

Article

Tension–Temperature Synergy in Tailoring Surface Polarity and Interfacial Properties of High-Modulus PAN-Based Carbon Fibers

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Highlights

- Temperature and tension exert decoupled control over crystallite size and axial orientation in high-modulus carbon fibers.
- A competitive balance keeps surface polarity nearly unchanged under varying tension at fixed temperature.
- Low-temperature high-tension processing achieves ~350 GPa modulus with 37.9% higher interfacial shear strength.
- The Sac parameter shows strong linear correlations with surface energy and interfacial shear strength.

Abstract

High-temperature graphitization inevitably compromises the surface polarity and resin wettability of polyacrylonitrile (PAN)-based high-modulus carbon fibers (HMCs), creating a long-standing trade-off between fiber modulus and interfacial adhesion that restricts its applications. Here we report a tension–temperature synergy to overcome this limitation. HMCs were fabricated at 1700–2100 K under axial tensions of 0–70 N, and the resulting microstructures and surface activity were characterized by X-ray diffraction, Raman spectroscopy, dynamic contact angle testing, and microdroplet debond measurements. Temperature dominates crystallite coarsening and surface-active carbon (Sac) concentration, whereas tension enhances axial lamellar orientation without inducing appreciable grain growth. At constant temperature, two competing effects, both slight crystallite growth and radial lamella rearrangement, keep Sac stable under varying tension. Fibers processed at 1900 K with 60 N tension achieve a modulus of ~350 GPa, equivalent to that of the 2100 K/10 N sample, while delivering a 13.5% higher Sac, elevated surface energy (26.3 mN·m^{−1}), and 37.9% stronger interfacial shear strength (IFSS). The Sac parameter exhibits strong correlations with surface energy and IFSS. This one-step in situ thermal strategy eliminates post-treatment and offers an industrially viable route to HMCs with balanced modulus and intrinsic interfacial bonding.

Keywords: high-modulus carbon fiber; tension–temperature synergy; surface polarity; interfacial shear strength; graphitization



Academic Editor: Yanxiang Wang

Received: 16 July 2026

Revised: 7 August 2026

Accepted: 17 August 2026

Published: 19 August 2026

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1. Introduction

Polyacrylonitrile (PAN)-derived high-modulus carbon fibers (HMCs, tensile modulus > 350 GPa) are indispensable lightweight reinforcements for aerospace primary load-bearing structures, owing to their exceptional specific modulus and dimensional stability at elevated temperatures [1–3]. However, conventional graphitization at temperatures exceeding 2000 K significantly enhances graphite crystallinity and crystallite dimensions, which inevitably eliminates edge-active carbon atoms on the fiber surface [4]. This surface degradation leads to low polarity, poor wettability by resin matrices, and consequently weak fiber–matrix interfacial shear strength (IFSS) [5]. Relative to medium-modulus carbon fibers (~290 GPa), HMCs typically exhibit a 30–40% reduction in interfacial performance, which severely constrains their application in composite structures subjected to complex alternating loads [2].

Conventional approaches to improving carbon fiber interfacial properties rely predominantly on post-surface treatments, including anodic oxidation [6–8], plasma etching [9–12], and chemical grafting [13–16]. Nevertheless, the effectiveness of these secondary modifications is fundamentally constrained by the intrinsic graphitic structure of the as-produced fibers. Highly graphitized HMCs possess few surface-active sites, establishing an inherent upper limit for interfacial enhancement regardless of post-treatment parameters [5,17,18]. This limitation underscores the need for an *in situ* thermal processing strategy that can generate polar surface structures during graphitization itself, without compromising the fiber's bulk mechanical properties.

