

EFFECTS OF DEFORMATION-INDUCED ORIENTATION ON CYCLIZATION AND OXIDATION OF POLYACRYLONITRILE FIBERS DURING STABILIZATION PROCESS*

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Abstract Orientation of copolymer polyacrylonitrile (PAN) chains during their deformation prior to stabilization and the further effect on the stabilization were investigated in detail. Results reveal that the orientation of PAN chains presents a saturation point of 69.51% when the deformation ratio reaches approximately 1.07, meanwhile the cyclization rather than the oxidation has a stronger dependence on the orientation of PAN chains during stabilization. The cyclization is facilitated that the cyclization degree is increasing while the activation energy is decreasing obviously as a consequence of the developing orientation of PAN fibers before the saturation point; however, it is restrained during the further deformation of PAN fibers after the point. The resulting carbon fibers obtained from the PAN fibers prepared at the saturation point possess the highest mechanical properties of 4.07 GPa in tensile strength and 249.0 GPa in tensile modulus.

Keywords: Polyacrylonitrile; Orientation; Deformation; Stabilization; Carbon fiber.

INTRODUCTION

The excellent tensile strength, the superior stiffness and low density have made the carbon fibers (CFs) become an ideal candidate for developing large load-bearing composites^[1–5]. It has been well established that copolymer polyacrylonitrile (PAN) fibers are the perfect precursors for preparing high-performance carbon fibers through a continuous thermal treatment of stabilization at 200–300°C in air followed by carbonization carried out at a temperature of up to 800–1500°C in an inert atmosphere^[6–9]. Recently, a pretreatment of hot-stretching prior to the stabilization at 160–180°C, which could improve the orientation of PAN chains remarkably, has become an indispensable process to produce high-quality PAN-based CFs and attracted numerous theoretical and technical researches^[5, 8–17]. During the hot-stretching, PAN chains are activated from frozen state as a consequence of the heat treatment, enabling PAN chains to align orderly with respect to fiber axis when they are stretched simultaneously. It is confirmed that the stretching-induced orientation in PAN chains is converted to the cyclized structures during stabilization, and the resulting CFs after carbonization exhibit an increase in mechanical properties^[5].

To the best of our knowledge, though there have been a few research efforts with the objective being targeted on developing the tensile strength of CFs through improving the orientation of PAN chains before stabilization^[18–24], we have not identified any previous literature concerning the effect of hot-stretching induced

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orientation of PAN chains on the cyclization and oxidation during stabilization. Such a situation has impeded us to further understand the influence mechanism of hot-stretching on the conversion of PAN fibers to CFs.

In this study, orientation of copolymer PAN chains during their deformation prior to stabilization and the further effect on the stabilization were investigated in detail. To approach the purpose, PAN fibers are stretched by various ratios at 180°C and the orientation degree of PAN chains was determined by polarized-FTIR. Furthermore, the cyclization degree and activation energy of both cyclization and oxidation during stabilization as well as the mechanical properties of the resulting CFs were taken into consideration. The objective of this work is to disclose the relationship between the orientation and the stabilization of PAN chains, and furnish a new concept for the development of high-performance CFs, particularly the PAN-based CFs by dominating the orientation of PAN chains just reaching its saturation point prior to the stabilization process.

EXPERIMENTAL

Preparation of Materials

PAN fibers used in this study were the Special Acrylonitrile Fibers (SAF 3K fibers) provided by the Courtaulds, Ltd in the UK. The SAF 3K fibers were made of the PAN copolymer with 92.8 wt% of acrylonitrile (AN), 1.2 wt% of itaconic acid (IA), and 6.0 wt% of methyl acrylate (MA), and they were in the form of bundle with 3000 fibers. PAN fibers (denoted by RT-0) was hot-stretched by various ratios (λ) ranging from 1.00 to 1.16 during pre-treatment at 180°C, and the deformation ratio (defined as $\lambda = l_i/l_0$, where l_i and l_0 were the length of stretched fibers and original fibers, respectively) was dominated by the rotating speed of two rollers set at the import and export of a treatment furnace, respectively. The deformation ratios and correlative samples are shown in Table 1.

