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A one-step hot pressing molding method of polyacrylonitrile carbon fibers: influence on surface morphology, microstructure and mechanical property

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ABSTRACT

Carbon fibers (CFs) have been the most popular material for decades and compound into various materials because of their excellent performance. Herein, a novel one-step hot pressing molding is proposed to prepare polyacrylonitrile (PAN) CFs, eliminating the time-consuming and energy-consuming thermal stabilization stage. The fibers are tiled and pressed tightly between the two plates. The unit is then carbonized in a tubular furnace. Hot pressing enforced the fiber structure to be cyclized and reduces the damage of fibers by mitigating the escape of heteroatoms gas. The thermoplasticity of PAN fibers is innovatively utilized in the preparation of carbon fibers by hot pressing, which is able to improve density and repair the cracks. The density and tensile strength of fibers at 900 °C have reached to 1.70 g cm^{-3} and 1.1GPa. The CFs obtained by hot pressing molding have not only a smooth surface morphology, but also a high degree of microstructure cyclization. Hot pressing molding can not only realize the function of thermal stability stage, but also simplify the process, save energy and time, and reduce the cost.

Introduction

For decades, carbon fibers (CFs) have been successfully applied in aerospace, automotive manufacturing, sports equipment, building materials [1, 2]. It is recognized as the material of light weight, high strength, temperature resistance and chemical corrosion resistance [3, 4]. Commonly, the commercial CFs can be manufactured from various precursors including polyacrylonitrile (PAN), pitch and rayon [5]. But the strength properties of pitch CFs are

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inferior to that of PAN CFs [6]. Although rayon fibers are cheaper than PAN fibers, PAN CFs still play the dominant role in the market because the carbon yield of PAN is almost double that from rayon [7]. Therefore, PAN precursor fiber was selected as the implementation object of this study.

The industrial manufacturing process of PAN CFs mainly involves two following steps: thermal stabilization and carbonization. During the thermal stabilization, the precursor fibers are heated and stretched at 200–300 °C in the air atmosphere, performing dehydrogenation, oxidation and cyclization reactions [8]. The main role of thermal stabilization is to transform the linear structure of the PAN into a heat-resistant trapezoid structure and to remove some heteroatoms [9]. PAN precursor fibers are converted from thermoplastic polymer to non-meltable PAN-stabilized fibers in order to carbonize steadily at subsequent high temperatures [10].

The thermal stabilization is considered as the complicated and most time/energy-consuming step in the whole manufacturing process of CFs. Too high heating temperature, too fast heating rate or too long holding time will lead to over intense or excessive dehydrogenation, oxidation and cyclization reactions of fiber [11, 12]. And it causes more oxygen or nitrogen compounds to form and embed in the rings, causing the internal structure to be messy [13]. Or the drastic evaporation of gas molecules destroys the fiber structure. These reflections on the fiber morphology are cracks, micropores and core-skin structure [14]. The defects can be decreased to some extent by stretching force applied to fibers in the thermal stabilization stage [15]. However, it is not practical to repair the disordered pore structure completely. These defects will continue to be retained or even deepened in the subsequent carbonization process, so that the surface morphology [16] and strength properties [17] of CFs will be affected. The aforementioned properties are the crucial indexes to evaluate the quality of CFs.

Whereafter, PAN-stabilized fibers are carbonized in the N_2 atmosphere at 700–2400 °C [18]. In the carbonization stage, the cyclized structure of the stabilized fibers develops into a larger planar heterocyclic structure [19]. And the planar structure is transformed into a stacked graphite-like structure. It is reported that fibers undergo severe mass loss (60%) during the temperature range of 300–500 °C [10] owing to the removal of heteroatoms from the structure like nitrogen, oxygen and hydrogen. Volatile products such as HCN, NH_3, CO_2, CO, H_2, N_2, H_2O, hydrocarbons and nitriles are escaped from the fiber [20]. This process will cause damage to the structure of the fiber, so that the defects formed in thermal stabilization deepen or produce new cracks, which leads to bad surface morphology and poor strength of CFs.

In order to obtain qualified CFs, the optimization of parameters for thermal stabilization and carbonization stage has been studied for more than 40 years. It is reported that 200 °C, 220 °C, 250 °C and 280 °C are considered to be key temperatures to stabilize PAN fibers in the thermal stabilization stage [21]. Thermal stabilization in nitrogen atmosphere [22] can improve the degree of cyclization and mechanical properties of the fibers [23]. And the application of mechanical tensile load during carbonization can enhance the mechanical properties of the fibers [24, 25]. But there has been little innovative progress. The complexity and time/energy consumption of thermal stabilization stage have not been solved.

Now, based on our years of research on polymers, we know that they are usually molded by hot pressing or injection molding, because polymers usually have good thermal plasticity. It is well known that PAN is a linear polymer [16]. The glass transition curve of PAN has a gentle glass transition peak and a very obvious exothermic peak related to molten state, which means that PAN precursor fiber is thermal plasticity [26]. The utilization of PAN fiber thermoplasticity in the CFs preparation process is a knowledge gap. Therefore, this paper presents a one-step method for preparing PAN CFs by hot pressing molding. It can not only realize the function of thermal stabilization, but also simplify the process, save energy and time, and reduce the cost.

In PAN-stabilized fiber, it is a non-meltable trapezoidal structure. PAN CFs is a heat-resistant material with graphite structure. Therefore, during the whole process, the fiber must have undergone a transition from thermoplastic material to implastic material. Molecular structure is transited from linear to trapezoidal to graphite-like structure. This paper illustrates that it is considered to be the processes of plasticizer volatilization and further cyclization of PAN fibers. Because the mass loss of fiber is known to be as high as 60% below 500 °C. The purpose of obtaining stabilized cyclized structure by thermal stabilization is to ease the pyrolysis of the fiber during carbonization, so as not to cause damage to the carbon fiber. In the one-step scenario, the thermal stabilization step is abandoned and the fiber is directly carbonized by thermocompression molding. Hot pressing can force the fiber structure to be cyclized and develop into graphite structure. Moreover, hot pressing makes it more difficult to release the gas molecules during fiber pyrolysis. So the intense pyrolysis of fiber can be slowed down during carbonization. In this way, the plasticizer can be retained in the fiber longer, and the thermoplasticity of the fiber can be maintained longer. Even if there are defects in thermoplastic fibers caused by pyrolysis in the carbonization process, it will be eliminated by hot pressing immediately. And slowing down the evaporation of plasticizer gas might also lessen defects such as fiber cracks, which is benefit to the morphology and mechanical properties of carbon fiber. Therefore, it is possible to achieve one-step hot pressing molding to produce high performance CFs.

Thereupon, we develop a simple and novel one-step hot pressing molding method to prepare PAN CFs. Remarkably, the whole course is carried out in the nitrogen atmosphere. The time/energy-consuming thermal stabilization step has been eliminated in this process. The PAN precursor fibers are placed and compressed between two hot pressing plates. Then the setup is placed in the constant temperature area of the tube furnace for rapid heating to achieve carbonization. In the process of carbonization, the hot pressing slows the escape of heteroatoms in the fiber in the form of gas, and all kinds of gas can be released slowly, which greatly reduces the damage caused to the fiber. Second, hot pressing can make better use of the thermoplasticity of PAN fiber, promote the cyclization of molecular structure and effectively repair fiber defects. The yield of carbon fibers will also increase because the hot pressing cushions the escape of organic molecules. The diagram is shown in Fig. 1.

The surface morphology, microstructure and mechanical properties of hot pressing CFs have been investigated via SEM, XPS and universal testing machine. The surface of CFs prepared by hot pressing is smooth nearly without cracks or other defects. The density and tensile strength/modulus of CFs by 900 °C hot pressing have reached to 1.70 g cm^{-3} and 1.1GPa/74GPa, respectively. The yield of hot pressing CFs has also increased by 27% compared with conventional CFs. These results demonstrate that the procedure in this study is simple, novel, and cost-effective, which can be a valuable theoretical exploration and data reference for the innovation of the preparation technology of PAN CFs.

Experimental

Fiber material

The PAN precursor fibers were a 6 k tow purchased from Jilin Chemical Fibre Co. Ltd., China. Fibers feed about 3 wt% methyl methacrylate (MMA) and 1 wt% itaconic acid (IA). The average molecular weight is 53000 ~ 106,000. The fibers are used without further refinement.