Tension applied during continuous high-temperature graphitization represents a critical adjustable parameter for tailoring carbon fiber microstructures [19]. Adequate axial tension restricts thermal shrinkage of the fiber and promotes alignment of graphite lamellae along the fiber axis, which effectively elevates tensile modulus without inducing excessive growth of graphite crystallites [20]. Previous studies have established that increased tension substantially improves microcrystalline orientation, whereas high graphitization temperatures simultaneously accelerate crystallite growth and diminish surface-active carbon content [21]. However, most earlier investigations examined the isolated effects of temperature or tension separately, with limited attention to the interactive influence of graphitization temperature and drawing tension on both the bulk graphite structure and intrinsic surface polarity [22,23]. Moreover, quantitative indicators for evaluating the surface polarity of HMCs remain scarce, resulting in an ambiguous correlation among processing parameters, microstructures, and interfacial performance.

In this paper, HMCs samples were prepared under gradient tension (0–70 N) at various graphitization temperatures (1700 K, 1900 K and 2100 K). X-ray diffraction (XRD), Raman spectroscopy, dynamic contact angle measurements, and microdroplet debond tests were employed to systematically elucidate the distinct roles of tension in modulating crystallite size, radial orientation, and surface-active carbon (Sac) content. A competitive mechanism between microcrystal coarsening and radial graphitic lamella exposure induced by axial tension is proposed to rationalize the nearly invariant surface polarity observed under variable tension. Furthermore, a tension–temperature synergistic regulation route is proposed. Substantial drawing tension combined with moderate graphitization temperature achieves comparable fiber modulus while preserving abundant edge-active carbon sites. This work offers a novel processing paradigm for fabricating HMCs with superior intrinsic interfacial activity.

2. Materials and Methods

2.1. Materials

Polyacrylonitrile (PAN) precursor fibers (0.78 dtex, linear density 0.940 g/m) were adopted as the starting fiber raw material, prepared by dry-wet spinning at the National Carbon Fiber Engineering Research Center (Beijing, China). E51 epoxy resin (bisphenol-A diglycidyl ether type), methyltetrahydrophthalic anhydride (MTHPA) curing agent, 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) accelerator were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemical reagents were used as received without further purification.

2.2. Preparation of HMCFs

A continuous multi-stage thermal treatment line was employed to produce the HMCFs. The production line consisted of an air stabilization furnace, a low-temperature carbonization furnace, and a high-temperature graphitization furnace, with high-purity nitrogen (99.999%) serving as the protective atmosphere throughout the entire heat treatment process.

Stabilization stage: The precursor tows were subjected to gradient heating temperatures ranging from 483 to 523 K under constant low tension to avoid molecular chain disorientation and to ensure uniform thermal oxidative stabilization across the filament cross-section.

Low-temperature carbonization: The stabilized fibers were passed through a furnace at temperatures ranging from 623 to 953 K to eliminate most of the hydrogen, oxygen, and partial nitrogen heteroatoms, thereby converting the stabilized PAN structure into a turbostratic carbon framework.

High-temperature graphitization: The residence time was fixed at 144 s for all experimental groups, and two independent variables were systematically regulated: graphitization temperature (1700 K, 1900 K, and 2100 K) and axial drawing tension (ranging from 0 N to 70 N). The fiber tension was precisely monitored and adjusted via a SCHMIDT DN1-5000 online tension tester installed at the outlet of the graphitization furnace. The tension gradient groups were set at approximately 10 N, 20 N, 30 N, 40 N, 50 N, 60 N, and 70 N, with a free-shrinkage control group (0 N). After stable temperature and tension equilibrium were achieved, the finished fiber tows were wound and collected for subsequent characterization. Figure 1 illustrates the preparation process. Table S1 lists the physical properties of HMCFs at different tension and temperature.

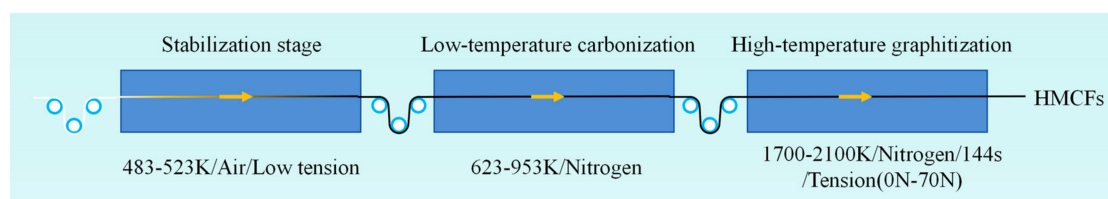


Figure 1. Schematic diagram of HMCFs preparation.