Table 1. Deformation ratios and correlative samples of PAN fibers

Sample	P-0	P-2	P-4	P-6	P-8	P-10	P-12	P-14	P-16
λ	1.00	1.02	1.04	1.06	1.08	1.10	1.12	1.14	1.16

Characterization

A Nicolet 6700 Fourier transform infrared spectrometer (FTIR) equipped with a gold-wire grid polarizer and a liquid nitrogen-cooled mercury-cadmium-telluride detector was used for orientation studies. Fibers were mounted under slight tension with double-sided sticky tape. When using the polarizer, spectra were acquired with the polarizer set both parallel and perpendicular to fibers. As an indication of orientation, dichroic ratios D for the nitrile absorption were determined, by which the orientation degree of chains f_{chain} was calculated according to the following formulae:

$$D = \frac{A_{\parallel}}{A_{\perp}}$$

$$D_0 = 2 \cot^2 \alpha$$

$$f_{\text{chain}} = \frac{3\langle \cos^2 \theta \rangle - 1}{2} = \frac{(D-1)(D_0+2)}{(D_0-1)(D+2)} \quad (1)$$

where, $A_{\parallel}$ was the absorption with the electric vector of polarized IR radiation parallel to the fiber axis, $A_{\perp}$ was the absorption with the electric vector of polarized IR radiation perpendicular to the fiber axis, α was the transition moment angle between the direction of the nitrile group's dipole moment and the chain axis, with an average value of about 70° for uniaxially drawn PAN fibers, and θ was the angle of the molecular segment relative to fiber axis^[5, 14]. From repeat experiments, confidence limits in values of D were ± 0.02 .

The wide-angle X-ray diffraction (WAXD) experiments were carried out by a Rigaku D/MAX-2500UBZ + PC X-ray diffractometer. The X-ray tube operating at 40 kV and 50 mA with the CuK α radiation (X-ray

wavelength $\lambda = 0.15418$ nm) was used. The 2θ scanning was carried out from 5° to 40° by step scanning mode with the parameters of 0.02° per step and 10 steps per minute.

To analyze the cyclization of PAN fibers, samples were prepared by grinding and pressing the fibers with potassium bromide (KBr); the FTIR spectra were acquired by scanning the samples (64 scans) from 500 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Ring closure index (τ) of PAN fibers was introduced and defined as the following formula:

$$\tau = \frac{I_{\text{C=N}}}{I_{\text{C=N}} + I_{\text{C}\equiv\text{N}}} \quad (2)$$

where, $I_{\text{C=N}}$ and $I_{\text{C}\equiv\text{N}}$ were the “C=N” absorbance centered at 1600 cm^{-1} and the “C $\equiv$ N” absorbance centered at 2243 cm^{-1} , respectively.

Thermal analysis experiments were carried out in nitrogen atmosphere using a Mettler DSC-1 differential scanning calorimeter (DSC). Less than 5.0 mg of sample was used for the DSC studies to avoid the potential thermal lag. The DSC curves were recorded from 50°C to 400°C , and the scanning rate was set as $0.25\text{--}5\text{ K/min}$. The activation energy of both cyclization and oxidation of various stretched PAN fibers is investigated by the Kissinger method.

The tensile strength and tensile modulus of CFs were evaluated according to ASTM D4018-99. The specimens were tested by a universal testing machine (model 5567, Instron Corp., Canton, MA) at a crosshead speed of 10.0 mm/min with gage length of 150 mm , and eight specimens were tested for each type of CFs. During the specimen preparation, the CFs were wound onto a rectangular framework in parallel and the aligned fibers were impregnated into a mixed solution (the mass ratio of acetone, epoxy 618 resin and triethylenetetramine was set at 20:10:1)^[5], and then, the samples were cured in an oven at 120°C for 2 h.

RESULTS AND DISCUSSION

Orientation of PAN chains

Orientation of PAN chains of these as-received PAN fibers (RT-0) and hot-stretched samples (P-0 to P-16) were measured by polarized-FTIR, respectively. Figure 1 shows the polarized-FTIR spectra attributed to the absorbance of nitrile groups between 2200 cm^{-1} and 2300 cm^{-1} , where the absorption of $A_\perp$ (the electric vector of the incident ray is perpendicular to fiber axis) is higher than $A_\parallel$ (the electric vector of the incident ray is parallel to fiber axis). The stronger the stretching applied on PAN fibers, the smaller the value of dichroic ratio “ D ” is observed (exhibited in Fig. 1), suggesting the development of orientation of PAN chains during deformation.

