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Evolution of the morphological and structural properties of plasticized spinning polyacrylonitrile fibers during the stabilization process

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Abstract: The morphological and structural properties of the plasticized spinning polyacrylonitrile (PAN) fibers during the stabilization process were investigated. The PAN fibers were subjected to stabilization treatment following a three-stage heating. It is found that the stabilization degree of the PAN fibers is significantly higher than commercial PAN fibers characterized by elemental analysis, fourier transform infrared spectroscopy and X-ray diffraction. For plasticized spinning fibers, the stabilization can occur at crystalline region even at low temperature of 180ºC, oxygen containing groups at crystalline region generated during the plasticized spinning process may be responsible for this phenomenon. At stabilization temperature of 230ºC, the cross-section of plasticized spinning fibers exhibits large block stacking structure with obvious grooves among them, while cross-section of the fibers shows sheet-like divergence structure at 260ºC. The mechanical properties and density test results further indicate that 260ºC is a critical stabilization temperature for plasticized spinning fibers. Meanwhile, it is observed that the slight skin-core structure can be formed during the stabilization process.

Key words: plasticized spinning; PAN fibers; stabilization; structure; skin-core.

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1. Introduction

Carbon fibers (CFs) with excellent properties are fabricated from polyacrylonitrile (PAN) precursor fibers through the thermal treatments of stabilization and carbonization[1]. The PAN-based CFs with high strength-to-weight ratio and superior stiffness are popularly considered as an ideal candidate for developing large load-bearing composites[2-4]. The production of PAN-based CFs involves spinning of precursor fibers, stabilization, carbonization and so on, all of which are crucial to improve the mechanical properties of the CFs[5-7]. The PAN fibers are generally fabricated by solution spinning method[8-10], and the use of large amounts of organic solvents causes environmental and health problems[11]. Moreover, the uneven skin-core structure can be generally observed in PAN fibers owing to the non-uniformity of double diffusion during the forming process of the as-spun fibers[12]. These structural imperfections of PAN precursor give rise to the deterioration of mechanical properties. External plasticized spinning is a promising method to prepare PAN fibers without disadvantages of uneven skin-core structures and micro-pores[13]. Moreover, compared with internal plasticized spinning[14-16], the prepared PAN fibers possess high acrylonitrile monomer content so as to maintain their characteristics, which will facilitate the subsequent stabilization and carbonization stages.

The quality of resulting CFs is also critically dependent on stabilization stage, which is time and energy consumption stage[17]. Therefore stabilization has been considered as a significant step in determining the cost of final CFs[18]. In order to reduce the consumption during the stabilization stage, catalytic modification methods[19-23] have been widely adopted. However, the amount of the chemicals has to be carefully controlled and optimized

as excess diffusion of chemicals to fibers may lead to the damage of fibers[24]. In addition, the introduction of catalytic modification processes also makes the stabilization stage more complicated. Thus it makes sense to look for a simpler and effective method to improve the efficiency of stabilization. In our previous study[4,11], we found that the special cyclization structure and oxygen-containing groups were generated during the plasticized spinning process, which would significantly shorten the time of stabilization stage.

Nevertheless, we have not exhaustively compared stabilization degree of plasticized spinning fibers with commercial fibers (wet spinning) under the same stabilization temperature. Moreover, to the best of our knowledge, there are few reports concerning the effect of temperature on the morphological and structural properties of the plasticized spinning fibers during the stabilization process. Consequently, those problems will be systematically studied in this paper and the most suitable stabilization temperature for plasticized spinning PAN fibers will be discussed as well.

2. Experimental Section

2.1 Materials

The plasticized spinning PAN fibers were fabricated by our laboratory, and commercial PAN fibers were purchased from Shanghai Synthetic Fiber Institute.

