

Research on the Influence of Polyacrylonitrile Precursor on the Properties of Carbon Fibers and Pultruded Composite Materials

Zheng Wei^{1*}, Guoping Hao², Yongqiang Zhang²

¹Zhejiang Baowan Carbon Fiber Co., Ltd., Shaoxing 312075, Zhejiang, China

²Shaoxing Baojing Composite Materials Co., Ltd., Shaoxing 312073, Zhejiang, China

**Author to whom correspondence should be addressed.*

Copyright: © 2025 Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY 4.0), permitting distribution and reproduction in any medium, provided the original work is cited.

Abstract: Polyacrylonitrile (PAN) precursor is a core precursor for the preparation of high-performance carbon fibers. Its unique chemical structure and physical properties directly contributes to the microstructure and mechanical properties of carbon fibers, and therefore affect the overall performance of pultruded composites. This study systematically investigated the influence of PAN precursor properties on the degree of graphitization, surface morphology and mechanical properties of carbon fibers by regulating the molecular weight distribution, stretching ratio and impurity content of PAN precursor, and analyzed the mechanism of action of carbon fiber properties on the interfacial bonding strength and tensile/bending properties of composites in combination with the pultrusion process. The results showed that when the filament stretchability was increased to 4.5 times, the axial orientation of carbon fibers increased by 18% and the tensile strength reached 520 MPa; Filaments with impurity content below 0.3% increase carbon fiber yield by 5.2% and interlaminar shear strength of composites by 23%. This study provides a theoretical basis for raw material screening and process optimization of high-performance carbon fibers and their composites.

Keywords: Polyacrylonitrile precursor; Carbon fiber; Pultrusion; Composites; Performance effects

Online publication: 4th September 2025

1. Introduction

Carbon fiber is highly resistant to corrosion and has high strength but low density. Due to its advantages and characteristics, carbon fiber is now widely used as a key structural material in aerospace, new energy equipment and other fields ^[1]. Among them, PAN -based carbon fibers have a relatively high global output, occupying 90% of the market ^[2].

In the manufacturing process, the primary factor determining its quality was the performance of the precursor, such as the impurity content and orientation of the precursor, which would affect the degree of graphitization and

defect distribution of the carbon fiber to a certain extent ^[3]. As for the preparation of carbon fiber composites, the pultrusion process has stood out due to its own advantages, such as the ability to achieve continuous production and high fiber volume fraction (65–75%), and has now developed into an important technology for the preparation of carbon fiber materials ^[4].

However, there is not enough study in the industry on the correlation between the properties of the precursor and the properties of pultruded composites, especially the mechanism by which the microstructure of the precursor affects the interfacial bonding behavior of the composites ^[5]. Hence, this paper takes different specifications of PAN precursor as the research object, attempts to explore the influence of key performance indicators of precursor on the structure and performance of carbon fiber by using the control variable method, and also constructs a performance transfer model of “precursor - carbon fiber - composite” in combination with the pultrusion forming process. The primary aim is to provide more theoretical support for the selection of raw materials and the optimization of processes for high-performance composites.

2. Materials and methods

2.1. Experimental materials

Three different specifications of PAN precursor (A, B, C) were selected, and their basic properties are shown in Table 1.

Table 1. Basic performance parameters of PAN precursor

Filament number	Average molecular weight ($\times 10^4$)	Molecular weight distribution (Mw/Mn)	Stretching ratio	Impurity content (%)	Monofilament diameter (μm)
A	15	2.1	3.0	0.5	18 ± 2
B	18	1.8	4.5	0.3	16 ± 1
C	22	2.5	2.0	0.8	20 ± 3

Note: The impurity content mainly includes metal ions, undissolved polymer particles, etc.

2.2. Carbon fiber preparation process

Carbon fiber is produced by pre-oxidation (air atmosphere, 220–280 °C, heating rate 2 °C/min, residence time 90 mins) and carbonization (nitrogen atmosphere, 1200 °C, residence time 30 mins) of the precursor ^[6]. The pre-oxidation stage focused on controlling the degree of oxidation (10–12% oxygen content), while the carbonization stage controlled the structural evolution by adjusting the rate of heating (5–10 °C/min).

2.3. Preparation of pultruded composite materials

The epoxy resin (E-51)/methyltetrahydrophthalic anhydride (curing agent, mass ratio 100:80), with 3% silane coupling agent (KH-550) was added in the resin system ^[7]. After the carbon fibers were impregnated with resin in an impregnation tank, they were cured and formed through a heated mold (temperature gradient: 80 °C → 120 °C → 160 °C), with a traction speed of 1.5 m/min and a fiber volume fraction of approximately 65% ^[8]. The sizes of the prepared composite specimens were: tensile specimens (250 × 25 × 3 mm), bending specimens (80 × 10 × 3 mm), interlaminar shear specimens (40 × 10 × 3mm).

