristic absorption band at

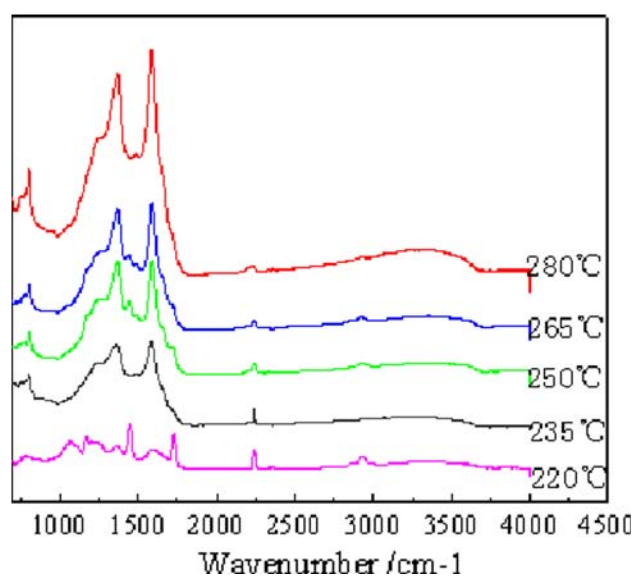


Fig. 2 Infrared Spectroscopy of different samples under different pre-oxidation temperature

2,243 cm^{-1} is decreasing. The absorption peaks of –C = N– band characteristics at 1,590 cm^{-1} and C – H features in the band at 1,363 cm^{-1} increase significantly with the pre-oxidation temperature increasing after 235 °C. Which indicates that cyclization and dehydrogenation reaction have occurred in the pre-oxidation process of PAN nanofibers [9]. A new peak appears in the band at 810 cm^{-1}. It indicates that –C = C– has come into being in the molecules during pre-oxidation process. Which shows that aromatic structure and heat-resistant structure have formed.

Cyclization degree analysis

DSC curves of different samples are showed in Fig. 3 and effect of pre-oxidated temperature on cyclization index is showed in Fig. 4.

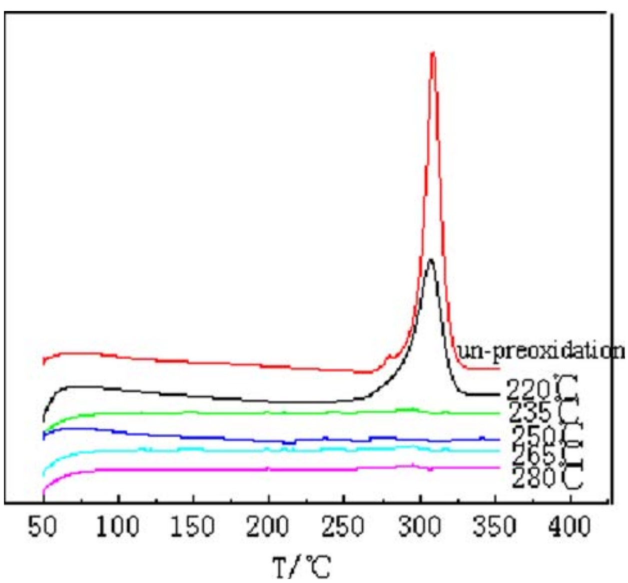


Fig. 3 DSC curves of different pre-oxidation webs under different pre-oxidation temperature

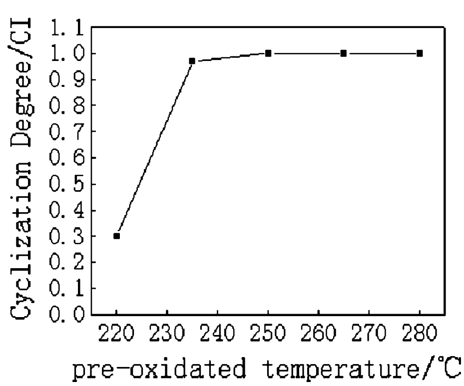


Fig. 4 Effect of pre-oxidated temperature on cyclization index

In Fig. 3, it is clear that there is a heat release peak of PAN un-preoxidated nanofiber web in about 300 °C. The heat release peak decreases with pre-oxidated temperature increasing and the heat release peak completely disappeared when pre-oxidated temperature is over 250 °C.

In Fig. 4, it is obvious that cyclization degree of pre-oxidated nanofiber web is equal to 1 when pre-oxidation temperature is over 250 °C. Cyclization occurs mainly in the 220–235 °C and cyclization was basically complete in 250 °C, at this time, heat-resistant ladder structure has been formed, which achieve the purpose of pre-oxidation.

Moisture content

Moisture content of pre-oxidated nanofiber web is closely related with the oxygen content of pre-oxidated nanofiber web, which can reflect the pre-oxidation degree of the fiber web.If the moisture content is high, the pre-oxidation degree of the fiber web is high too. Oxidation reaction during the process of pre-oxdation is showed in Fig. 5.

