

The Fourth International Conference on Surface and Interface Science and Engineering

Chemical Modification for PAN Fibers during Heat-treatment Process

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Abstract

Chemical modification for Polyacrylonitrile (PAN) fibers during heat-treatment process were systematically studied by DSC, FT-IR, EA, XPS, etal. Comparing with original PAN fibers, chemical reactions, structures and elemental compositions of fibers modified with potassium permanganate (KMnO₄) solutions were totally changed at a certain extent. KMnO₄ had reduced the activation energy of cyclization, decreased the area and widened the peak of exothermic curve, decreased the velocity of cyclization reaction, increased the oxygen content about 67%, hence increased C—O—C and C=O groups and the core/shell ratio.

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PACS: 81.05.Lg; 81.65.Mq

Keywords: Potassium permanganate; Modification; Polyacrylonitrile(PAN) fibers

1. Introduction

Chemical modification of copolymer PAN precursors was useful for preparing high-tension and high-strain carbon fibers [1, 2]. Heat-treated in the air, the original PAN fibers always had a large area and a narrow peak of exothermic curve, which would easily result to surface defects, therefore, increasing the defects of resultant carbon fibers and decreasing the mechanical performance of carbon fibers. Comparing with the original PAN precursors, fibers pretreated with KMnO₄ had reduced the activation energy of cyclization, decreased the area and widened the peak of exothermic curve, and decreased the velocity of cyclization reaction [3-6]. Hence, it was important for improving inner and outer defects of PAN fibers during preoxidation and carbonization to systematically study thermo-chemical reactions of fibers modified with KMnO₄.

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2. Materials and Methods

A wet-spun precursor with a comonomer (6 wt %methyl acrylate and 1 wt % itaconic acid) was selected for this study. The fibers, containing 3000 filaments with 1.2 dtex for a single one, were thermally stabilized and carbonized on a bench scale in a laboratory system.

The modified fibers, named as G, or original fibers, named as U, were passed continuously through a furnace for stabilization, which was divided into three zones with a temperature gradient in the range of 220~300°C. The stabilization atmosphere was clean air. The preoxidized fibers were finally heated in oxygen-free nitrogen up to 1350°C to obtain PAN-based carbon fibers.

Differential scanning calorimetry (DSC) experiments were carried out on an American Perkin—Elmer DSC-2 instrument. Experiments were performed in air at a heating rate of 5°C/min. Elemental analysis was carried out with a Carlo Erba Azione 1106 model elemental analyzer (Milano, Italy). A fiber sample was first washed with acetone, dried in vacuo at 105°C, and then analyzed for carbon, hydrogen, and nitrogen. The oxygen content was determined from the difference between these three. In addition, the K and Mn contents were measured with a Hitachi Z-8000 atomic emission spectrometer (Tokyo, Japan). X-ray photoelectron spectra were recorded using a Scienta ESCA300 spectrometer with a Mg K α X-ray source(1254eV). Depth profile data were obtained after sputtering with an argon (Ar) ion beam. The ion gun was operated at 15kV with an ion current of 10 mA and the beam rastered over a 5mm \times 5mm area of the film. 1 cm \times 1cm sized pieces of Kapton were used.

3. Results and Discussion

3.1 Differential scanning calorimetry (DSC) study.

As shown in figure 1, the range of the exotherm for modified fibers (G) was from 204.8°C to 308.2°C, a spread of 103.4°C, whereas for original fibers (U) the range was from 211.9°C to 301.1°C, a spread of 89.2°C. A lower value of the exotherm spread over a wide temperature range was more desirable than a larger value spread over a narrow temperature range, since in the latter case there were more chances of damage to the structure of the material during oxidation.