2.4. Testing and characterization

2.4.1. Carbon fiber performance testing

The degree of graphitization was analyzed by X-ray diffraction (XRD, Cu K α radiation, $\lambda = 0.154$ nm), and the (002) interplanar spacing (d_{002}) and microcrystalline size (Lc) were calculated; The surface morphology was observed by scanning electron microscopy (SEM, acceleration voltage 5kV); The tensile strength of the filaments was measured using an Instron5948 microforce tester with a gauge length of 20 mm and a tensile rate of 1 mm/min, with 50 filaments tested in each group with the average value recorded ^[9].

2.4.2. Composite material performance test

Tensile and flexural strength were tested in accordance with GB/T3354-2014 and GB/T3356-2014 standards at a loading rate of 2 mm/min; Interlayer shear strength was tested using the short beam shear method (GB/T3357-2014), with a span of 20 mm and a loading rate of 1 mm/min; Interfacial bonding performance was analyzed by observing the fracture morphology via SEM.

3. Results

3.1. The effects of PAN precursor properties on carbon fiber structures

3.1.1. The effect of stretching ratio on carbon fiber orientation

The stretching ratio directly affects the orientation degree of the precursor molecular chains ^[10]. **Figure 1** shows the XRD patterns of carbon fibers prepared from filaments with different stretching ratios. As the stretch ratio increased from 2.0 (precursor C) to 4.5 (precursor B), the intensity of the diffraction peak (002) significantly increased and the half-height width narrowed, indicating an improvement in the orientation of the graphite microcrystals along the fiber axis. The Lc value of the carbon fiber prepared from precursor B was 21.5 nm, which was 21% higher than that from precursor C (17.8 nm), and d_{002} decreased from 0.342 nm to 0.338 nm, indicating an increase in graphitization.

The stretching ratio directly affected the orientation degree of the precursor molecular chains ^[10].

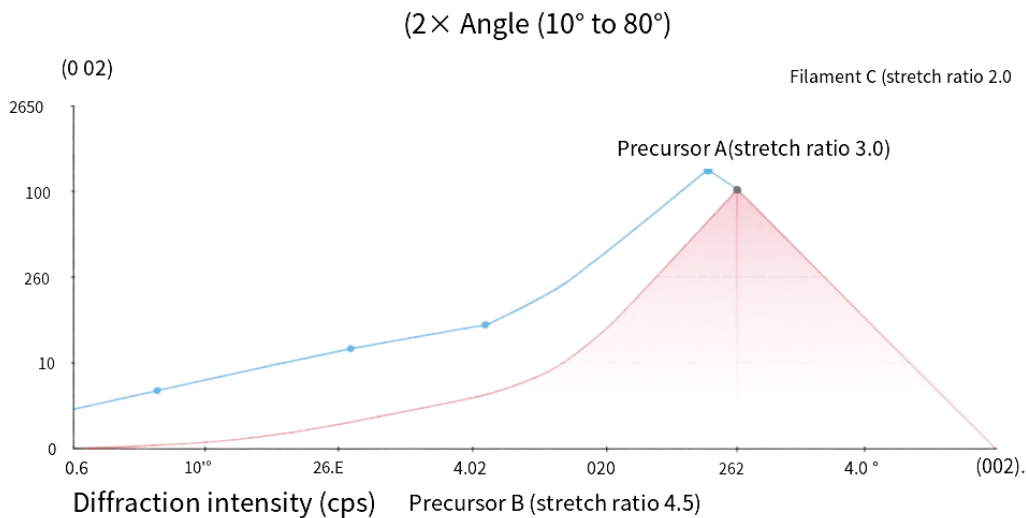


Figure 1. XRD patterns of carbon fibers prepared from filaments with different stretching ratios.

3.1.2. The effect of impurity content on carbon fiber defects

Impurities in the precursor (such as metal ions) can catalyze the cracking of graphite sheets during the carbonization process, resulting in structural defects^[12]. **Figure 2** shows the SEM images of carbon fibers prepared from precursor A (0.5% impurity) and precursor B (0.3% impurity). There are obvious longitudinal grooves and protrusions on the surface of precursor A carbon fiber, while the surface of precursor B carbon fiber is smooth with grooves less than 2 μm deep. Energy spectrum analysis showed that the Fe content in precursor A carbon fiber was 85 ppm, significantly higher than 32 ppm in precursor B. Metal impurities act as catalysts for REDOX reactions, intensifying the intense exothermic process during the pre-oxidation stage, resulting in microcracks within the fibers and surface defects after carbonization.