Tows of 12 cm length are laid flat on one hot pressing plate. Another plate was then placed on top, so that the fibers were sandwiched between the two plates. Then we tightened the screws on both ends of the custom plate. The fibers were compacted and the device was placed in the constant temperature zone of the tubular furnace (KTL 1600, Nanjing University Instrument Co., Ltd.) with a stable nitrogen atmosphere (20 ml/min) to obtain the effect of one-step hot pressing carbonization. The sample was compressed between two iron plates ($180 \times 35 \times 4$ mm^3), the two ends of plates were tightened with two screws (M4, A2-70). The pressure (890 MPa) exerted on the fibers was calculated by the formula ($F = 0.5\sigma s \times As$) ($\sigma s = 640$, $As = 8.78$). The carbonization temperatures were 400 °C, 600 °C, 800 °C and 900 °C at a rate of 10 °C/min. The samples were recorded as 4HSPAN, 6HSPAN, 8HSPAN and 9HSPAN. The temperature was kept at the set final temperature for 1 h.

The corresponding blank carbonization was to place PAN precursor fibers in a crucible. Then the crucible was placed in the tubular furnace (KTL 1600, Nanjing University Instrument Co., Ltd.) with stable nitrogen atmosphere (20 ml/min). The crucible was also heated to 400 °C, 600 °C, 800 °C and 900 °C at a rate of 10 °C/min. The samples were denoted as 4PAN, 6PAN, 8PAN and 9PAN.

Characterization

The morphological photographs on the surfaces of PAN CFs were obtained by field emission scanning electron microscope (FE-SEM, JSM-7600F, Japan

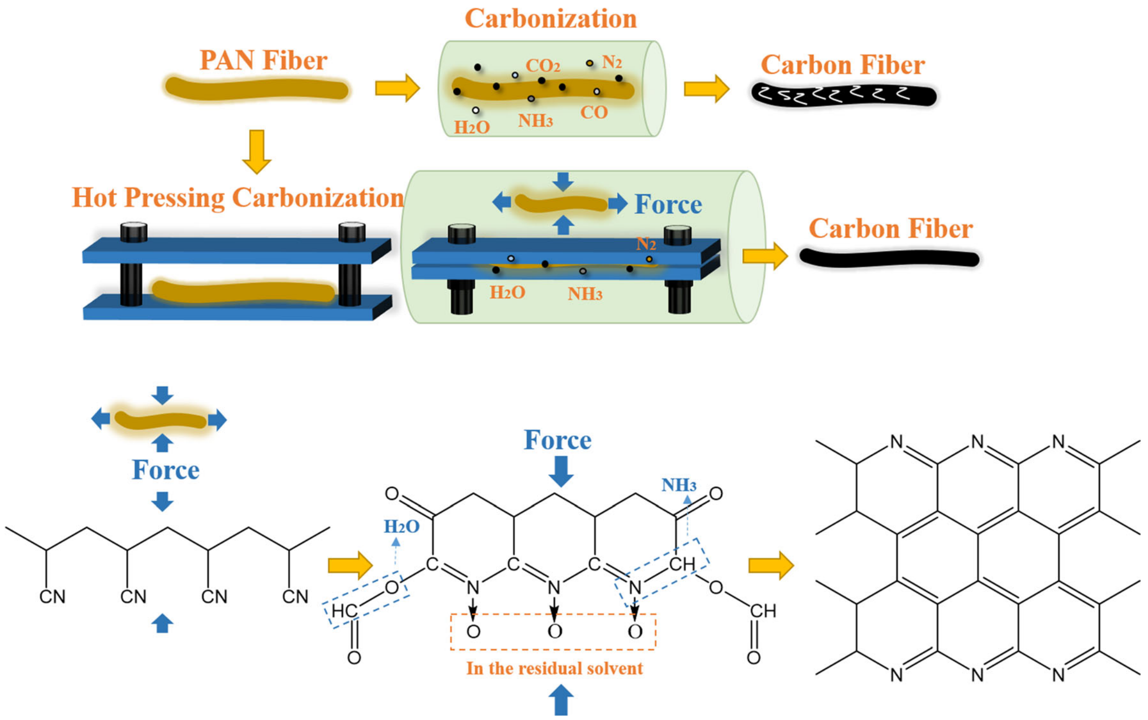

Figure 1 Schematic illustration of the hot pressing carbonization process and structural formula for samples.

Electronics Co., Ltd). The density of samples was measured by a density balance (XS205DU, Mettler Toledo) according to GB/T 1033.1–2008. Thermogravimetrical (TG) analysis was conducted on a thermogravimetry analyzer (TGA, TG 209 F1, NETZSCH) in nitrogen atmosphere (flow rate 20 ml/min). Differential scanning calorimetry (DSC) analysis was done on a DSC 214 device (NETZSCH) in nitrogen atmosphere (flow rate 40 ml/min). The X-ray photoelectron spectroscopic (XPS) results were obtained on an instrument (AXIS UltraDLD, Shimadzu, Japan). The Raman spectra were acquired using a Raman spectrometer (DXR532, Themor, USA) with wavelength of 532 nm. The tensile properties were tested by an Electromechanical Universal Testing Machine (CMT8502, MST SYSTEM Co., LTD, China) on the basis of GB/T 3362–2005.

Results and discussion

The surface morphology of the samples was analyzed by SEM as shown in Fig. 2. It can be seen that the surface of the sample 4PAN is uneven. This is because drastic denitrification, dehydrogenation and deoxygenation reactions begin to take place since 300 °C [19]. The gases produced by pyrolysis first leave the fiber through phase separation and then spill out into the environment. The surface morphology can be damaged in the phase separation, which makes the fiber surface morphology rough. Then the volatilization of gas molecules further damages the fibers and makes the fibers defective. The significant gully-shaped cracks can be seen in the 6/8/9PAN samples. It was reported that the total weight loss of PAN fibers was about 63% at 700 °C [27]. It means a huge amount of volatile substances escape from the fiber. So lots of defects can be formed in the 6/8/9PAN fibers. Obviously, with the increase of temperature, the cracks from 4 to 9PAN increased and deepened gradually. These cracks can cause fatal damage to the mechanical strength of the carbon fiber and cannot be remedied in subsequent processes.

The corresponding 4/6/8/9HSPAN samples all show a flat and smooth morphology in Fig. 2, which strongly proves the superiority of hot pressing molding. It is reported that fibers undergo severe mass loss (60%) in the temperature range of 300–500 °C [10]. However, from 4 to 6HSPAN, it can be observed that the surface morphology of 6HSPAN does not deteriorate due to pyrolysis. This result proved our hypothesis that thermoplasticity of fiber and hot pressing were mutually utilized to mold fiber