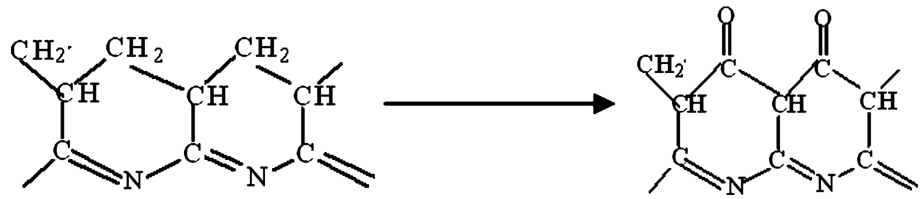
In pre-oxidation process, the role of oxygen is to form the heat-resistant ladder structure in original fibers. If too much oxygen in the pre-oxidated nanofibers web, it would escape Co and CO_2 during carbonization process, so that the carbon fiber have too many flaws [10]. Hefu et al. reported that high-performance carbon fibers could be made when the oxygen content is generally controlled by 8–10% in pre-oxidation fibers, corresponding to the control of moisture content by 6–8%. To electrospinning PAN nanofibers web, moisture content of pre-oxidation web gradually increased with pre-oxidated temperature increasing (see in Fig. 6). Therefore, at pre-oxidation temperature of 250 °C, we could obtain higher pre-oxidation degree of nanofiber web.

Tensile property

Fibers in Fig. 7a are almost unwinding though they are not directional. Fibers in Fig. 7b become disordered. These behaviors imply that electrospinning PAN nanofibers shrinked during oxidatively stabilizing, so the fibers were under stress during oxidatively stabilizing which made the nanofibers disordered and blended at last.

Figures 8 and 9, with the preoxidated temperature increasing, the breaking strength of preoxidated web gradually increased, the breaking elongation has been gradually reduced, and the initial modulus increased. With the preoxidated temperature increasing, the intermolecular forces weakened. However, due to fibers in the preoxidated nanofiber web were bonded with each other, the resistance among the fibers increased, and the breaking strength, initial modulus also increased. As a result of the ability to

Fig. 5 Oxidation reaction during the process of pre-oxidation



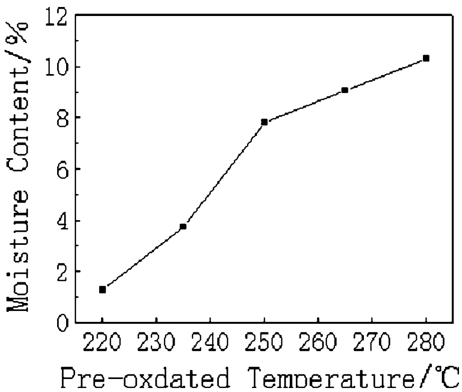


Fig. 6 Effect of pre-oxidated temperature on moisture content of pre-oxidated nanofiber web

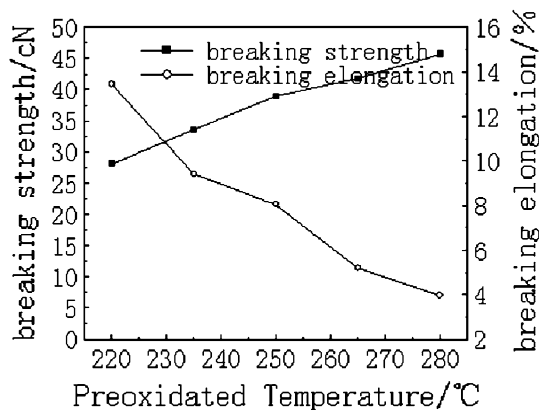


Fig. 8 Effect of preoxidated temperature on breaking strength and breaking elongation

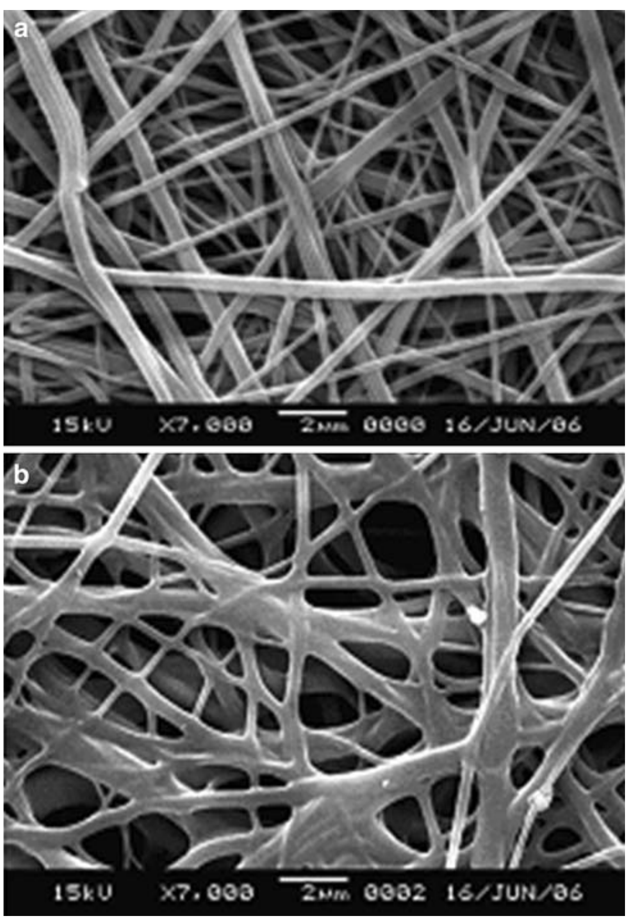


Fig. 7 SEM of electrospinning nanofibers web (**a**) and preoxidated fibers web (**b**)