The change of orientation degree of PAN chains (f_{chain}) during the thermal stretching process determined by the polarized-FTIR measurement is depicted in Fig. 2. An extraordinary decrease in f_{chain} is observed as a consequence of the increased entropy of PAN chains when the as-received PAN fibers RT-0 are heated up from RT to 180°C at a constant initial length. The residual stress generated during the spinning process of PAN precursor fibers will be released when fibers are heated up to a temperature higher than their glass transition temperature (104°C for co-PAN precursors), giving rise to the spontaneous disorientation of PAN chains^[5, 6–8]. However, the value of f_{chain} turns to increase significantly when the fibers are stretched by a series of ratios from 1.00 to 1.08 at 180°C , and is almost invariable when the ratio is greater than 1.08, which indicates that the orientation of PAN chains has reached an equilibrium state (in Fig. 2, a saturation point possessing a value of 69.51% is observed).

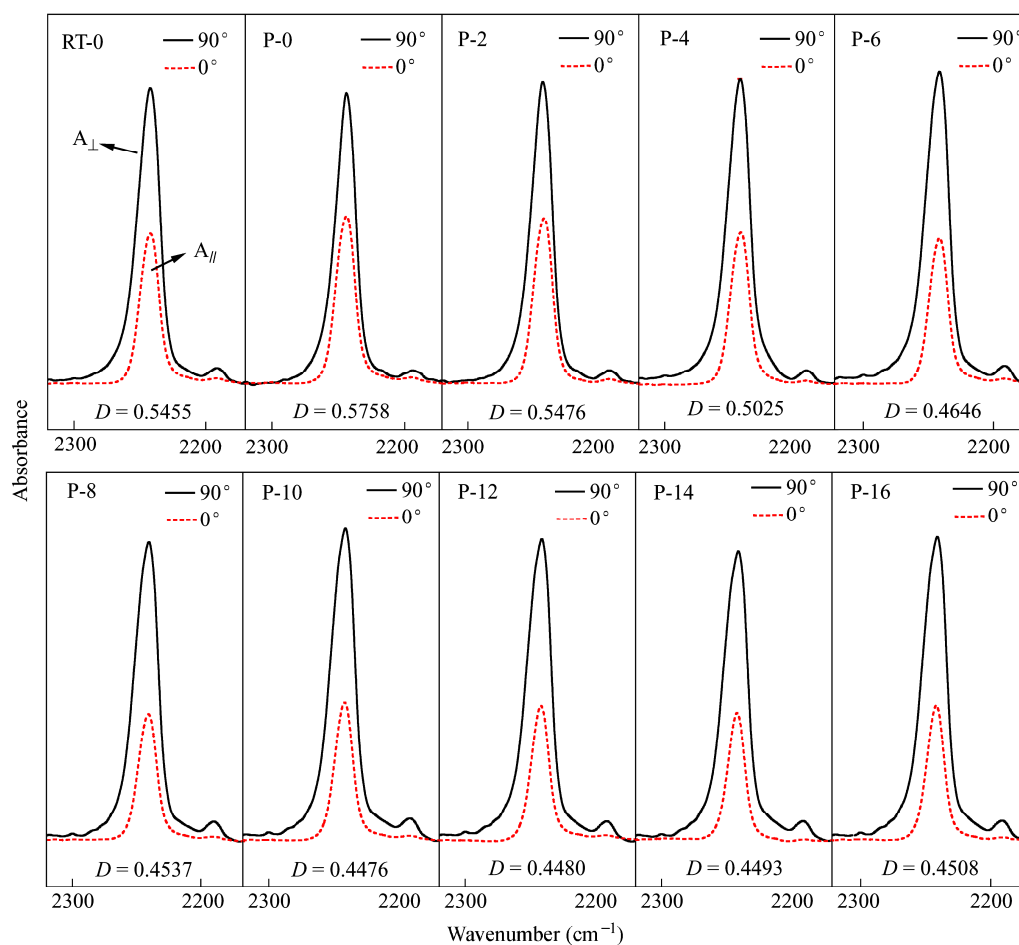


Fig. 1 The polarized-FTIR spectra attributed to the absorbance of nitrile groups

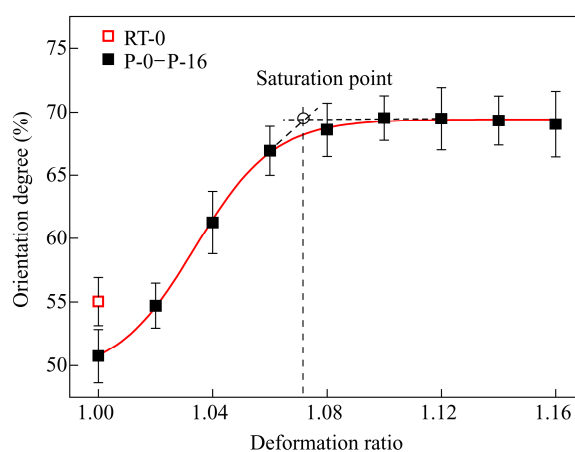


Fig. 2 The change of orientation of PAN chains during the thermal stretching process

Stabilization of PAN Fibers