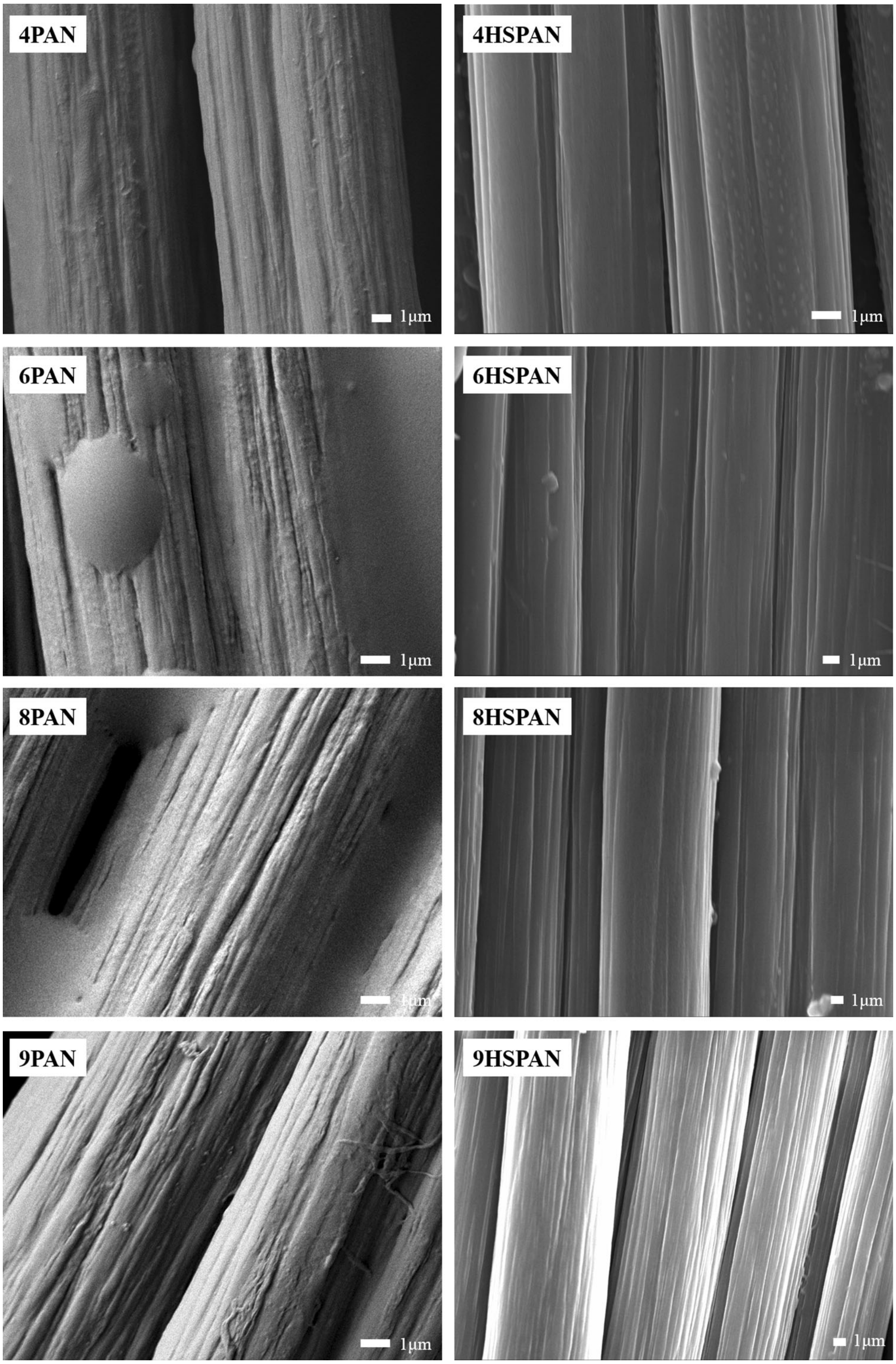

Figure 2 SEM images of the surface morphology of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

and eliminate defects. Hot pressing carbonization proceeds according to the process we inferred in Fig. 1. Most of the defects in the carbon fiber are known to be caused by the free escape of heteroatoms [20]. Hot pressing not only effectively slows down the release rate of heteroatoms, but also smooths out the tiny defects. Second, it can be concluded from the flat appearance of 4/6/8/9HSPAN samples that there was deformation during the carbonization by hot pressing, which indicated that hot pressing made full use of the thermal plasticity of PAN fiber and played a role in molding CFs.

The average diameter of samples is listed in Table 1. The diameter of 4/6/8/9PAN is universally larger than that of 4/6/8/9HSPAN. Probably on account of violent pyrolysis, the 4/6/8/9PAN fibers crazed and expanded in an unrestrained manner. The fibers range in size from 10 to 12 µm. 4/6/8/9HSPAN fibers are only 7–9 µm in size, which also proves the effect of hot pressing molding. Hot pressing has a compacting and shaping effect on fibers. The obtained CFs are compact and regular.

Subsequently, the density of samples measured by a density balance according to GB/T 1033.1–2008 is shown in Fig. 3a. It can be seen that with the rise of temperature, the trend of density in two groups is both increased. The density of 4/6/8/9HSPAN samples is significantly higher than that of corresponding blank samples, while the density of the 4/6/8/9PAN samples was not ideal. From 4 to 9HSPAN, the density increases from 1.36 to 1.70 g cm^{-3}. The density of 4PAN-9PAN varied from 1.25 to 1.36 g cm^{-3}. Generally, the density of commercial CFs at 900 °C is in the range of 1.7–1.8 g cm^{-3} [28]. It is reported that the density of the modified acrylonitrile carbon fibers prepared by the conventional carbonization process with thermal stabilization is 1.73 g cm^{-3} [26]. Therefore, the density of CFs in hot pressing carbonization has reached the level of commercial CFs. This data strongly supports the effect of thermocompression molding on CFs. It can reduce the damage caused by pyrolysis gas and repair fiber defects to obtain compact carbon fiber. This is also consistent with the SEM photo analysis results above.

The yield of the samples is recorded in Fig. 3b, which referred to the residual mass of fibers under different experimental conditions at characteristic temperatures. It can be seen that the sample yield of the hot pressing group is significantly higher than that of the blank group. Compared to 4PAN (60%), the yield of 4HSPAN is as high as 74%. Similarly, the yield of 6HSPAN (61%) is 13% higher than that of 6PAN (48%). The escape of gas molecules [29] was effectively buffered by hot pressing. This scheme reduces the product loss during the process and increases the yield of CFs. As can be seen from the horizontal comparison in Fig. 3b, both groups suffered the greatest mass loss between 400 and 600 °C. It has been studied that a large number of dehydrogenation and deoxygenation reactions take place during the initial carbonization stage (300–600 °C) [30, 31]. It can be seen from the SEM photographs that the surface cracks of 6PAN were more and deeper than those of 4PAN. However, the morphology of 6HSPAN was not greatly affected and even became more flat under the action of thermocompression molding. Therefore, the one-step hot pressing molding of carbon fiber has a remarkable effect.

Table 1 Average diameter of samples

Sample	4PAN	6PAN	8PAN	9PAN
Average diameter	11.85 µm	11.71 µm	11.13 µm	10 µm
Sample	4HSPAN	6HSPAN	8HSPAN	9HSPAN
Average diameter	7 µm	8.08 µm	8.36 µm	8.87 µm

Next, the yield of 8PAN is only 41%. This is basically consistent with the reported yield (~ 37%) of the sample carbonized at 700 °C without thermal stabilization [10]. The yield of 8HSPAN is 53%, which is 12% higher than that of 8PAN after the effective control of the free escape of gas molecules by hot pressing carbonization. This result is similar to the mass loss (52%) of PAN CFs carbonized at 700 °C after thermal stabilization at 250 °C for 30 min [10]. Therefore, it can be inferred that one-step hot pressing carbonization may have the same effect on the conventional process (thermal stabilization and carbonization). The yield of 9HSPAN is 47%, while that of 9PAN is only 37%. The yield of 900 °C has been markedly increased by 10%. Hot pressing can effectively buffer gas escape from pyrolysis and improve the yield of CFs. And it has the advantages of simplicity, energy conservation and saving time compared to thermal stabilization.

Figure 4a shows the TG curves of PAN precursor fibers and samples. It can be seen that the mass loss of PAN precursor fibers is about 60% when they are carbonized to 900 °C at a heating rate of 10 °C/min. Severe pyrolysis begins at about 276 °C. It is consistent with other studies [10]. By comparing the curves of 4PAN and 4HSPAN, it can be seen that the pyrolysis rate of 4HSPAN is higher than that of 4PAN when it exceeds 400 °C at the beginning. This is due to the suppression of heteroatomic gas escape by hot pressing. When the fibers were released, the heteroatoms escaped briefly and explosively. When the temperature increases gradually, it can be seen that the weight loss degree of 4HSPAN is lower than that of 4PAN. So the thermal stability of 4HSPAN is