2.3. Characterizations

2.3.1. X-Ray Diffraction

XRD patterns were recorded on an X'Pert PRO MPD diffractometer (Malvern Panalytical, Almelo, Overijssel, The Netherlands) equipped with Cu K α radiation ($\lambda = 0.154$ nm). Equatorial scanning over the 10–90° range with a step width of 0.01313° was used to determine the interlayer spacing d_{002} from the (002) peak position via Bragg's law (Equation (1)), and the apparent crystallite size perpendicular to the basal plane (L_c) from the (002) peak

width via the Scherrer equation (Equation (2)). Meridional scans were collected for the (100) diffraction peak to determine the apparent crystallite size parallel to the basal plane (L_a) using the Scherrer equation (Equation (2)). Azimuthal scans from 90° to 270° with a step size of 0.5° at the (002) peak position were employed to evaluate the graphite microcrystalline orientation factor (π) via Equation (3).

$$2d \sin \theta = n\lambda \quad (1)$$

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

$$\pi = \frac{180 - 2Z}{180} \times 100\% \quad (3)$$

while d is the interlayer spacing; θ is the diffraction angle; n is the diffraction order; λ is the X-ray wavelength (0.154 nm); L is the average microcrystal size perpendicular to the crystal plane; K is the shape factors (0.9 for L_c , 1.84 for L_a); π is the orientation degree; $2Z$ is the half-width at half maximum of the azimuthal intensity distribution, which quantifies the degree of preferred alignment of graphite basal planes along the fiber axis. All peak deconvolution and parameter extraction were performed using the instrument's accompanying software package. The equatorial, meridional, and azimuthal XRD patterns are presented in Figures S1–S3. For each sample condition, XRD patterns were acquired from a single representative specimen, consistent with standard practice in carbon fiber structural characterization.

2.3.2. Raman Spectroscopy

Raman spectra were acquired using an inVia RM2000 micro-Raman spectrometer (Renishaw plc, Wotton-under-Edge, Gloucestershire, UK) with a 532 nm excitation laser to probe the carbon chemical structure and to establish the surface-active carbon index (Sac). Three sampling methods were designed to distinguish surface cross-section radial skin-core structure. For surface analysis, single filaments were mounted flat onto glass slides and measured with a $50\times$ objective, using 10% laser power over the $1000\text{--}1900\text{ cm}^{-1}$ spectral range with an acquisition time of 15 s and five accumulations per specimen. For cross-sectional radial profiling, fibers were transversely sectioned to expose the full circular face, and spectra from the skin and core regions were collected separately under a $100\times$ objective.

The Sac indicator, reflecting the relative proportion of edge-active carbon atoms exposed on the fiber surface, was defined as:

$$Sac = \frac{I_D}{I_D + I_G} \quad (4)$$

where I_D and I_G are the integrated areas of the D band ($\sim 1350\text{ cm}^{-1}$, associated with defects and edge carbons) and the G band ($\sim 1580\text{ cm}^{-1}$, corresponding to in-plane sp^2 graphitic carbons), respectively.

For comparison, the conventional graphitization index $R = I_D/I_G$ was also calculated for each specimen. All spectral data were baseline-corrected and normalized prior to peak fitting using a mixed Gaussian–Lorentzian function.

2.3.3. Dynamic Contact Angle and Surface Energy Calculation

Dynamic contact angles were measured using a DCAT21 tensiometer (Dataphysics Instruments GmbH, Filderstadt, Baden-Württemberg, Germany) following the Wilhelmy plate method. Four monofilaments of 8 mm length were mounted in parallel on the sample holder. The immersion speed was set to 0.08 mm/s, the immersion depth to 5 mm, and

the force threshold to 0.08 mg. Three consecutive measurement cycles were performed for each test liquid, and the average advancing angle test is shown in Figure 2.