2.2 Preparation of samples

Stabilization was carried out at a self-designed continuous production line composed of 3 tube furnaces, as illustrated in Fig 1. The applied tension was adjusted through controlling frequency of godet roller and was 0.5 cN per dtex. The stabilization temperature in 3 tube furnaces (1 to 3) was designated in sequence as 180ºC, 230ºC and 260ºC. B_1, D_1, B_2, D_2, B_3

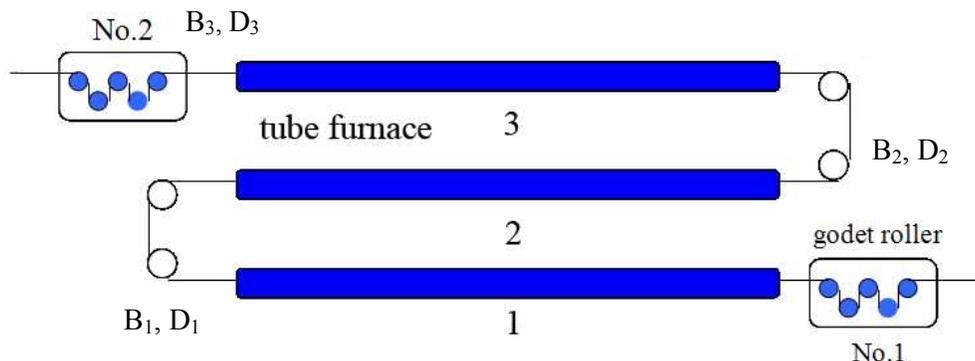and D_3 represent stabilized fibers at different stages, as shown in Fig 1.

Fig. 1. The schematic of stabilization of PAN fibers.

2.3 Measurements

Elmentar elemental analyzer (Vario EL III, Elmentar, Germany) was using to measure the carbon, hydrogen, nitrogen and oxygen contents of stabilized fibers and carbon fibers.

The Infrared spectra (IR) spectrum was recorded using a FTIR (Spectrum BX□, Perkin Elmer, US) spectrometer in the range of 400-4000cm^{-1} using KBr pellets, 32 scans were collected at a resolution of 1 cm^{-1}.

The X-ray diffraction analysis(XRD) using CuKα (λ=0.1542 nm) for PAN fibers was conducted under the X-ray diffractometer (D/Max-2550 PC, RIGAKU, Japan), the operation voltage and electricity were 30kv and 10mA respectively. The average crystal size (Lc) was calculated using the Scherrer equation[25]:

$$L_C = \frac{k\lambda}{\beta\cos\theta}$$ (1)

where K is the apparatus constant, which was taken to be 0.89; λ=0.1542 nm is the wavelength of the X-rays; β is the full width at half maximum in radians at 2θ =17°.

The crystallinity was determined from the XRD patterns of the fibers according to the

formula calculated by Hinrichsen's method[26]:

$$C\% = \frac{Ac}{Ac + Aa} \qquad (2)$$

where Ac is the integral area of the crystalline region, and Aa is the integral area of the amorphous region.

The orientation in crystalline of the fibers was measured by XRD diffraction, the fibers was scanned around $2\theta=17°$, and the degree of orientation was determined by the following equation[27]:

$$\pi = \frac{180 - H}{180} \times 100\% \qquad (3)$$

where H is the full width at half the maximum intensity at $2\theta=17°$ diffraction.

Peakfit soft (v4.12) was utilized for peak fitting of nritile groups for FTIR spectra of the fibers.

Field emission scanning electron microscopy (FESEM, S-4800, HITACHI, Japan) (operating voltage, 2 kV) was used to observe the cross-section of the fibers. The fibers were washed with alcohol for several times and dried in an oven, some fibers were embedded in epoxy resin followed by brittle fracture in liquid nitrogen, some fibers were embedded in haci slicer and then cut by blade.

Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) (operating voltage, 150 kV) was employed to microstructures of stabilized fibers, the fibers were embedded in epoxy resin, then embedded samples were ultramicrotomed to the thickness of nanoscale.

The fiber tensile strength machine (XQ-1, Shanghai New Fiber Instrument Co., Ltd., China) was used to measure the mechanical properties of PAN fibers at a gauge length of 20mm and at a cross-head speed of 20mm/min. The statistical results came from 20

measurements for each sample.

The density of fibers was measured by flotation technique. n-Heptane (0.68 g cm^{-3}) and 1,2-dibromoethane (2.17 g cm^{-3}) were mixed in different proportions to form mixtures in the range of 1.11 g cm^{-3} to 1.58 g cm^{-3}.

3. Results and discussion

3.1 Elemental analysis

Table 1 shows the properties of plasticized spinning and commercial PAN fibers. It can be observed that various performance parameters of plasticized spinning fibers are close to those of commercial fibers. Thus it makes sense to compare morphological and structural properties of two kinds of fibers under the same stabilization conditions.

Table 1 The properties of plasticized spinning and commercial PAN fibers.