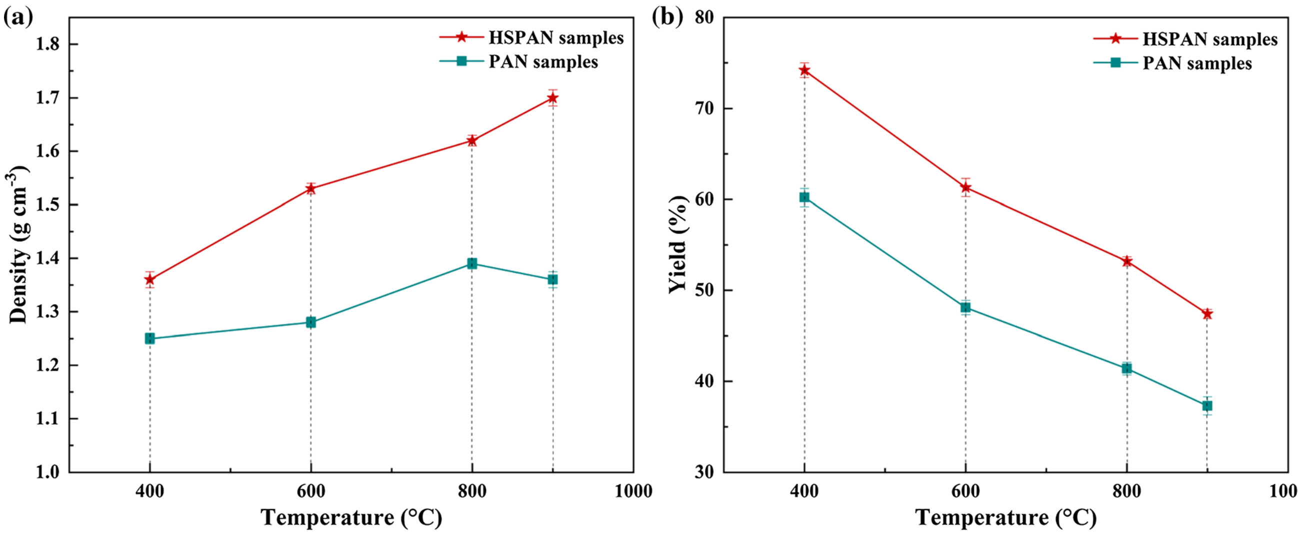

Figure 3 **a** Density of 4/6/8/9PAN and 4/6/8/9HSPAN samples. b. Yield of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

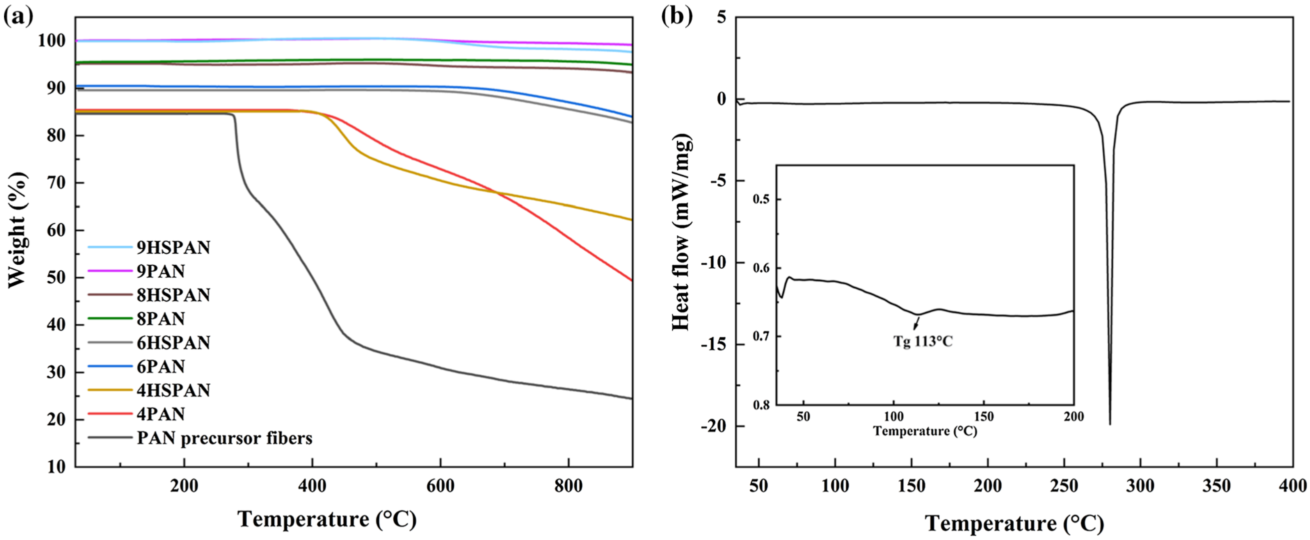

Figure 4 **a** TG curves of PAN precursor fibers, 4/6/8/9PAN and 4/6/8/9HSPAN samples **b** DSC curve of PAN precursor fibers.

better than that of 4PAN. This indicates that hot pressing can not only buffer the damage caused by the escape of gas molecules, but also promote the internal cyclization of the fiber and improve the stability of the fiber. The contrast between the three sets of curves at 600 °C, 800 °C and 900 °C is not obvious. But the samples in the hot pressing group still have a small amount of mass loss at high temperature. This is to be expected. Because hot pressing has a certain buffer effect on the pyrolysis of nitrogen, oxygen and hydrogen, which results in more heteroatoms being retained in the 4/6/8/9HSPAN than in the 4/6/8/9PAN, and thus being released during TG analysis.

The DSC curve of PAN precursor fibers is shown in Fig. 4b. As shown in the figure, it exhibits a strong exothermic peak at about 280 °C, which represents the molten state of PAN fiber at 263–293 °C. Other scholars attribute the peak more to cyclization and oxidation reactions [26]. In fact, fibers in this temperature range undergo complex changes, including dehydrogenation, oxidation, cyclization and melting. Fibers can be damaged by the evaporation of various gases, but they are also the most easily repaired because they are in the molten state. This is where the hot pressing molding works best, helping to reorganize the structure within the fiber and eliminating the damage caused by escaping heteroatoms. In addition, the enlarged area of the image shows a small peak at 113 °C, which is the glass transition temperature (Tg) of the PAN polymer. Tg is the inherent property of polymer materials [32], at that point the polymer motion form happen to transformation [33], the materials become plastic [34]. At this point thermo-compression molding can also come into play. Based on above analysis, the thermoplasticity and melting properties of PAN fibers are known to weaken gradually with the occurrence of dehydrogenation, deoxygenation and denitrification. They can be well utilized by hot pressing molding to solve cracks and promote cyclization, etc.

Subsequently, chemical bonds of samples and the composition of C, N and O are analyzed in detail by XPS. The element composition of samples are compared in Table 2. The carbon content of blank group is from 55.08 (4PAN) to 82.41% (9PAN), while that of hot pressing group is from 51.36 of 4HSPAN to 78.71% of 9HSPAN. As expected, the carbon content of 4/6/8/9HSPAN is lower than that of 4/6/8/9PAN. It also means that the hot pressing samples have higher heteroatom content. This is in line with the previous analysis that the hot pressing cushions the escape of heteroatomic gases and reduces fiber damage. And the heteroatoms (plasticizer) make the fibers' thermal plasticity, or molten state, last longer. Therefore, the fiber density is higher and surface morphology is better under the interaction of thermoplastic fibers and hot pressing.

As can be seen from Table 2, C-composition increases in both PAN and HSPAN, O-composition decreases. Because carbonization and deoxidation occur primarily in this work. N-composition trend is not-regular. Because deoxidation and carbonization are dominant, and N hardly participates in the pyrolysis reaction below 600 °C [19, 31]. N-composition relatively changes due to the decrease of the overall fiber mass and the change of the ratio of C and O in the fiber. At temperatures above 600 °C, denitrogenation occurs, leading to the lateral growth of graphite-like ring systems [20, 30]. Carbonization and deoxidation are also occurring. N-composition trend is jointly determined by the denitrification reaction and the reduction of the total fiber mass. These cause the irregular trend of N-composition. Then, N-composition of PAN and HSPAN is analyzed by combining Fig. 3b with Table 2. It can be seen from Fig. 3b that the overall quality of HSPAN group is higher than that of PAN group. The fibers in PAN group undergo a violent deoxidation reaction, but N-composition does not participate in the pyrolysis reaction, which leads to the increase of N relative content. The pyrolysis reaction of HSPAN is moderated by hot pressing, so the overall quality of HSPAN fiber is higher. The deoxidation reaction was slowed down to some extent, and the carbonization reaction continued with the increase of temperature, which resulted in the irregular fluctuation of N-composition in the HSPAN group, and the relative content of N was low.