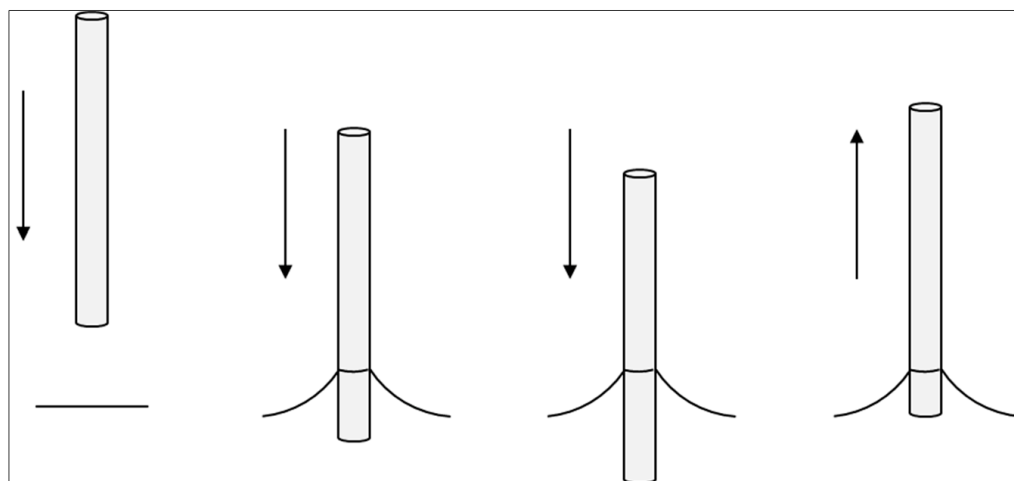


Figure 2. Schematic diagram of dynamic contact angle test [2].

Surface energy of the fibers was calculated using the Owens–Wendt–Rabel–Kaelble (OWRK) method. The OWRK equation, which separates the surface energy into dispersive and polar components, is expressed as:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_L^p \gamma_s^p)^{1/2} + 2(\gamma_L^d \gamma_s^d)^{1/2} \quad (5)$$

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (6)$$

where γ_s is the total surface energy of the fiber ($\gamma_s = \gamma_s^d + \gamma_s^p$); γ_L is total surface energy of the liquid; γ_s^d and γ_s^p is the dispersive and polar components of the fiber surface energy; γ_L^d and γ_L^p is the dispersive and polar components of the liquid surface tension; θ is advancing contact angle. The properties of the two testing liquids used in this study are summarized in Table S2.

2.3.4. Single-Fiber Microdroplet Debond Test

The IFSS between the carbon fiber and the epoxy matrix was assessed through the single-fiber microdroplet debond test, a widely accepted method for characterizing fiber–matrix adhesion. The test followed an established laboratory protocol based on the microdroplet debond method [2], consistent with procedures commonly reported in the carbon fiber literature [3,15]. The epoxy matrix was prepared from E51 epoxy resin, with MTHPA as the curing agent and DMP-30 as the accelerator, at a weight ratio of EP:MTHPA:DMP-30 = 100:85:1.

Single filaments were mounted on custom-designed metal frames, and small epoxy droplets with an embedded length of 40–60 μm were deposited onto the fiber surface, followed by curing at 120 $^\circ\text{C}$ for 3 h. During testing, the resin droplet was clamped by two blades while the fiber was pulled at a constant displacement rate of 0.1 mm/min, as shown in Figure 3. Identical testing parameters, including displacement rate, droplet curing conditions, blade gap settings, and data acquisition criteria, were applied consistently across all fiber groups to ensure the comparability of IFSS measurements.

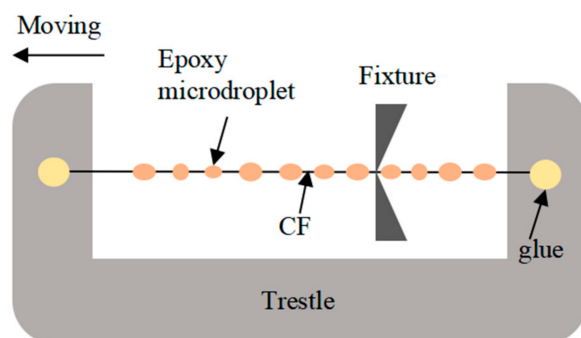


Figure 3. Schematic diagram of microdroplet debond test [2].