Fibers type	Strain to failure /%	Tensile strength cN/dtex	Tensile modulus /cN/dtex	Crystallinity/%	Orientation in crystalline/ %
Plasticized spinning fibers	9.26	5.95	100.92	67.6	92.4
Commercial fibers	11.18	5.57	105.4	68.7	94.3

The elemental analysis of the stabilized fibers was listed in Table 2. It is interesting to observe that the oxygen content of plasticized spinning PAN fibers and their stabilized fibers is obviously higher than commercial PAN fibers, which is attributed to the occurrence of cyclization and oxidation reactions during the plasticized spinning process[4,11]. Comparing the oxygen content of two kinds of fibers under the same temperature, it can be seen that the oxidation degree of plasticized spinning fibers is significantly higher than that of commercial fibers, indicating that oxygen-containing groups and special cyclization structures generated

during the spinning process[4,11] significantly accelerate stabilization process for plasticized spinning PAN fibers. The hydrogen content of B_3 is lower than D_3, revealing that the unique chain structures of plasticized spinning fibers also facilitate the dehydrogenation reaction. It is proposed[13] that the oxygen content of stabilized fibers should be controlled within the range of 8-12%, consequently, 260ºC can be considered as a suitable stabilization temperature for plasticized spinning fibers.

Table 2 The elemental analysis of the stabilized fibers.

Fibers type	Fibers name	O/%	N/%	H/%	C/%
Plasticized spinning PAN fibers	A	4.98	23.21	5.23	66.58
Stabilized fibers	B_1	5.12	23.44	5.17	66.27
	B_2	8.24	23.5	4.94	63.32
	B_3	12.5	22.82	4.12	60.56
Commercial PAN fibers	C	1.96	25.09	5.66	67.29
Stabilized fibers	D_1	2.18	25.12	5.59	67.11
	D_2	3.87	25.09	5.24	65.8
	D_3	5.12	24.04	5.05	65.79

3.2 FTIR analysis

For FTIR spectra of PAN fibers, the peaks in the range of 2180-2260cm^{-1} can be ascribed to three types of C≡N groups, un-reacted nitrile at 2242cm^{-1}, conjugated nitrile at 2210cm^{-1} and β-amino nitrile at 2190cm^{-1}[28,29]. As shown in Table 3 and Fig. 2, B_3 shows a higher Φ_c as compared to D_3. The conjugated nitrile is generated upon dehydrogenation[30], thus dehydrogenation reaction is significantly accelerated for plasticized spinning fibers. The Φ_b is formed as a consequence of termination of cyclization[30], which causes chain scission. Accordingly the higher ratio of Φ_c/Φ_b for B_3 as compared with D_3 suggests lower degree of chain scission and fewer defects in the B_3.

Table 3 Peak fitting for FTIR spectra of plasticized spinning and commercial PAN fibers after stabilization.

B₃				D₃			
Φ_c/%	Φ_b/%	Φ_c/Φ_b	Φ_d/%	Φ_c/%	Φ_b/%	Φ_c/Φ_b	Φ_d/%
45.62	11.77	3.88	42.61	8.87	8.8	1.008	82.33

Note: Φ_c: Percentage of conjugated nitrile, Φ_b: Percentage of β-amino nitrile, Φ_d: Percentage of unreacted nitrile.
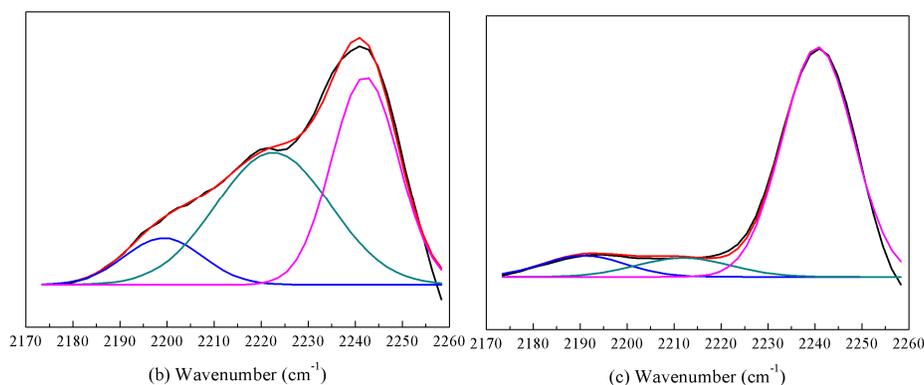
Fig. 2. Nitrile peak fitting of FTIR spectra of stabilized PAN fibers: (a) B₃, (b) D₃.