Those PAN fibers are subjected to a stabilization treatment carried out at a temperature ranging from 210°C to 280°C, and the stabilized fibers are investigated by the FTIR analysis. Figure 3 shows the FTIR spectra of these PAN fibers after the stabilization. The most prominent structural change is the variation in the intensities of the

bands at 2200–2260 cm^{-1} , attributed to $-\text{C}\equiv\text{N}$ groups retained in fibers after the cyclization. The relative absorption intensity of $-\text{C}=\text{N}-$ (centered at *ca.* 1600 cm^{-1}) and $-\text{C}\equiv\text{N}$ (centered at *ca.* 2243 cm^{-1}) groups^[2, 15, 16] in stabilized fibers are exhibited in Table 2. Thus, the cyclization degree (τ) of stabilized fibers could be evaluated by Eq. (2), and the results are shown in Fig. 4.

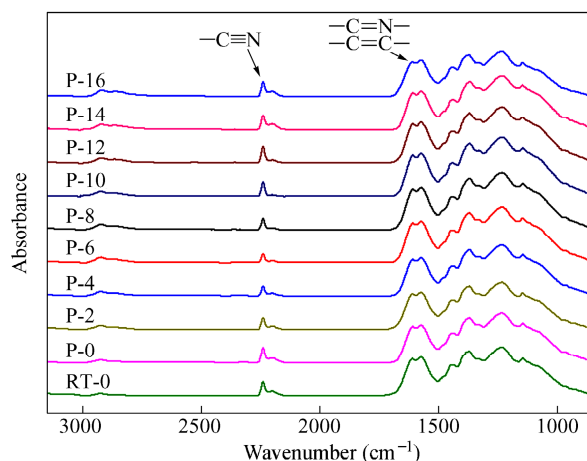


Fig. 3 The FT-IR spectra of various PAN fibers after the cyclization reaction

Table 2. The relative absorption intensity of $-\text{C}=\text{N}-$ and $-\text{C}\equiv\text{N}$ groups in various stabilized fibers determined by FTIR

	RT-0	P-0	P-2	P-4	P-6	P-8	P-10	P-12	P-14	P-16
$I_{-\text{C}=\text{N}-}$ (%)	26.46	25.45	26.09	24.99	24.48	25.04	23.77	23.90	20.40	19.31
$I_{-\text{C}\equiv\text{N}}$ (%)	11.27	11.82	9.40	7.71	6.70	8.19	10.09	12.06	11.03	10.58