Figure 2. SEM images of the surface of carbon fibers prepared from filaments with different impurity contents.

3.2. The effect of PAN precursor properties on the mechanical properties of carbon fibers

The data on the mechanical properties of carbon fibers prepared with different precursor materials was presented in **Table 2**. The carbon fiber tensile strength of precursor B (high stretch ratio, low impurities) reached 520 MPa, and the elastic modulus was 23.5 GPa, which were 48% and 31% higher, respectively, than that of precursor C (low stretch ratio, high impurities). This difference is mainly due to two aspects: (1) The high elongation ratio improves the orientation of the molecular chain and reduces the stress concentration points; (2) Low impurity content inhibits the formation of defects during carbonization. It is notable that the molecular weight of precursor A is higher (22×10^4), but its mechanical properties are lower than those of precursor B, indicating that the broadening of the molecular weight distribution ($M_w/M_n = 2.5$) led to uneven molecular chain entanglement and local overheating degradation during pre-oxidation, reducing the density of the carbon fiber^[13].

Table 2. Comparison of mechanical properties of carbon fibers

Filament number	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation at break (%)	Yield (%)
A	410 \pm 15	20.1 \pm 1.2	3.2 \pm 0.3	48.5
B	520 \pm 20	23.5 \pm 1.5	3.8 \pm 0.4	53.7
C	350 \pm 12	17.9 \pm 1.0	2.8 \pm 0.2	43.2

3.3. The influence of carbon fiber properties on the interfacial bonding of pultruded composites

3.3.1 The influence of surface morphology on interfacial shear strength

The groove structure on the surface of carbon fibers enhance mechanical meshing with the resin ^[14]. **Figure 3** shows the SEM images of the fracture surfaces of composite materials prepared with different filaments. The surface grooves of precursor B carbon fiber were uniform, the embedding depth of the resin matrix is about 5 μm , and the fracture shows a large number of resin tear marks, indicating that the interfacial bonding is mainly the combined effect of chemical adsorption and mechanical locking; In contrast, the surface of precursor C carbon fiber is rough but the grooves are irregular, and cavities after fiber extraction can be seen at the fracture. The interfacial shear strength is only 32.5 MPa, which is 23% lower than that of precursor B (42.1 MPa). This suggests that a moderate surface roughness (such as $R_a = 1.2 \mu\text{m}$ for precursor B) was beneficial for improving interfacial bonding, while excessive defects (such as $R_a = 2.3 \mu\text{m}$ for precursor C) was shown to cause a stress concentration and reduce interfacial compatibility.

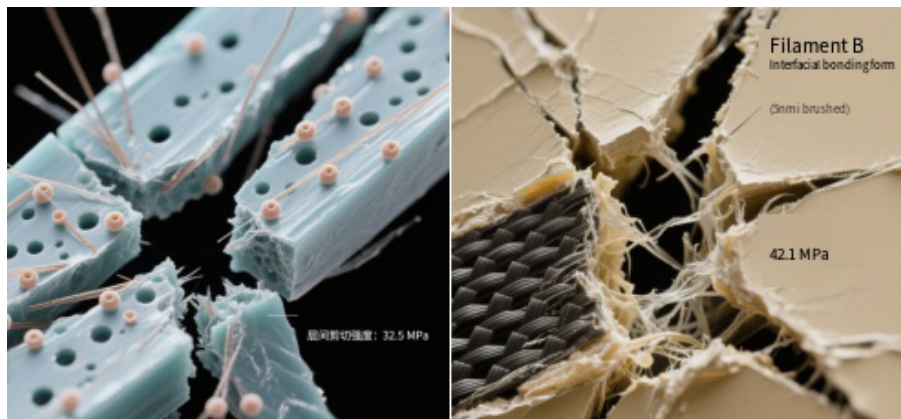


Figure 3. SEM image of the fracture surface of the composite.

3.3.2. The effect of oxidation degree on the adsorption of coupling agent

Controlling the content of oxygen-containing functional groups (such as hydroxyl and carboxyl groups) on the carbon fiber surface during the pre-oxidation stage can enhance the chemical bond interaction of the coupling agent ^[15]. **Figure 4** shows that the O/C atomic ratio in the XPS profile of precursor B carbon fiber is 0.18, which is higher than 0.12 for precursor A, indicating a better degree of surface oxidation. The silane coupling agent forms hydrogen bonds with the carbon fiber surface through hydroxyl groups, and after curing, it generates Si-O-C chemical bonds, which increase the interlamellar shear strength of the composite. Infrared spectroscopy analysis showed that the absorption peak intensity of the precursor B composite at 1020 cm^{-1} (Si-O-C stretching vibration) was 35% higher than that of the precursor A, confirming the enhanced inter-interface chemical bonding.