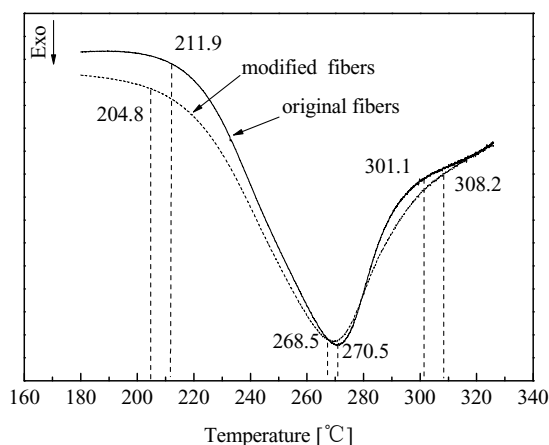


Fig.1. DSC curves of Courtelle fibers

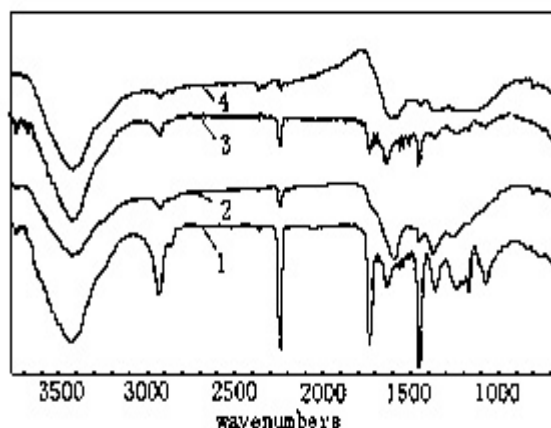


Fig.2. The FT-IR spectrum of fiber U and G
1. fiber U 2. U in 240°C 3. fiber G 4. G in 240°C

3.2 Infrared (IR) spectra study.

The spectrum of original PAN fibers contained prominent peaks at 2930 and 2240 cm^{-1} due to stretching vibration of the methylene ($-\text{CH}_2-$) and the nitrile groups ($-\text{C}\equiv\text{N}$). When PAN fibers was treated with KMnO_4 solutions, the spectrum gave rise to a new peak at 2340 cm^{-1} , which, together with widen of peak between 1580 and 1625 cm^{-1} , indicates the formation of the >C=N- conjugated structure that was relevant to PAN fibers pretreated with KMnO_4 solutions. The manganese atom attracted the $-\text{C}\equiv\text{N}$ groups of AN unit to initiate the cyclization reaction, consequently enabling the cyclization reaction to occur at a low temperature. And with the increasing of extent of preoxidization, the peak of this kind of conjugated structure had intensified, causing the decrease of content of the nitrile groups in macromolecule chains. Besides the prominent peaks mentioned above, the peak at 1361 cm^{-1} was intensified in FT-IR of modified fibers, which indicated increasing of C=C groups content in the KMnO_4 modified fibers possibly caused by partial dehydrogenation reaction. The peaks at 2920 cm^{-1} and 1450 cm^{-1} , due to stretching vibration and binding vibration of the C=C respectively, also took place notable changes. Stretching vibration of the >C=N- groups at 1600 cm^{-1} was representative for the formation velocity of pyridine cycle. And the peak at 800 cm^{-1} caused by vibration of pyridine cycle and binding vibration of the methylene on the cycle could also prove the formation velocity of pyridine cycle. The value of 1380 cm^{-1} /2240 cm^{-1} could be used to disclosure the velocity of cyclization reaction at a certain extent.

3.3 Elemental analysis (EA) study.

Tab. 1 Elemental Compositions of the PAN precursor and Preoxidized Fibers

Fiber type	C/%	H/%	N/%	O/%	K/%	Mn/%	C/N/H/O
Original fibers	66.21	5.76	24.18	3.68	0.0008	0.009	3.00/0.94/3.11/0.13
Modified fibers	64.63	5.58	23.51	6.15	0.336	0.208	3.00/0.94/3.09/0.19
Unmodified preoxidized fibers ^a	63.75	4.18	22.52	8.4	—	—	3.00/0.91/2.34/0.30
Modified preoxidized fibers	62.98	4.6	22.33	8.62	—	—	3.00/0.91/2.61/0.31

^a Obtained after heat treatment at 280 $^{\circ}\text{C}$

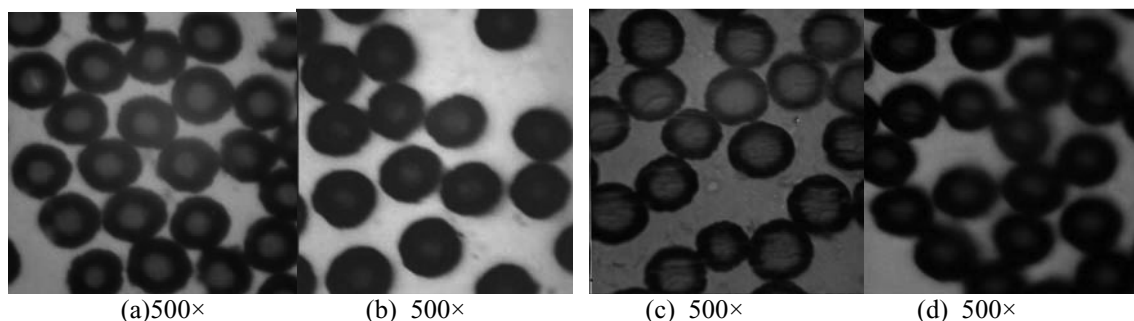


Fig.3. Skin/core morphology of preoxidized fibers developed from modified fibers at (a) 250 and (b) 300 $^{\circ}\text{C}$ and of unmodified fibers at (c) 250 and (d) 300 $^{\circ}\text{C}$.