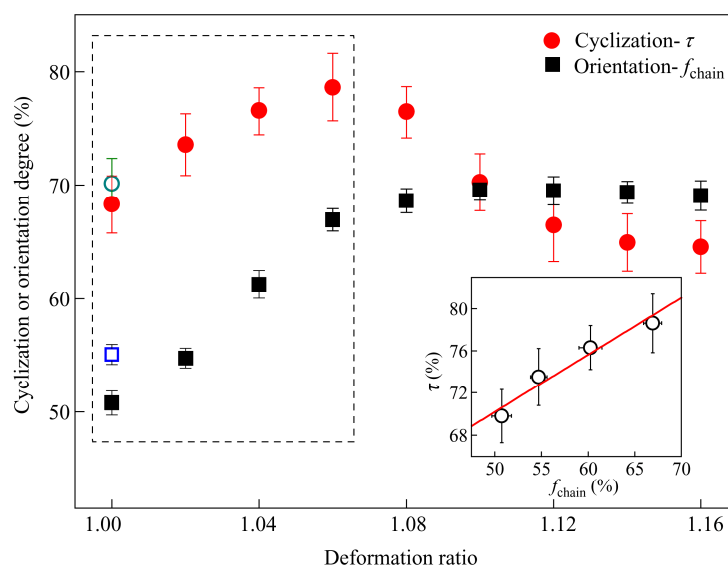


Fig. 4 The orientation degree of PAN chains after the hot-stretching at 180°C and their cyclization degree after the stabilization

The inserted figure shows the relationship between the two indexes; The large open symbols represent the values obtained from as-received PAN fibers RT-0.

In order to investigate the relationship between orientation and cyclization of PAN chains, values of f_{chain} are also depicted in Fig. 4 for a comparison. When the deformation ratio of PAN fibers is less than 1.06, an obvious increase in τ is observed, meanwhile, the orientation of PAN fibers is also increased. The orientation of PAN chains with respect to fiber axis, which is beneficial to prevent chains from crossing and/or snarling and overcome the steric hindrance and dipole repulsions generated by $-\text{C}\equiv\text{N}$ groups, could facilitate the cyclization reaction during the stabilization. Giving a careful attention to Fig. 4, a perfect linear relation between f_{chain} and τ is observed when the deformation ratio is less than 1.06, and the fitted result shows that τ may possess a value of 97.02% in the case of fully oriented PAN chains (*i.e.*, f_{chains} reaches 100%), as the insert figure in Fig. 4 shows. Thus, we tentatively put forward that the cyclization of the highly oriented PAN chains is apt to carry out completely. However, τ turns to decrease dramatically once the deformation ratio is greater than 1.08, while the orientation of PAN chains is almost terminated (exceeds the saturation point in Fig. 2). The stronger deformation of PAN fibers has induced the yield extension of PAN chains and increased the gap for the cyclization between $-\text{C}\equiv\text{N}$ groups^[5].

Furthermore, in order to verify the close influence of orientation of PAN fibers on the cyclization and oxidation during the stabilization, the activation energy of both cyclization (E_c) and oxidation (E_o) of various stretched PAN fibers is investigated by DSC analysis^[2]. In this section, sample P-0, P-4, P-8, P-12 and P-16 were selected for the DSC analysis. Figures 5(a) and 5(b) show the exothermal curves of the five samples, where the heating rate is 1 K/min. Two exothermal peaks are observed centered at about 240°C and 284°C, which are attributed to the cyclization and oxidation, respectively. The peak temperatures (T_c for cyclization and T_o for oxidation) and the enthalpy (ΔH_c for cyclization and ΔH_o for oxidation) are exhibited in Table 3. With the increase of the deformation ratio of PAN fibers, the value of T_c decreases first and then increases, while the ΔH_c shows the opposite trend, however, the change of ΔH_o is feeble. The variation of ΔH_c , which reveals the degree of cyclization carried out in PAN fibers, is in consistent with the change of τ in Fig. 4.

Table 3. Indexes of thermal reaction of PAN fibers determined by DSC (1 K/min)

	P-0	P-4	P-8	P-12	P-16
T_c (°C)	241.19	239.96	238.59	240.32	242.05
T_o (°C)	284.26	284.14	284.39	284.06	284.31
ΔH_c (J/g)	1578.2	1643.5	1694.7	1665.2	1586.8
ΔH_o (J/g)	1777.8	1785.9	1759.0	1772.6	1789.3