3.3 XRD analysis

The XRD data and curves of stabilized fibers are listed in Table 4 and Fig. 3. For plasticized spinning fibers, it is evident that crystallinity, crystal size and orientation are sharply decreased with increasing temperature. It is noted that the crystallinity of D_1 is basically unchanged compared with that of C, while crystallinity of B_1 is reduced from 67.6% to 66% at stabilization temperature of 180ºC. This reveals that stabilization can take place at crystalline region of plasticized spinning fibers even at low temperature of 180ºC. The possible reason is that the oxygen-containing groups at crystalline region formed during the plasticized spinning process may initiate the cyclization reaction, leading to the reduction in regularity of molecular chains at crystalline region. Meanwhile, the crystallinity of B_3 is significantly reduced as compared with B_2, suggesting that the temperature of 260ºC markedly promotes the stabilization reaction.

Table 4 XRD data of stabilized fibers.

Fibers name	Crystallinity/%	Crystal size/nm	Orientation in crystalline/%
A	67.62	4.7	92.4
B_1	66.13	4.32	91.8
B_2	59.85	3.98	74.1
B_3	47.11	3.15	57.5
C	68.73	5.24	94.3
D_1	68.41	5.18	94.0
D_2	65.76	4.97	87.8
D_3	62.45	4.71	83.7

(a) 2θ /(°)   (b) 2θ /(°)
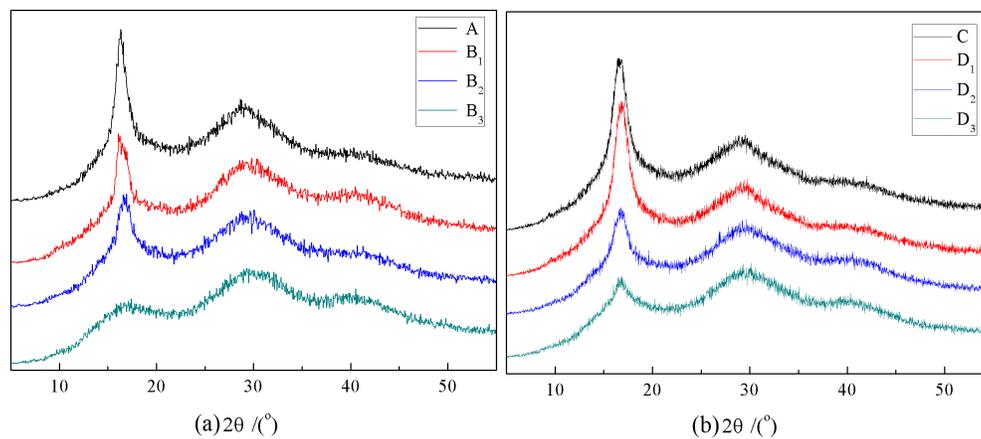
Fig. 3. XRD curves of of stabilized fibers.

3.4 SEM and TEM analysis

As depicted in Fig. 4 (a) and Fig. 4 (b), it can be observed that plasticized spinning PAN precursor with high tenacity tends to deform during the cutting process. And the cross-section of stabilized PAN fibers is very close to circular (in Fig. 4 (c) and Fig. 4 (d)), suggesting that the stabilized PAN fibers exhibit fragility and are prone to brittle fracture under stress. It is worth noting that there exists some small holes on cross-section of the stabilized fibers, which can not be observed on PAN fibers, this requires further analysis.

As shown in Fig. 4 (e) and Fig. 4 (f), the cross-section of commercial PAN fibers after