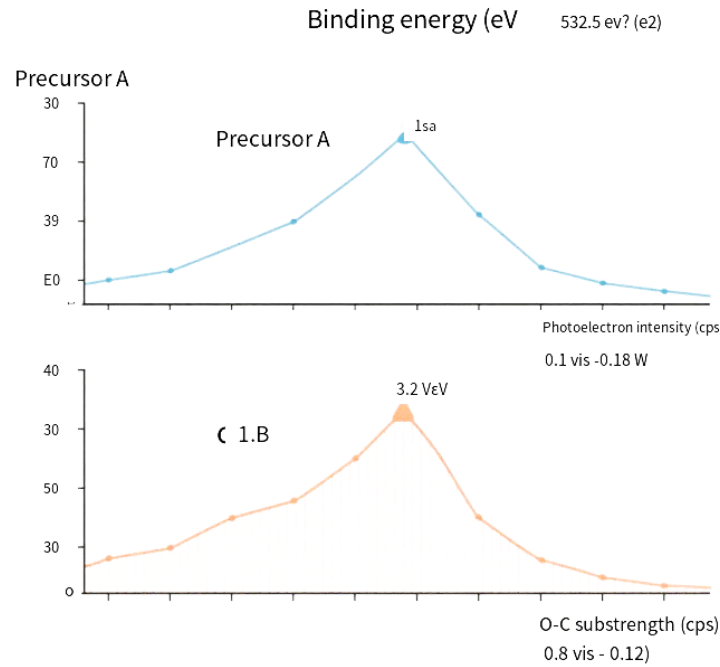


Figure 4. XPS spectra of carbon fiber surface.

3.4. Analysis of mechanical properties of pultruded composites

Table 3 shows the data of mechanical properties of composites with different precursor systems. Precursor B composites have tensile strength of 1280 MPa, flexural strength of 1120 MPa, and interlaminar shear strength of 42.1 MPa, all significantly superior to other systems. Correlation analysis shows that the tensile strength of carbon fibers is linearly positively correlated with the tensile strength of composites ($R^2 = 0.96$), and the correlation coefficient between interfacial shear strength and interlayer shear strength is 0.92.

Table 3. Mechanical properties of pultruded composites

Filament number	Tensile strength (MPa)	Flexural strength (MPa)	Interlaminar shear strength (MPa)
A	1050 ± 40	910 ± 35	35.8 ± 2.1
B	1280 ± 50	1120 ± 45	42.1 ± 2.5
C	890 ± 30	780 ± 30	32.5 ± 1.8

4. Discussion

In this study, the effects of precursor properties on the structural and mechanical performance of carbon fibers and their composites were investigated. It was observed that increasing the stretching ratio significantly improved the orientation of the carbon fibers, which led to enhanced graphitization and better mechanical properties.

The tensile strength and elastic modulus of precursor B carbon fiber, prepared with a high stretching ratio and low impurity content, were notably higher than those of precursor C. The impurities present in the precursor materials had a detrimental effect on the carbon fiber structure, promoting defects during the carbonization process. This was evident from the SEM analysis, where precursor A, with higher impurity content, showed

more surface defects. The relationship between impurity content and fiber quality highlights the importance of controlling impurity levels to reduce defects and improve fiber performance.

Surface morphology also played a critical role in the interfacial bonding between carbon fibers and the resin matrix in the pultruded composites. Moderate surface roughness ($R_a = 1.2 \mu\text{m}$) was found to optimize the interfacial shear strength, while excessive surface defects could lead to stress concentration and poor bonding. Additionally, controlling the degree of oxidation of the carbon fiber surface during pre-oxidation enhanced the chemical bonding with the coupling agent, further improving the interfacial properties. The overall mechanical properties of the pultruded composites were also heavily influenced by the precursor properties. Composites made from precursor B fibers exhibited superior performance, demonstrating the importance of both fiber orientation and surface treatment in achieving high-quality composite materials.

5. Conclusion

The drawing ratio and impurity content of PAN precursor are key factors affecting the structure and performance of carbon fibers. An increase in the drawing ratio to 4.5 times increases the carbon fiber orientation by 18%, and when the impurity content is below 0.3%, the carbonization yield increases by 5.2% and the defect density decreases.