The activation energy of E_c and E_o of the five selected samples is calculated by the Kissinger method (Fig. 5c), where the heating rate is changing from 0.25 K/min to 5 K/min, and the exothermal peaks attributed to the cyclization and oxidation are separated by the Gaussian fitting function. In Fig. 5(d), with the increase of deformation ratio, E_c decreases slowly when the ratio is below 1.08 and increases extraordinary when PAN fibers are further stretched with the ratio greater than 1.08. When PAN fibers are stretched by a proper ratio (*e.g.*, 1.00 to 1.08 in this study), the tangled PAN chains are improved and oriented with respect to the fiber axis, which makes it easier for PAN chains to change their conformation for the initiation of cyclization, meanwhile, the cyclization is also easier to be delivered through those highly oriented PAN chains^[5]. As a result, the stabilized fibers possess a relatively high cyclization degree. However, as Fig. 6 shows, the stronger the deformation applied on PAN fibers, the greater the stress will be released when those stretched fibers are heat treated again after their hot-stretching process. Thus, when PAN fibers are stretched by the extremely strong deformation (greater than 1.08, exceeds the saturation point in Fig. 2), more residual stress is generated, which makes it harder for PAN chains to change their conformation and result in the obviously increase of E_c as well as the decrease of cyclization degree. However, E_o attributed to the oxidation of PAN fibers possesses an almost constant value of about 126.5 kJ/mol with the increasing of deformation ratio. Thus, it is reasonable to reach a basic conclusion that the oxidation is independent on the orientation of PAN chains.