stabilization exhibits kidney-shaped morphology, cross-sectional structure is relatively compact and no small holes can be observed. However, non-circular cross-section is not conducive to homogenization transition of the PAN structure during the subsequent carbonization stage.
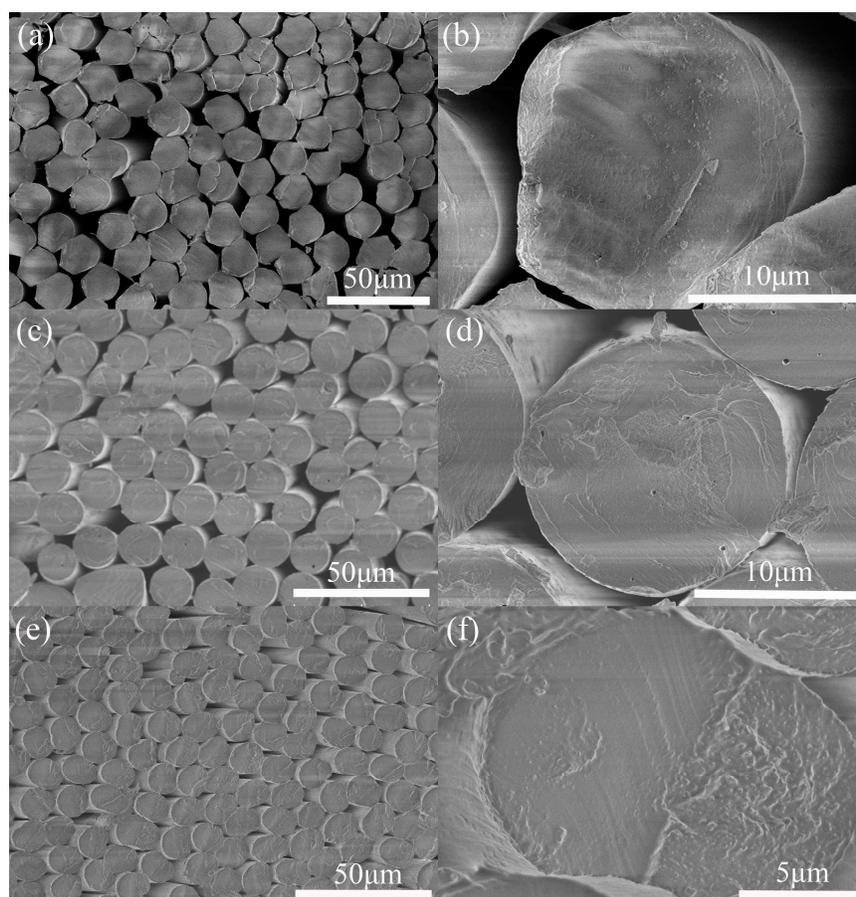

Fig. 4. The cross-section SEM images of plasticized spinning and commercial PAN fibers after stabilization：(a), (b) A；(c), (d) B$_3$；(e), (f) D$_3$; The samples were fabricated by haci slicer.

The cross-section morphology of stabilized PAN fibers whose precursor was fabricated by wet-spinning has been systematically studied[31]. Ko et al.[32,33] proposed that the fracture surface of the stabilized fibers show a radial structure from the center to the boundary. As shown in Fig. 5, the cross-section morphology of D$_3$ is consistent with the view of Ko[32,33]. Moreover, the radial fracture feature of D$_3$ also reveals that fracture first occurs in

the core, and then spreads to the border. Non-simultaneous fracture indicates that there exists obvious skin-core structure for stabilized fibers.
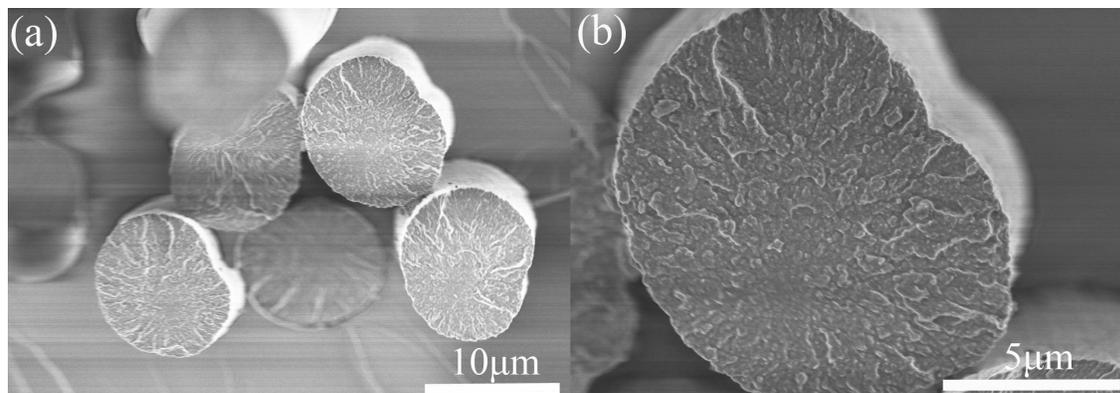

Fig. 5. The cross section images of D_3.