The modification of PAN fibers with KMnO_4 increased the oxygen content in a PAN fiber, as shown in Table 1. The carbon and hydrogen contents in a modified PAN fiber had no significant differences in comparison with those in an unmodified PAN precursor fiber, whereas the oxygen content, 6.15% in a modified PAN fiber, was higher than 3.68% in an unmodified fiber, with an increase of 67%. The oxygen, as an active site, would promote the cyclization and preoxidation rate, and this was in agreement with the fact that the concentrated oxygen in a modified PAN precursor fiber could result in a higher skin/core ratio during the process of thermal stabilization (see figure 3), demonstrating the improvement in the homogeneous structure in the inner and outer parts of preoxidized fibers. As a

result, the higher oxygen content in a modified PAN precursor fiber also resulted in much more oxygen-contained functional groups, such as $\text{C}=\text{O}$ and $\text{HO}-\text{C}=\text{O}$, which would increase the water absorption in a PAN fiber(not presented here), especially after its preoxidation stage.

3.4 X-ray photoelectron spectroscopy(XPS) study.

In figure 4, O 1s XPS spectra of original PAN fibers and modified PAN fibers, peak 1# at 532.46eV which was caused by $-\text{OH}$ groups mainly existing in the surface of fibers becomes stronger, indicating the content of $-\text{OH}$ was increased in the fiber due to chemical modification. Peak 2# at 532.93eV became weaker, which was caused by the decrease of $\text{C}-\text{O}-\text{C}$ groups. $\text{C}=\text{O}$ groups (534.67eV) also became weak. Comparing with modified fibers, from figure 5, O 1s XPS spectra of modified preoxidized fibers, the peak at 530.9eV became weak and the peak at 532eV became strong, which indicated the decrease of hydroxide groups and increase of ether bonds respectively. Changes of these chemical groups had evidenced the increase of oxygen-contained groups in IR while giving a forceful proof to the improvement of the content of O element and the increase of Skin/core ratio in modified fibers.

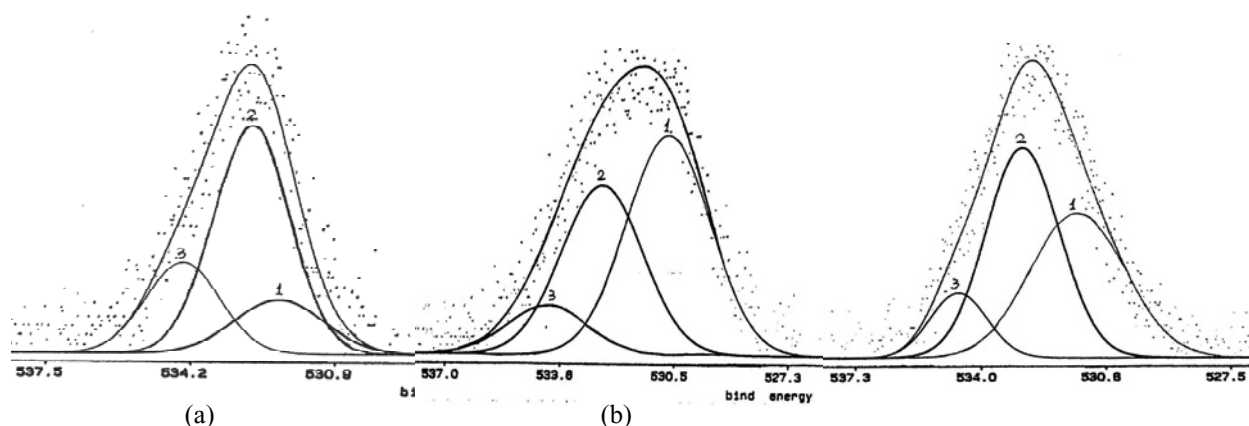


Fig.4. O 1s XPS spectra of fiber U and G
(a) Fiber U (b) Fiber G

Fig.5. O 1s XPS spectra of the preoxidized fiber of G

4. Conclusions

A modified PAN precursor fiber could be fully preoxidized at a lower temperature, showing a catalytic effect of KMnO_4 , which accelerated the rate of preoxidation and reduced the time of thermal stabilization. The modification also increased the oxygen content in a PAN precursor fiber, resulting in an increase in the skin/core ratio for preoxidized fibers developed from modified precursors and further improving the uniformity of the cross-section structure.

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