The C_{1s} ($\sim$ 285.0 eV) and O_{1s} ($\sim$ 532.0 eV) binding energy spectra are shown in Figs. 5 and 6, and fitted by Gaussian function. First, the evolution of C_{1s} bonds between the hot pressing and blank samples is clearly compared in Fig. 5a–d. The C_{1s} peak at $\sim$ 284.8 eV represents C–C in the carbon rings [10, 21]. From the two curves of each figure, it is clear that the C_{1s} peaks ($\sim$ 284.8 eV) of 4/6/8/9HSPAN is sharper and stronger than that of 4/6/8/9PAN. This indicates that there are more carbon rings and higher degree of cyclization in the hot pressing samples. This result strongly confirms that hot pressing is helpful to recombine intermolecular structure and promotes the cyclization reaction inside samples. The C_{1s} peak ($\sim$ 286.4 eV) represents C–O/ = N–O on the chain. And the C_{1s} peak ($\sim$ 288.4 eV) represents O–C = O at the junction of rings and chains [35, 36]. From the curves of 4HSPAN to 9HSPAN, the intermolecular binding law of the hot pressing samples is very obvious. In addition to the carbon ring peak ($\sim$ 284.8 eV) with the highest strength, there is the C–O/ = N–O on the chain and the O–C = O at the junction of rings and chains. This indicates that the heteroatoms retained in the fibers are then connected to the carbon rings by ester or ether bonds under the

Table 2 The element composition of samples

Sample/Content(%)	4PAN	4HSPAN	6PAN	6HSPAN	8PAN	8HSPAN	9PAN	9HSPAN
C	55.08	51.36	68.41	62.71	78.58	71.34	82.41	78.71
O	44.12	47.46	25.72	34.28	12.85	27.41	9.47	18.74
N	0.8	1.18	5.68	3.01	8.57	1.25	8.12	2.55

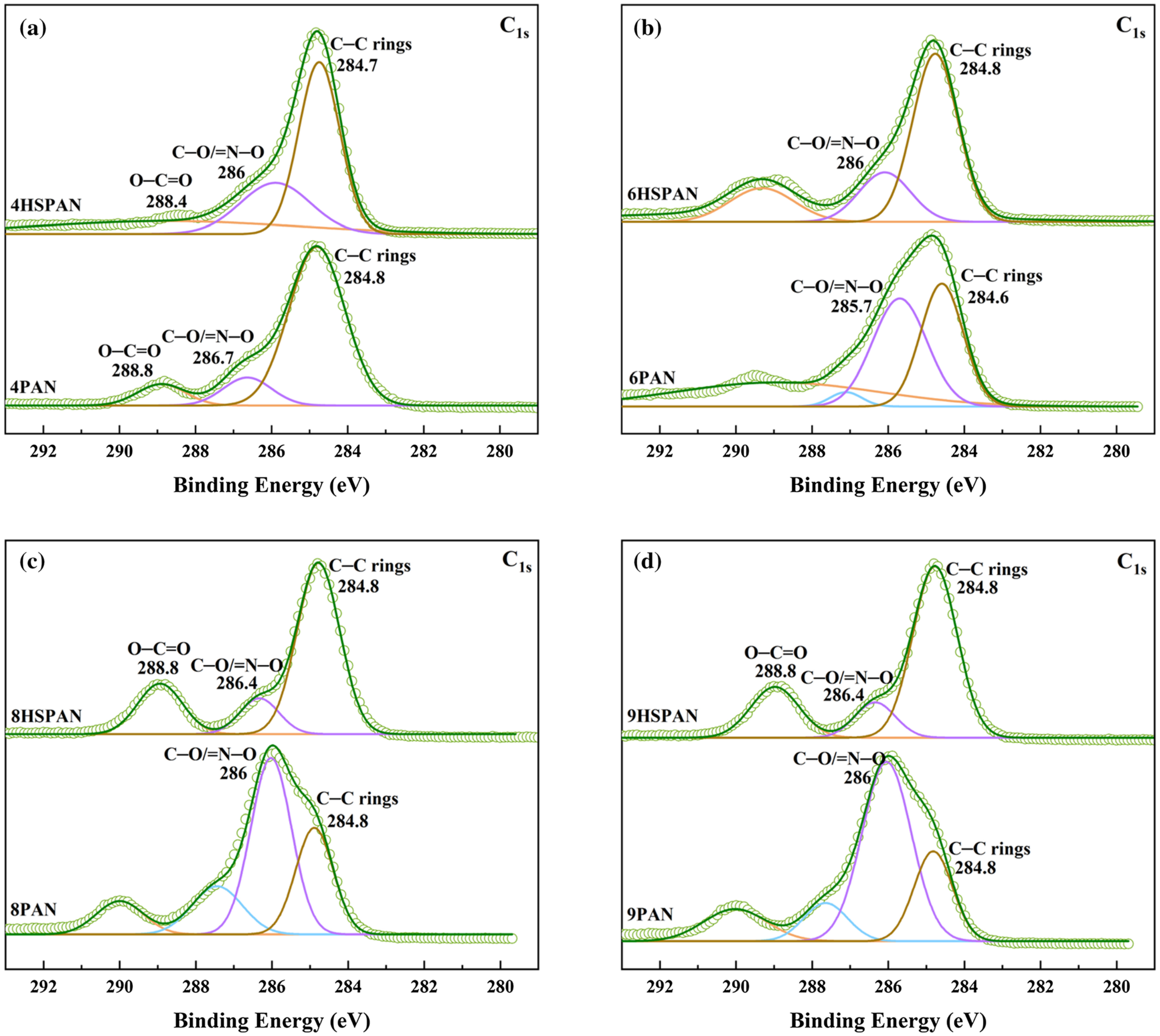

Figure 5 XPS C_{1s} peaks of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

hot pressing. And these ether and ester bonds are what keep the fibers thermoplastic for longer [37]. This explains the mechanism of hot pressing molding fundamentally. The possible evolution of the molecular structure during hot pressing carbonization is also given in Fig. 1. By observing Fig. 5a–d, we can find that the carbon ring peaks are gradually weakened in 4/6/8/9PAN curves. C–O/ = N–O hybrid peaks are dominant. It indicates that wanton pyrolysis makes more C–O/ = N–O compounds to form and embed in the rings, causing the internal structure to be messy [13].

The O_{1s} curves are given in Fig. 6a–d. Except for the consistent oxygen bond in the C_{1s} spectrum, the most conspicuous O_{1s} peak is at ~ 532 eV, which represents C–C = O in the rings [21]. The peak is observed in the 4/6/8/9HSPAN pattern and keeps getting stronger. This indicates that oxygen atoms are more connected to the carbon ring as ester bonds with the increase of carbonization temperature, which helps to retain the melting properties of the fiber. Therefore, hot pressing can help the thermoplastic fiber eliminate defects and increase the density. The results of 6/8/9PAN are consistent with the carbon spectra, with only C–O/ = N–O peaks. It is