In this paper, the PAN fibers, prepared by plasticized spinning, present different structural feature, as shown in Fig 6. D_2 and D_3 present different cross-sectional structures, D_2 exhibits large block stacking structure with obvious grooves among them. While D_3 shows sheet-like divergence structure. Accordingly, 260ºC is a critical stabilization temperature, the stabilization degree is remarkably improved and structural transition is apparent at this temperature, which is in agreement with the XRD results.
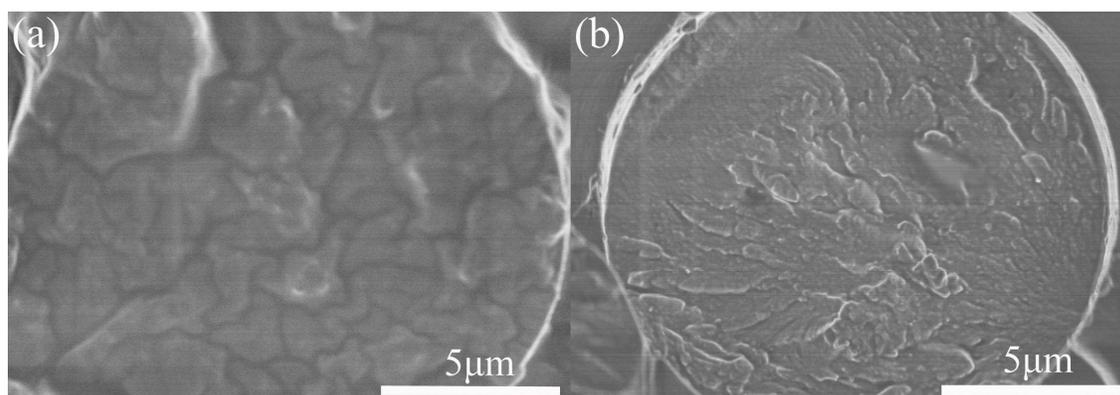

Fig. 6. The cross section images of stabilized fibers: (a): D_2, (b): D_3.

In order to accurately observe the differences between core and skin layer of the structure, TEM was employed. As can be seen in Fig. 7 (a') and (b'), skin layer structure is

dense, but core structure is relatively loose. It can be visually observed that crystal size in skin layer is obviously smaller than core in 20nm scale (in Fig. 7 (a'') and (d'')). For those PAN fibers prepared by wet spinning, skin-core structure is easily formed during the wet spinning process, which is induced by double diffusion process[9]. But for plasticized spinning PAN fibers, skin-core structure can not be generated during the spinning process. Consequently, this reveals that the skin-core structure is still possible to form during the stabilization stage.
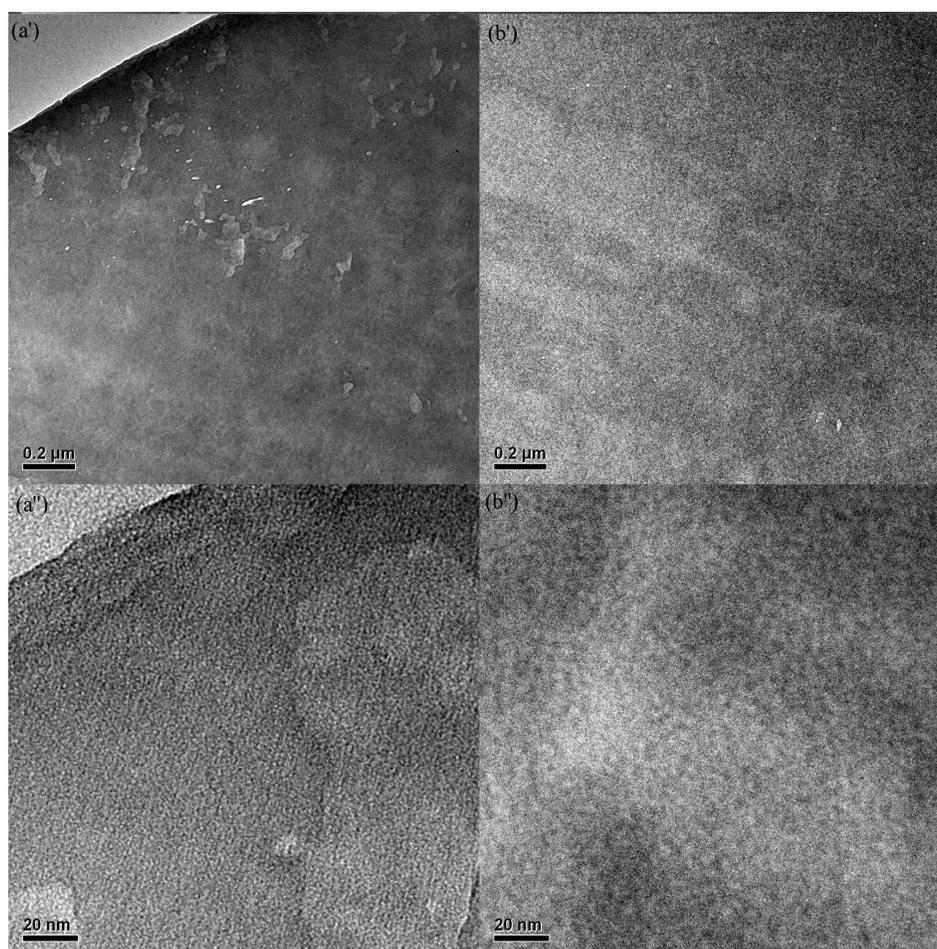