The surface morphology of carbon fibers and the degree of oxidation significantly affect the interfacial properties of pultruded composites. Moderate surface grooves ($R_a = 1.0\text{--}1.5\mu\text{m}$) and oxygen-containing functional groups ($\text{O/C} = 0.15\text{--}0.20$) can increase interlaminar shear strength by more than 20%.

A transfer mechanism of “precursor properties - carbon fiber structure - composite properties” was established: high regularity precursor \rightarrow low defect carbon fiber \rightarrow strong inter-interface bonding composite. In actual production, PAN precursor with a narrow molecular weight distribution ($M_w/M_n \leq 2.0$), stretching ratio 4.0–5.0, and impurity content $< 0.3\%$ is recommended for the preparation of high-performance carbon fibers and pultruded composite materials.

Further research could be conducted on the effects of precursor spinning processes (such as dry-wet spinning parameters) on the microporous structure of carbon fibers, as well as the optimization effect of nano-filler modification on interfacial thermal stress matching to promote the application of carbon fiber composites in extreme environments.

Disclosure statement

The authors declare no conflict of interest.

References:

- [1] Ge G, Wang L, Gou P, 2025, Analysis of the Relationship Between the Viscosity Increase of PAN Spinning Solution and the Properties of Precursor and Carbon Fiber, *High Technology Fibers & Applications*, 50(02): 51–57.
- [2] Lan Z, Zhou H, Wang Y, et al., 2025, The Mechanism of Air Pressure in the Pre-oxidation Process of Polyacrylonitrile Precursor, *Polymer Materials Science and Engineering*, 41(02): 78–86.
- [3] Su B, 2024, Preparation and Properties Study of Polyacrylonitrile-Based Nanofiber Composites, thesis, Inner Mongolia Agricultural University.

- [4] Li X, Han X, Zhao H, et al., 2024, Research Progress on Green Adsorption of Polyacrylonitrile-Based Carbon Fibers in Water Treatment, *Aging and Application of Synthetic Materials*, 53(05): 81–83.
- [5] Wang Z, Zhong J, Zhou Z, et al., 2024, Study on the Effect of Lignin Structure on Mechanical Properties of Polyacrylonitrile/Ground Wood Lignin-Based Carbon Fibers, *Chemical and Biological Engineering*, 41(10): 44–49 + 63.
- [6] A Spinning Assembly for Large Filament Carbon Fiber Precursor and a Method for Preparing Polyacrylonitrile-Based Large Filament Carbon Fiber Precursor, 2024, *Qilu Petrochemical Industry*, 52(03): 239.
- [7] Preparation Method of a Low Grain Size Polyacrylonitrile Precursor, 2024, *High Technology Fibers & Applications*, 49(04): 76.
- [8] Qin Q, Xu L, Chen T, et al., 2024, Research on the Preparation Process of High Performance Polyacrylonitrile-Based Carbon Fiber Precursor, *Synthetic Fibers*, 53(08): 45–49.
- [9] Wang J, Zhao Y, Li J, et al., 2024, Research Progress on Polymerization Process of High Molecular Weight Polyacrylonitrile, *Synthesis Technology & Application*, 39(02): 28–32.
- [10] Gu L, Fan B, Sun Q, et al., 2024, Analysis of Influencing Factors of Oxygen Content Detection in Polyacrylonitrile-Based Carbon Fiber Precursor, *Synthetic Fibers*, 53(06): 54–55.
- [11] Xu J, 2024, Preparation and Performance Study of Oiling Agent for High Heat Resistance Carbon Fiber Precursor, thesis, Changzhou University.
- [12] Yang X, 2024, The Effect of Methyl Acrylate on the Structure and Properties of Polyacrylonitrile Fibers, thesis, Jilin Institute of Chemical Technology.
- [13] A High-Performance Polyacrylonitrile-Based Carbon Fiber Precursor and Its Preparation Method and Application, 2024, *High Technology Fibers & Applications*, 49(02): 75.
- [14] Geng Y, Zhang K, 2023, Research on the Production Process of Polyacrylonitrile-Based Carbon Fiber Precursor, *Shanxi Chemical Industry*, 43(10): 16–17 + 22.
- [15] Zhang M, Gu H, Zhang S, et al., 2021, Effects of Polyacrylonitrile Precursor on the Properties of Carbon Fibers and Pultruded Composites, *New Materials for Chemical Industry*, 49(12): 153–157.

Publisher's note

Bio-Byword Scientific Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.