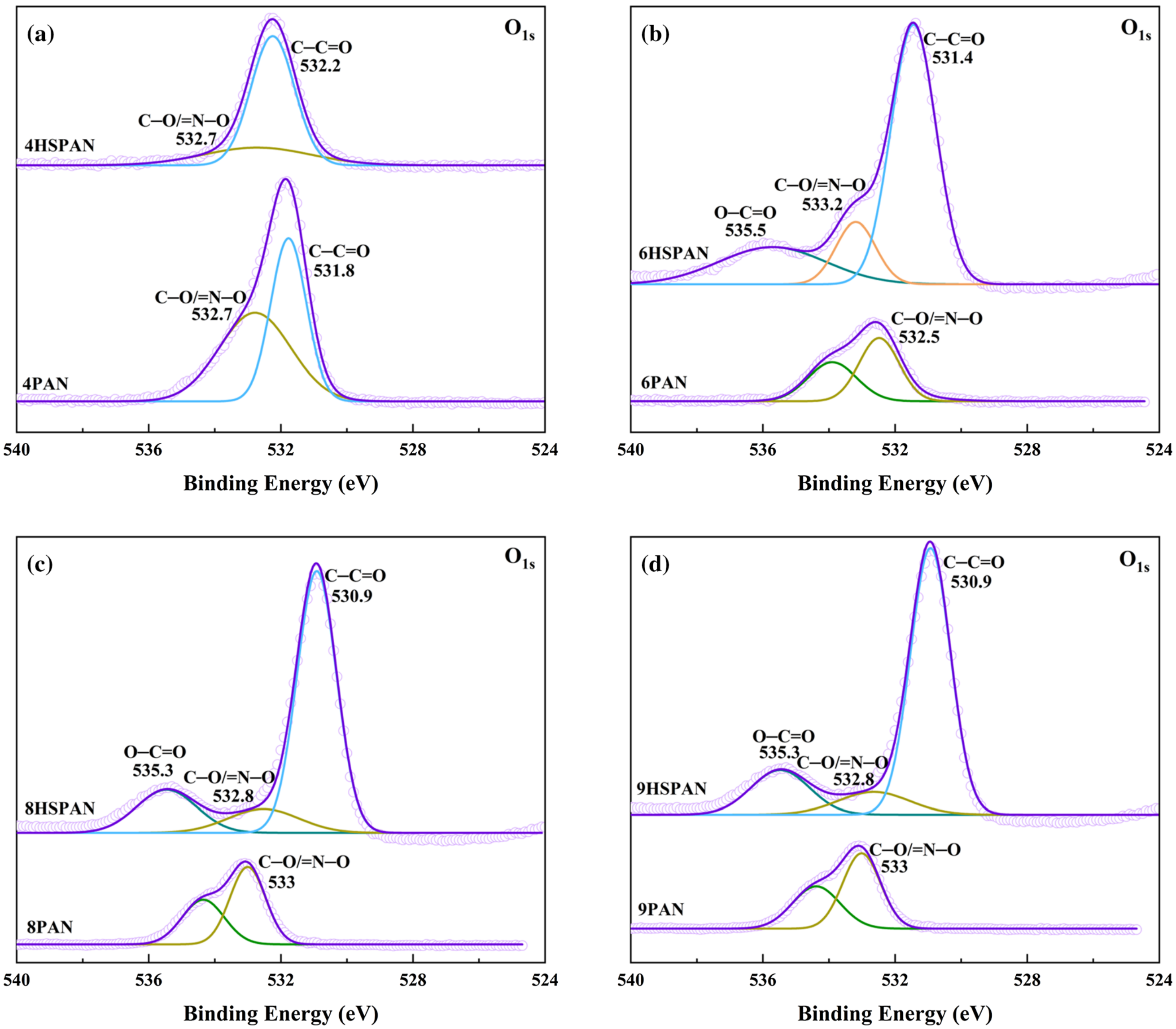

Figure 6 XPS O_{1s} peaks of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

also proved that the internal structure of blank samples is seriously damaged during carbonization.

Raman spectroscopy is usually used to detect the degree of lattice defects and graphitization of carbon materials [31, 38]. Figure 7a–d shows the Raman spectra curves of 4/6/8/9PAN and 4/6/8/9HSPAN, which are fitted with Lorentzian function. The intensity of the D-band around 1360 cm^{-1} usually represents the degree of carbon lattice defects [39]. The G-band at 1580 cm^{-1} is caused by the E_{2g} mode vibration of graphite [40]. I(D)/I(G) is an important index used to measure the degree of carbon lattice defects in carbon materials [41]. It can be observed that the D-band and G-band of 4/6/8/9HSPAN have very significant changes. The G-band representing graphite structure becomes stronger and the ratio of I(D)/I(G) decreases from 2 to 1.34. However, the I(D)/I(G) of CFs obtained by conventional carbonization process (1000 °C) is ~ 3.4[31], which is obviously higher than that obtained by thermo-pressing molding in this paper. It indicates that under the promotion of hot pressing, the internal defects of the fibers are corrected, and the molecular structure develops steadily toward the graphite-like structure. In contrast, the D-band and G-band of the 4/6/8/9PAN in the blank group are weaker and wider from beginning to end. The value of I(D)/I(G) ranges from 2.67–1.64, indicating that there are

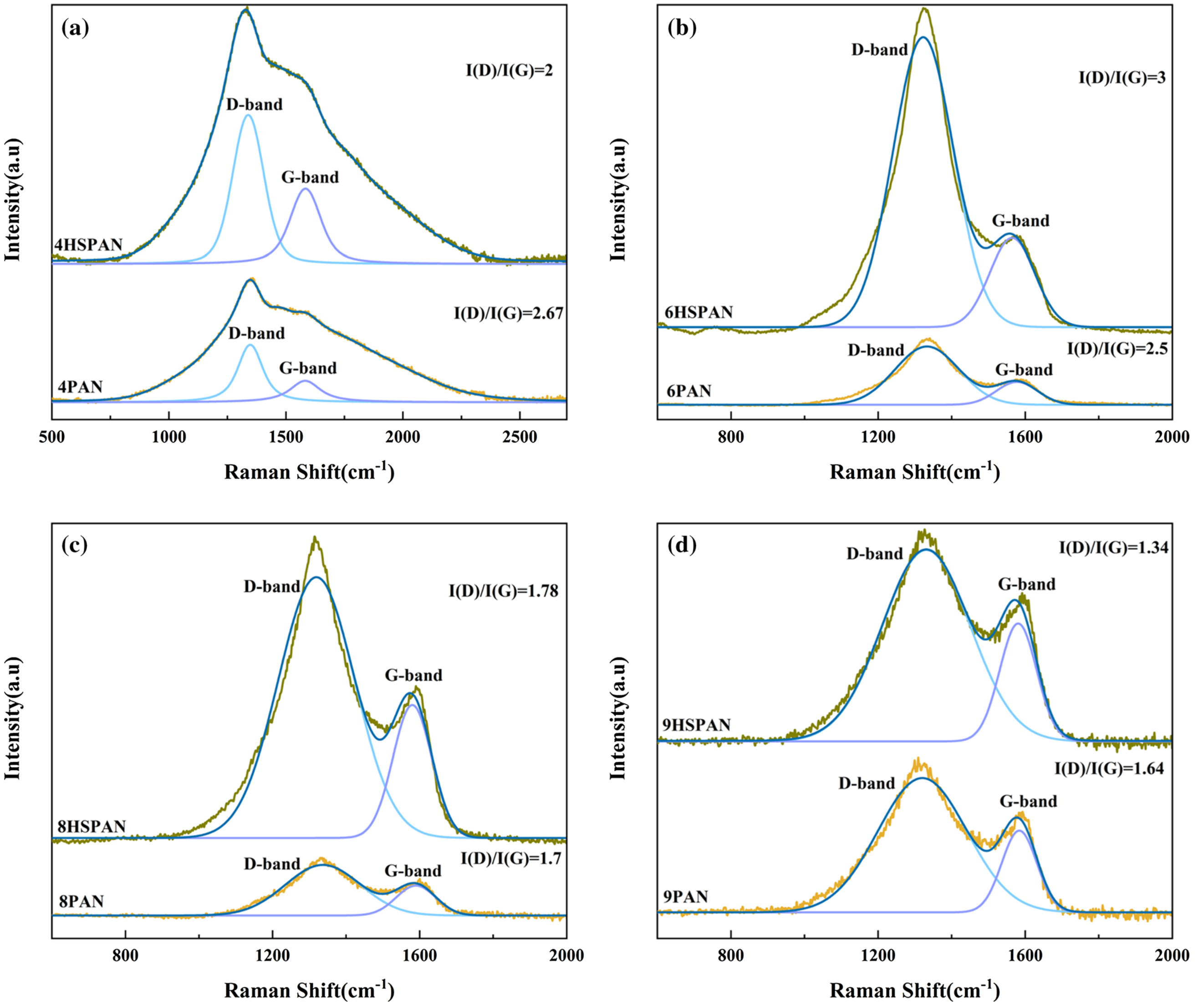

Figure 7 The Raman spectra of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

many carbon lattice defects and irregular structure in the 4/6/8/9PAN fibers. The result is in good agreement with those of XPS.