Fig. 7. The TEM photographs of stabilized fibers (D$_3$): (a') and (a'') skin layer, (b') and (b'') core.

3.5 Physical properties

It is well known that the decrease in mechanical properties of stabilized fibers are due

to the loss of inter-chain cohesive energy as a consequence of chemical reactions[34]. Fig. 8 display the mechanical properties of stabilized fibers. For plasticized spinning fibers, the tensile strength (in Fig. 8 (a)) and tensile modulus (in Fig. 8 (b)) are sharply decreased as the temperature reaches 260ºC. This further confirms that stabilization process is significantly accelerated at this temperature. Meanwhile, the significant reduction in tensile strength and tensile modulus for plasticized spinning fibers indicates that stabilization degree of plasticized spinning fibers is obviously higher than that of commercial fibers.

It is noted that the elongation at break of plasticized spinning fibers is increased at first, and then decreased, while elongation at break of commercial fibers is firstly decreased, and then increased. This indicates that there exists different stabilization behaviors for two kinds of fibers under the same stabilization temperature. For plasticized spinning fibers, stabilization reactions have propagated to crystalline region at low temperature of 180ºC, which has been confirmed by XRD data. Amorphization transition causes relaxation of molecular chains, leading to the increase in elongation at break. Ladder structure may be formed and molecular chains may be crosslinked at the stabilization temperature of 260ºC. These changes increase the the rigidity of the molecular chains, resulting in the decrease in elongation at break. Similarly, for commercial fibers, it is reasonable to speculate that stabilization reactions occur mainly at amorphous region as the stabilization temperature is lower than 260ºC. Rigidity of molecular chains at amorphous region is increased with increasing stabilization temperature, leading to the reduce in elongation at break. The increase in elongation at break of the fibers as the temperature reaches 260ºC reveals that stabilization process is apparently accelerated at crystalline region at this temperature.
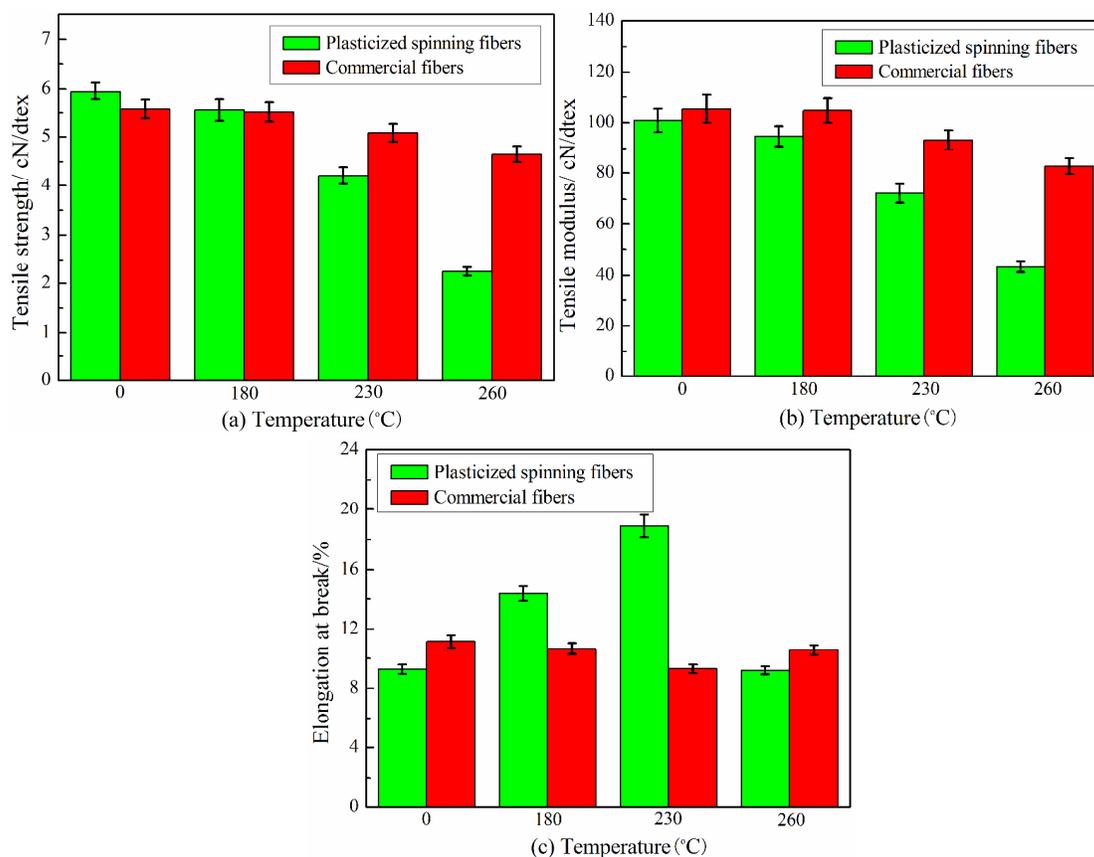
Fig. 8. The mechanical properties of stabilized fibers.