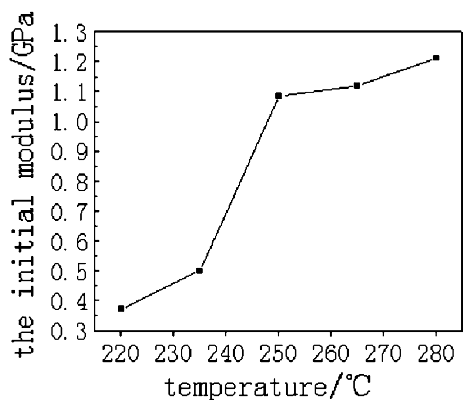


Fig. 9 Effect of preoxidated temperature on modulus

slip between the molecules and the fibers weakened, the breaking elongation reduced.

To sum up, at preoxidated temperature of 250 °C, we obtained the preoxidated web with better breaking strength, elongation at break, and the initial modulus.

SEM of carbon nanofibers

According to preoxidated temperature of 250 °C, we got carbon nanofibers nonwoven by carbonization. SEM of carbon nanofibers are showed in Fig. 10. It is obvious that the surface is smooth and fiber dispersion is small in Fig. 10a, the carbon fiber structure of the section was solid and no empty in Fig. 10b. Which implies that the pre-oxidation temperature of 250 °C is appropriate.

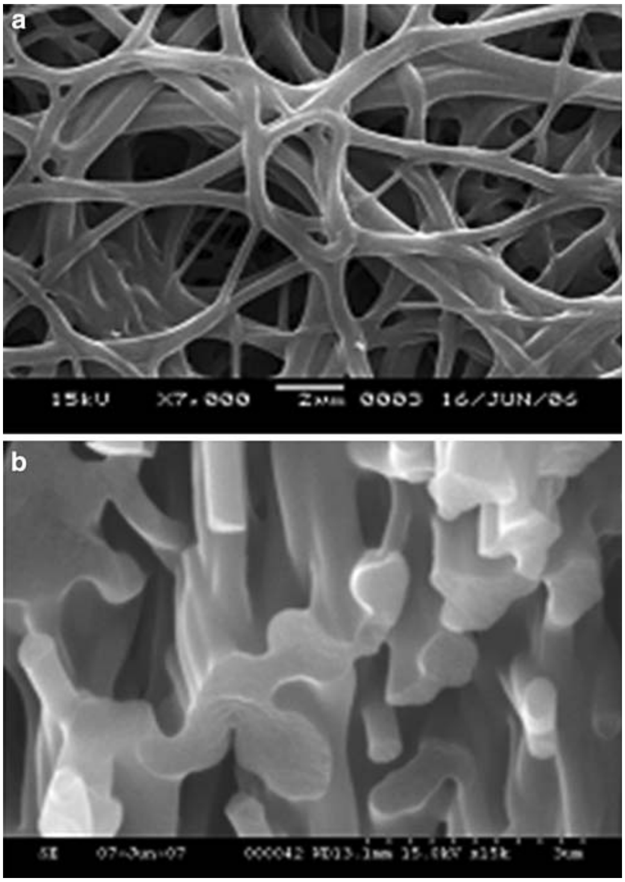


Fig. 10 **a** SEM of carbon nanofibers; **b** SEM of a cross section carbon nanofibers

Conclusions

To sum up, 250 °C is the best pre-oxidation temperature to electrospinning PAN nanofibers web:

(1) DSC curves and cyclization degree analysis showed that cyclization was basically complete at pre-oxidation temperature 250 °C, at this time, heat-resistant ladder structure has been formed, which achieve the purpose of pre-oxidation. Infrared Spectroscopy showed that cyclization and dehydrogenation reaction have occurred in the pre-oxidation process of PAN nanofibers at this temperature.

(2) By analyzing moisture content of pre-oxidated nanofiber web, it is found that moisture content can be controlled from 6% to 8% when pre-oxidation temperature is 250 °C, which is appropriate moisture content to pre-oxidated nanofiber web.

(3) At preoxidated temperature of 250 °C, we obtained the preoxidated web with better breaking strength, elongation at break, and the initial modulus. And better level of pre-oxidation, high-performance carbon nanofibers can be obtained at this pre-oxidation temperature by analyzing the structure and performance of the pre-oxidation web.

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