Tensile tests were performed on both blank and hot pressing samples, as shown in Fig. 8a–c. The tensile strength and modulus of 4/6/8/9PAN decreases gradually, which is also consistent with the SEM results. With the rise in carbonization temperature, dehydrogenation, deoxygenation and denitrification reaction takes place violently. It results in a large number of furrowed cracks in the fibers. And the defects have a huge effect on fiber strength, which leads to the results shown in the figure. This can also be related to the results of the loose density of 4/6/8/9PAN described above. Loose and porous will inevitably lead to poor fiber strength. In contrast, the tensile strength and modulus of the samples in the hot pressing group increase steadily. The tensile strength of 4HSPAN 0.34GPa, slightly higher than that of 4PAN is 0.3 GPa. This result is close to the tensile strength (0.308 GPa) of the fibers carbonized to 400 °C after thermal stabilization in other studies [10]. There is little difference in the strength of the sample obtained at 400 °C. This indicates that the pyrolysis at the initial stage of carbonization is not very intense and has no significant effect on the fiber strength. The strength of 6HSPAN carbonized at 600 °C is obviously higher than that of 6PAN. It has been studied that the highest amount of heteroatom removal occurs between 300 and 500 °C. This is the reason

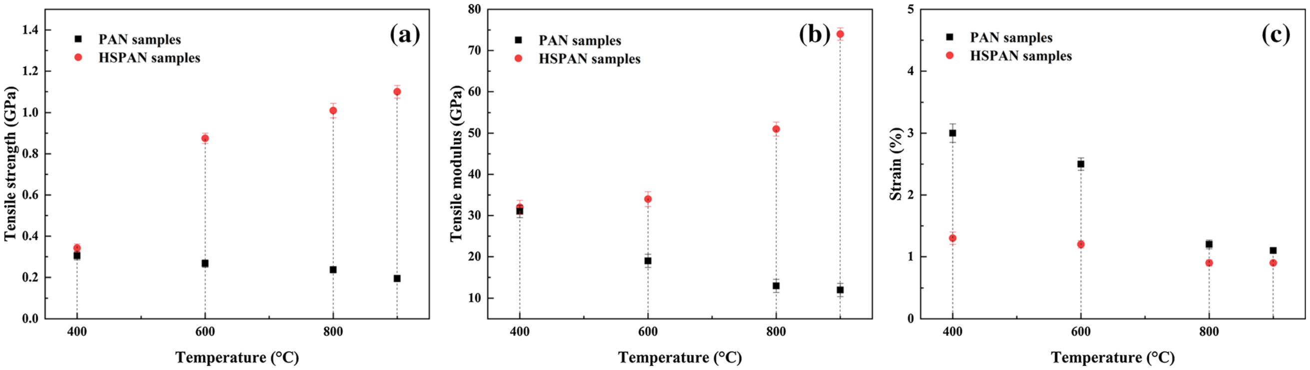

Figure 8 **a** Tensile strength of 4/6/8/9PAN and 4/6/8/9HSPAN samples. b. Tensile modulus of 4/6/8/9PAN and 4/6/8/9HSPAN samples. c. Strain of 4/6/8/9PAN and 4/6/8/9HSPAN samples.

why the strength of 6PAN cannot be further improved. The severe pyrolysis reaction causes irreversible damage to the fiber and affects its strength. The pyrolysis reaction of 6HSPAN is effectively controlled by hot pressing, which buffers the escape of gas molecules, reduces the heteroatom damage to the fibers. Meanwhile, thermoplastic fibers and hot pressing are mutually utilized, eliminating cracks in the fibers. Thus, the strength is greatly improved, reaching 0.87 GPa. It is also higher than the strength (0.5 GPa) of the fibers obtained by carbonization (600 °C) with thermal stabilization [31]. The same is true for samples of 800 and 900 °C. The tensile strength of 9HSPAN is 1.1 GPa, while the strength of 9PAN is only 0.195 GPa due to a large number of irreparable defects. The conventional process of acrylonitrile carbon fiber (1400 °C) strength is only 1.05 GPa [26]. Hot pressing promotes the formation of C–C rings and the stacking of graphite-like structures. From the density results, the fiber structure in the HSPAN group is obviously more compact. SEM pictures also show that the fiber morphology of HSPAN is smoother and has fewer defects. All these lead to the improvement in mechanical properties of fibers. Therefore, the effect of hot pressing carbonization process is remarkable.

Figure 8c shows strain comparison of 4/6/8/9PAN fibers and 4/6/8/9HSPAN fibers. It is known that the smaller the strain of the material, the greater the brittleness [24]. The strain of HSPAN group is significantly lower than that of PAN group, indicating that the brittleness of HSPAN group is greater than that of PAN group. With the increase of temperature, the strain of HSPAN decreases slightly, indicating that the brittleness of HSPAN group increases slightly. The strain of 4PAN is 3%, which is higher than that of 4HSPAN (1.2%) and lower than that of the fiber carbonized with thermal stabilization (4.9%) [10]. This is because the degree of carbonization of 4PAN fibers is low. The fibers tend to be similar to polymer fibers [31], so the strain is slightly higher. However, due to the fact that 4PAN is carbonized without thermal stabilization, there are lots of defects in fibers, resulting in lower strain than that of fibers carbonized with thermal stabilization. The reason for the high brittleness of HSPAN can be deduced from the XPS results. Compared with PAN group, the C_{1s} peak at ∼ 284.8 eV (C–C rings) and O_{1s} peak at ∼ 532 eV (C–C = O in the rings) of HSPAN are stronger and sharper, which implies high cyclization in the HSPAN group. It is reported that the higher the cyclization, the greater the brittleness of the fiber [24, 31]. Therefore, we obtained the reason for the high brittleness in the HSPAN group. As the temperature increases, the C–C ring peak in HSPAN group becomes sharper and stronger, which indicates higher degree of cyclization. So the brittleness of HSPAN CFs increases. The strain of 4/6/8/9HSPAN is relatively stable at about 1%, closely to the 1.09% of conventional acrylonitrile CFs [26]. Since there is nearly no defect in the hot pressing CFs, the strain (brittleness) is mainly affected by the increase of carbon content and graphite-like structure of the fiber. The strain of 4/6/8/9PAN also decreases gradually. That is because the fiber becomes brittle due to the increase of carbonization temperature. Moreover, it is also caused by the cracks inside the fiber as shown in SEM photos.

Conclusion

In this paper, PAN CFs was successfully prepared by one-step hot pressing molding. It realizes the cyclization reaction of thermal stabilization and eliminates the complex and time/energy-consuming thermal stabilization stage. Hot pressing does buffer the violent escape of gas molecules and reduce the damage of fiber caused by heteroatom removal. Atoms such as oxygen and nitrogen were well integrated into the cyclization structure as ether or ester bonds, which promotes the retention of fiber thermoplasticity and molten state. So the defects of the fiber can be easily repaired by hot pressing and the cyclization of the molecular structure can be promoted. The obtained PAN CFs have higher degree of cyclization microstructure, good surface morphology and excellent mechanical properties. The density of 9HSPAN is 1.7 g cm^{-3}, and tensile strength is 1.1 GPa. We provide a novel experimental idea and theoretical support for the preparation of CFs. The proposed one-step method preparation for CFs is practicable to reduce the cost, decrease the loss and evolving technologies.

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Declarations

Conflicts of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Edie DD (1998) The effect of processing on the structure and properties of carbon fibers. Carbon 36:345–362. https://doi.org/10.1016/S0008-6223(97)00185-1

[2] Lu S (2021) Research on electromagnetic properties and microwave deicing performance of carbon fiber modified concrete. Constr Build Mater. 286:122868

[3] Kim T, Chung DDL (2003) Carbon fiber mats as resistive heating elements. Carbon 41:2436–2440. https://doi.org/10.1016/S0008-6223(03)00288-4

[4] Khayyam H, Jazar RN, Nunna S et al (2020) PAN precursor fabrication, applications and thermal stabilization process in carbon fiber production: experimental and mathematical modelling. Prog Mater Sci 107:100575. https://doi.org/10.1016/j.pmatsci.2019.100575

[5] Lu J, Li W, Kang H et al (2020) Microstructure and properties of polyacrylonitrile based carbon fibers. Polym Test 81:106267. https://doi.org/10.1016/j.polymertesting.2019.106267

[6] Lü Y-G, Wu D, Zha Q-F et al (1998) Skin-core structure in mesophase pitch-based carbon fibers: causes and prevention. Carbon 36:1719–1724. https://doi.org/10.1016/S0008-6223(97)00172-3

[7] Xue Y, Liu J, Liang J (2013) Correlative study of critical reactions in polyacrylonitrile based carbon fiber precursors during thermal-oxidative stabilization. Polym Degrad Stab 98:219–229. https://doi.org/10.1016/j.polymdegradstab.2012.10.018