The density of fibers as a function of stabilization temperature is plotted in Fig .9. The density of stabilized fibers is increased with increasing stabilization temperature, which is in agreement with the changing trend of oxygen content (in Table 1). This indicates that the incorporation of oxygen to fibers contributes greatly to the increase in density. It is obvious that the density of plasticized spinning fibers is higher than that of commercial fibers under the same stabilization temperature. For plasticized spinning fibers, the density is markedly increased from 1.192 to 1.353 g/cm^3 as the temperature reaches the 260°C. It is suggested[35] that the appropriate density of stabilized fibers should be in range of 1.34-1.39g/cm^3, this further confirms that 260°C can be suggested as a suitable stabilization temperature for plasticized spinning fibers.
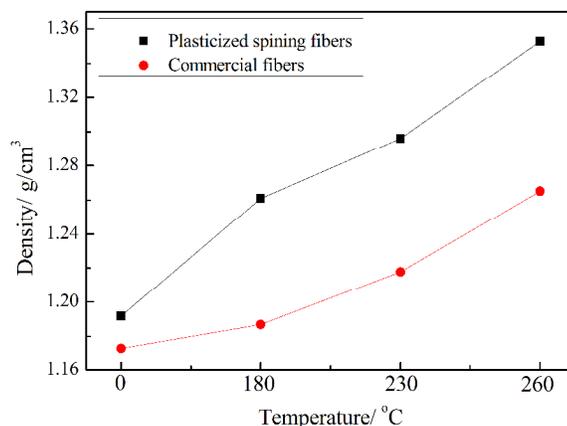
Fig. 9. The density of stabilized fibers.

Conclusion

In this paper, the effect of temperature on morphological and structural properties of plasticized spinning PAN fibers was studied. It is observed that the stabilization degree of plasticized spinning fibers was significantly higher than commercial fibers.

At 230ºC, the plasticized spinning fibers exhibit large block stacking structure with obvious grooves among them, while the fibers show sheet-like divergence structure at 260ºC. Meanwhile, the skin layer structure of stabilized fibers was dense, but core structure was relatively loose, indicating that the slight skin-core structure of PAN fibers was generated during the stabilization.

After stabilization at the temperature of 260ºC, the oxygen content and density of plasticized spinning fibers were 12.5% and 1.353 g/cm^{-3} respectively. This indicated that 260ºC was suitable as a stabilization temperature for plasticized spinning fibers.

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