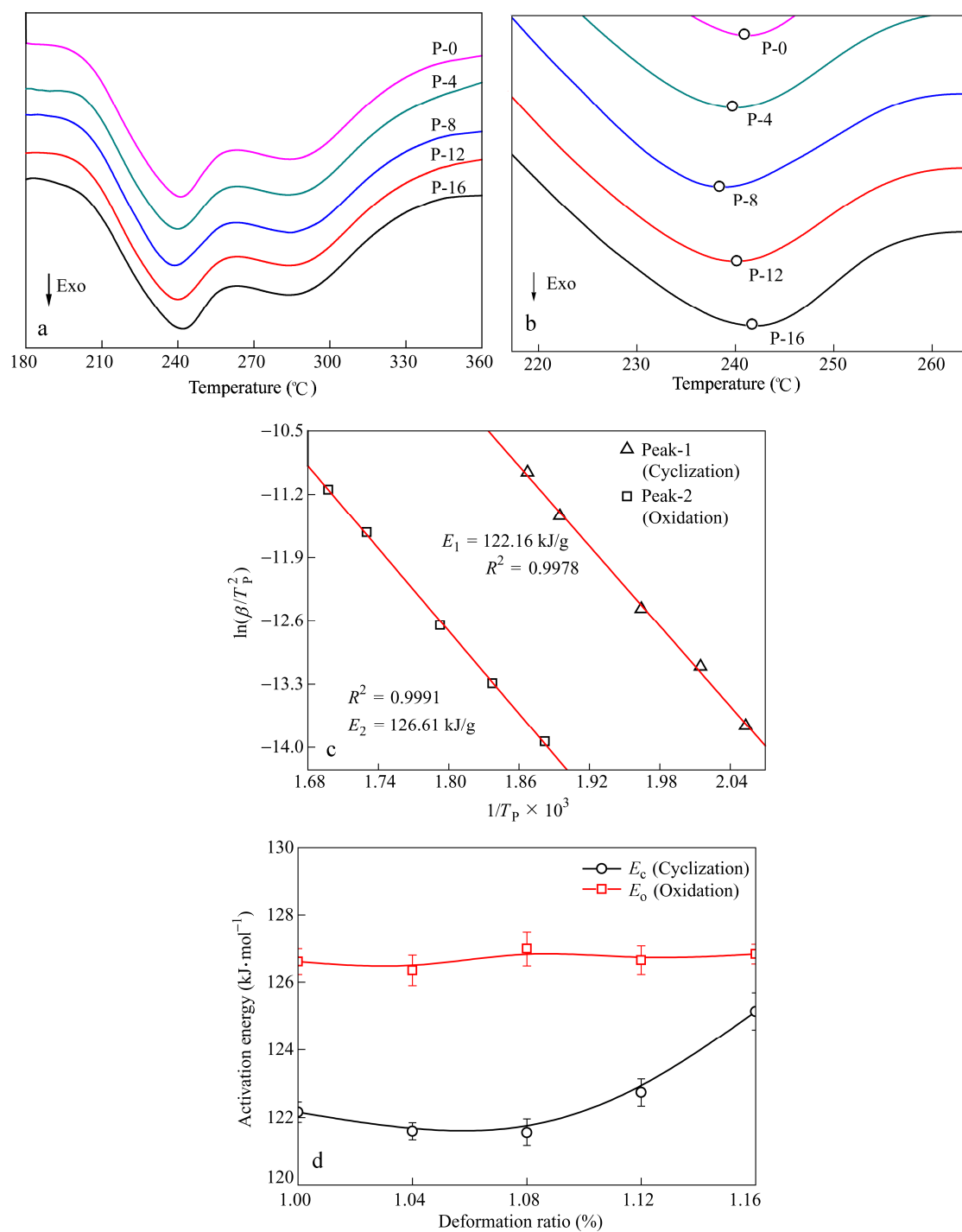


Fig. 5 DSC analysis on the stabilization of PAN fibers, (a) DSC curves of various stretched PAN fibers (1 K/min in air), (b) the change of peak temperature attributed to cyclization in (a), (c) Kissinger method to calculate E_c and E_o , (d) activation energy of cyclization and oxidation for various stretched PAN fibers

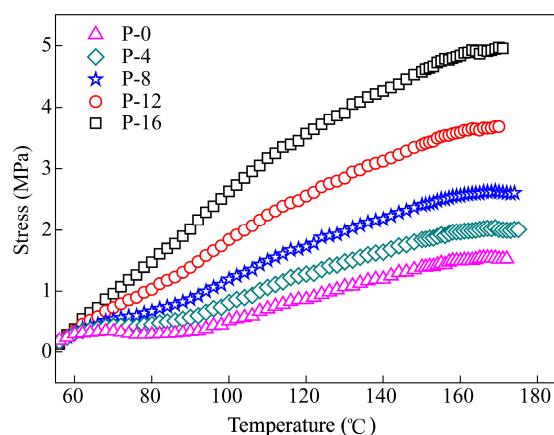


Fig. 6 Stress release of various stretched PAN fibers

Structure and Properties of CFs

The structure and mechanical properties of the resulting CFs obtained by those PAN fibers are investigated in detail. The structural parameters, *i.e.* stacking height (L_c), lattice spacing (d_{002}), crystallinity (β), orientation of graphite crystallites (f_c), density (ρ) and porosity (V_p) of CFs are determined and the results are exhibited in Table 4. The index of V_p is evaluated by an empirical equation:

$$V_p = 1 - \frac{\rho \cdot d_{002}}{\rho_g \cdot d_g} \quad (3)$$

where, ρ and d_{002} represent the measured density and lattice spacing of CFs; ρ_g and d_g are these indexes of ideal graphite with a theoretical value of $2.266 \text{ g} \cdot \text{cm}^{-3}$ and 0.3354 nm , respectively.

Table 4. Structural characteristics of the resulting CFs obtained by various PAN fibers

	RT-0	P-0	P-2	P-4	P-6	P-8	P-10	P-12	P-14	P-16
L_c (nm)	1.82	1.80	1.87	1.92	1.94	1.88	1.50	1.42	1.40	1.34
d_{002} (nm)	0.352	0.352	0.350	0.349	0.348	0.346	0.346	0.347	0.348	0.347
β (%)	61.18	60.29	63.23	65.92	68.60	71.51	71.25	69.41	64.19	59.26
f_c (%)	81.53	81.08	81.45	82.29	83.37	84.38	84.23	83.73	83.41	82.82
ρ ($\text{g} \cdot \text{cm}^{-3}$)	1.7816	1.7801	1.7830	1.7869	1.7932	1.7956	1.7926	1.7875	1.7821	1.7813
V_p (%)	17.49	17.56	17.89	17.95	17.90	18.26	18.39	18.39	18.41	18.67

On the one hand, CFs has a strong inheritance of both the perfect and defective structures from PAN precursor fibers, hence the stretching-induced oriented structures in PAN chains are converted to cyclized, ladder-like structures during thermal oxidative stabilization, and the higher degree of orientation is retained through the resulting CFs after carbonization^[5, 9, 11]. On the other hand, some small fragment crystallites probably formed from the ultra-stretched or even cracked PAN chains during the carbonization exhibit a random orientation, which will impede the growth and orientation of the turbostratic graphite crystallites^[12]. As a result, the structural changes of CFs exhibit a different dependence on the deformation of PAN chains before and after 1.08.