[8] Ruhland K, Frenzel R, Horny R et al (2017) Investigation of the chemical changes during thermal treatment of polyacrylonitrile and 15N-labelled polyacrylonitrile by means of in-situ FTIR and 15N NMR spectroscopy. Polym Degrad Stab 146:298–316. https://doi.org/10.1016/j.polymdegradstab.2017.10.018

[9] Rahaman MSA, Ismail AF, Mustafa A (2007) A review of heat treatment on polyacrylonitrile fiber. Polym Degrad Stab 92:1421–1432. https://doi.org/10.1016/j.polymdegradstab.2007.03.023

[10] Lee S, Kim J, Ku B-C et al (2012) Structural evolution of polyacrylonitrile fibers in stabilization and carbonization. Adv Chem Eng Sci 02:275–282. https://doi.org/10.4236/aces.2012.22032

[11] Ozbek S, Isaac DH (2000) Strain-induced density changes in PAN-based carbon fibres. Carbon 38:2007–2016. https://doi.org/10.1016/S0008-6223(00)00060-9

[12] Ruixue Z, Xudong Z, Zhongmin G et al (2017) Influence of thermal temperature on the structure and sealed micropores of stabilized polyacrylonitrile fibers. Chem Res Chin Univ. 33(2):312–317

[13] Salleh SNM, Abdullah MZ, Wahab AA (2014) Chemical and physical characterization of stabilized polyacrylonitrile (PAN) fiber. MATEC Web Conf 13:04016. https://doi.org/10.1051/matecconf/20141304016

[14] Xiao H, Lu Y, Zhao W, Qin X (2014) A comparison of the effect of hot stretching on microstructures and properties of polyacrylonitrile and rayon-based carbon fibers. J Mater Sci 49:5017–5029. https://doi.org/10.1007/s10853-014-8206-3

[15] Johnson JW, Marjoram JR, Rose PG (1969) Stress graphitization of polyacrylonitrile based carbon fibre. Nature 221:357–358

[16] Tse-Hao K, Tzy-Chin D, Jeng-An P, Ming-Fong L (1993) The characterization of PAN-based carbon fibers developed by two-stage continuous carbonization. Carbon 31:765–771. https://doi.org/10.1016/0008-6223(93)90013-Z

[17] Sauder C, Lamon J, Pailler R (2004) The tensile behavior of carbon fibers at high temperatures up to 2400 °C. Carbon 42:715–725. https://doi.org/10.1016/j.carbon.2003.11.020

[18] Mittal J, Konno H, Inagaki M, Bahl OP (1998) Denitrogenation behavior and tensile strength increase during carbonization of stabilized pan fibers. Carbon 36:1327–1330. https://doi.org/10.1016/S0008-6223(98)00113-4

[19] Goodhew PJ, Clarke AJ, Bailey JE (1975) A review of the fabrication and properties of carbon fibres. Mater Sci Eng 17:3–30. https://doi.org/10.1016/0025-5416(75)90026-9

[20] Jain MK, Abhiraman AS (1987) Conversion of acrylonitrile-based precursor fibres to carbon fibres: Part 1 A review of the physical and morphological aspects. J Mater Sci 22:278–300. https://doi.org/10.1007/BF01160584

[21] Zhao R-X, Sun P, Liu R et al (2018) Influence of heating procedures on the surface structure of stabilized polyacrylonitrile fibers. Appl Surf Sci 433:321–328. https://doi.org/10.1016/j.apsusc.2017.09.252

[22] Szepcsik B, Pukánszky B (2019) The mechanism of thermal stabilization of polyacrylonitrile. Thermochim Acta 671:200–208. https://doi.org/10.1016/j.tca.2018.12.004

[23] Qin X, Lu Y, Xiao H, Song Y (2012) Improving stabilization degree of stabilized fibers by pretreating polyacrylonitrile precursor fibers in nitrogen. Mater Lett 76:162–164. https://doi.org/10.1016/j.matlet.2012.02.103

[24] Hameed N, Sharp J, Nunna S et al (2016) Structural transformation of polyacrylonitrile fibers during stabilization and low temperature carbonization. Polym Degrad Stab 128:39–45. https://doi.org/10.1016/j.polymdegradstab.2016.02.029

[25] Tarakanova NV, Bondarenko VM, Azarova MT (1995) Structural changes in thermal stabilization of polyacrylonitrile fibre. Fibre Chem 27:15–17. https://doi.org/10.1007/BF00551522

[26] Huang J, Ouyang Q, Li M et al (2019) Thermal behavior and thermal stabilization of guanidine hydrochloride-modified acrylic fiber for preparation of low-cost carbon fiber. J Therm Anal Calorim 136:2195–2203. https://doi.org/10.1007/s10973-018-7848-9

[27] Qian X (2015) Surface structural evolvement in the conversion of polyacrylonitrile precursors to carbon fibers. Appl Surf Sci. 327:246–252

[28] Liu J, Wang PH, Li RY (1994) Continuous carbonization of polyacrylonitrile-based oxidized fibers: aspects on mechanical properties and morphological structure. J Appl Polym Sci 52:945–950. https://doi.org/10.1002/app.1994.070520712

[29] Chatterjee N, Basu S, Palit SK, Maiti MM (1995) An XRD characterization of the thermal degradation of polyacrylonitrile. J Polym Sci Part B Polym Phys 33:1705–1712. https://doi.org/10.1002/polb.1995.090331201

[30] Jing M, Wang C, Wang Q et al (2007) Chemical structure evolution and mechanism during pre-carbonization of PAN-based stabilized fiber in the temperature range of 350–600°C. Polym Degrad Stab 92:1737–1742. https://doi.org/10.1016/j.polymdegradstab.2007.05.020

[31] Gutmann P, Moosburger-Will J, Kurt S et al (2019) Carbonization of polyacrylonitrile-based fibers under defined tensile load: Influence on shrinkage behavior, microstructure, and mechanical properties. Polym Degrad Stab 163:174–184. https://doi.org/10.1016/j.polymdegradstab.2019.03.007

[32] Lebrón-Colón M, Meador MA, Gaier JR et al (2010) Reinforced thermoplastic polyimide with dispersed functionalized single wall carbon nanotubes. ACS Appl Mater Interfaces 2:669–676. https://doi.org/10.1021/am900682s

[33] Wang W, Wang C, Gao Q et al (2019) A new perspective on the internal structure of polyacrylonitrile-based preoxidized fibers through ultrathin sections. Polym Degrad Stab 167:269–276. https://doi.org/10.1016/j.polymdegradstab.2019.07.012

[34] Fu Z, Liu B, Sun L, Zhang H (2017) Study on the thermal oxidative stabilization reactions and the formed structures in polyacrylonitrile during thermal treatment. Polym Degrad Stab 140:104–113. https://doi.org/10.1016/j.polymdegradstab.2017.04.018

[35] Patterson BA, Galan U, Sodano HA (2015) Adhesive force measurement between hopg and zinc oxide as an indicator for interfacial bonding of carbon fiber composites. ACS Appl Mater Interfaces 7:15380–15387. https://doi.org/10.1021/acsami.5b03322

[36] Fitzer E, Müller DJ (1975) The influence of oxygen on the chemical reactions during stabilization of pan as carbon fiber precursor. Carbon 13:63–69. https://doi.org/10.1016/0008-6223(75)90259-6

[37] Jiang S, Uch B, Agarwal S, Greiner A (2017) Ultralight, thermally insulating, compressible polyimide fiber assembled sponges. ACS Appl Mater Interfaces 9:32308–32315. https://doi.org/10.1021/acsami.7b11045

[38] Wang Y (2017) Preparation of carbon nanosheets from petroleum asphalt via recyclable molten-salt method for superior lithium and sodium storage. Carbon. 122:344–351

[39] Ferrari AC, Robertson J (2000) Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B

61:14095–14107. https://doi.org/10.1103/PhysRevB.61.14095

[40] Miyagawa H, Sato C, Mase T et al (2005) Transverse elastic modulus of carbon fibers measured by Raman spectroscopy. Mater Sci Eng A 412:88–92. https://doi.org/10.1016/j.msea.2005.08.037

[41] Cheng X-B, Tian G-L, Liu X-F et al (2013) Robust growth of herringbone carbon nanofibers on layered double hydroxide derived catalysts and their applications as anodes for Li-ion batteries. Carbon 62:393–404. https://doi.org/10.1016/j.carbon.2013.06.023