The values of tensile strength (TS) and tensile modulus (TM) of CFs are normalized to their initial values to show the influence of thermal treatment and deformation on the mechanical changes, as depicted in Fig. 7. The initial values show a natural statistical variance for the different CF bundles obtained from as-received PAN fibers, $\text{TS}_{\text{mean}}(\text{RT-0}) = (3.36 \pm 0.13) \text{ GPa}$ and $\text{TM}_{\text{mean}}(\text{RT-0}) = (231.7 \pm 9.2) \text{ GPa}$. The relative increment (RI) of TS and TM is defined as below:

$$RI = \frac{\chi_i - \chi_0}{\chi_0} \quad (4)$$

where, χ_0 and χ_i represent the value of TS and TM of CFs obtained by the PAN fibers RT-0 and P- i , respectively.

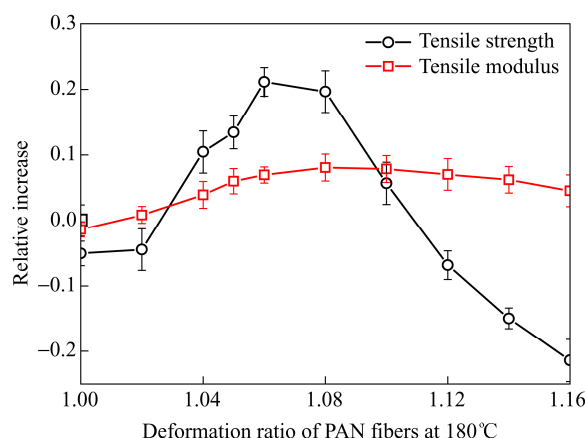


Fig. 7 Relative increase of mechanical properties of the resulting CFs prepared with various stretched PAN fibers
The large open symbol represents the values of CFs obtained from as-received PAN fibers RT-0.

Compared with CFs obtained from as-received PAN fibers RT-0, the CFs prepared from sample P-0 have an obvious decrease of about 5% in TS (Fig. 7). The result is due to the entropy-induced disorientation of PAN chains once they are heated up to a temperature higher than their glass transition temperature in the absence of further stretching^[5]. Both TS and TM increase with the increasing deformation of PAN fibers at 180°C, which is in agreement with the noteworthy development of orientation in PAN chains. The resulting CFs possesses the maximum increase of 21.13% in TS and 7.29% in TM when the PAN fibers just right reach their saturation point of orientation. Thus, optimizing the orientation of precursor fibers is efficient to improve the microstructure (e.g., increase in orientation degree, decrease in d_{002} and L_c) and to develop mechanical properties of CFs. When the deformation ratio is greater than 1.08 (exceeds the saturation point in Fig. 2), the orientation of PAN chains has terminated and the strong deformation has induced the ultra-straightening or even breaking of the helical PAN chains, which will make the cyclization harder and form some imperfections in the resulting CFs (the value of V_p is increased remarkably once the deformation ratio exceeds 1.08). Hence the mechanical properties especially the TS of CFs are seriously decreased.

CONCLUSIONS

In this study, the orientation of copolymer PAN chains during their deformation prior to stabilization and the further effect on the stabilization is investigated in detail.

(1) The orientation of PAN chains presents a saturation point of about 69.51% (determined by the polarized-FTIR) when the deformation ratio of PAN fibers reaches approximately 1.07 at 180°C.

(2) During stabilization, the cyclization rather than the oxidation has a strong dependence on the orientation of PAN chains. The activation energy of oxidation E_o possesses an almost constant value of about 126.5 kJ/mol with the increasing of deformation ratio.

(3) The cyclization is facilitated as a consequence of the developing orientation of PAN chains before the saturation point that the cyclization degree τ is increased obviously from 68.28% to 78.51% while the activation energy of cyclization E_c is decreased from 122.05 kJ/mol to 121.56 kJ/mol. However, the cyclization is impeded

by the further deformation of PAN fibers after the point (up to 1.16) that E_c increases to 125.13 kJ/mol while τ decreases to 64.60% remarkably. The resulting CFs obtained from the PAN fibers prepared at the saturation point possesses the highest mechanical properties of 4.07 GPa in tensile strength and 249.02 GPa in tensile modulus.

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