The IFSS value was calculated using Equation (7):

$$\text{IFSS} = \frac{F_{\max}}{\pi d L} \quad (7)$$

where $F_{\max}$ is the maximum debonding force; d is the fiber diameter; L is the embedded length of the droplet. For each fiber group, fifteen valid droplets were tested to minimize statistical scattering.

2.3.5. Tensile Mechanical Properties

Tensile modulus of the fiber tows was determined using an Instron 5967 universal testing machine (Instron Corporation, Norwood, MA, USA), in accordance with GB/T 3362-2017 (Test methods for tensile properties of carbon fiber multifilament) [24]. This standard is applicable to the determination of tensile strength, tensile modulus of elasticity, and elongation at break for 1 K–24 K carbon fiber multifilaments after impregnation and curing. In our work, the fiber tow (12 K) was impregnated with epoxy resin and cured, following the guidelines of GB/T 3362-2017, to prevent filament sliding and ensure uniform load transfer during testing.

Specimens of 200 mm in length were prepared by impregnating the tows with epoxy resin, followed by curing. Reinforced end tabs were attached at both ends to prevent premature failure at the grips. The crosshead speed was set at 2 mm/min, and an extensometer was used for accurate strain measurement during modulus determination. For each sample group, ten replicate specimens were tested. The tensile modulus was calculated from the linear slope of the stress–strain curve in the elastic deformation region, and the measured modulus values were normalized by linear density and bulk density before averaging.

3. Results and Discussion

3.1. Modulus Evolution Under Different Tension–Temperature Combinations

Figure 4 shows the tensile modulus of PAN-based carbon fibers as a function of axial tension at different graphitization temperatures (1700 K, 1900 K and 2100 K). At every fixed temperature, fiber modulus increases steadily as the applied axial tension increases from 0 N to 70 N. Regardless of tension level, fibers treated at higher graphitization temperature consistently yield higher modulus values, confirming that both thermal energy and axial tensile load contribute synergistically to improving stiffness [25].

For specimens graphitized at 2100 K, the modulus starts at 343 GPa under zero tension and gradually climbs to nearly 396 GPa at the maximum tension. The rate of modulus growth diminishes when tension exceeds 50 N, suggesting that axial alignment of graphite lamellae approaches saturation under high tension, and further increasing tensile load cannot substantially improve the preferred orientation of crystallites along the fiber axis [26]. The same trend is observed for 1700 K, 1900 K and 2100 K groups.

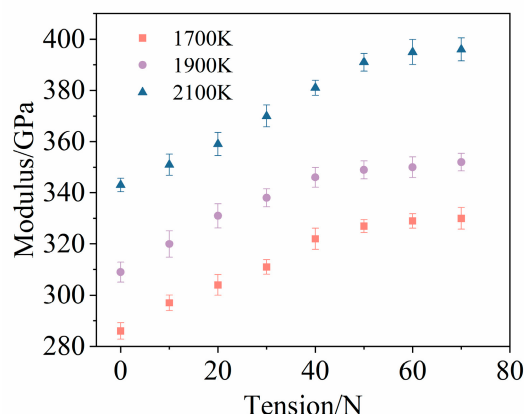


Figure 4. Tensile modulus of carbon fibers at different tension–temperature.

A comparison of the modulus increments reveals that both graphitization temperature and axial tension contribute significantly to modulus enhancement within the experimental range. Raising tension from 0 N to 70 N at 1900 K increases the modulus by approximately 43 GPa, while elevating the temperature from 1900 K to 2100 K under identical tension brings about a modulus increment of 28–45 GPa. This range overlaps considerably with the tension-induced increment, indicating that both parameters play substantial and comparable roles in modulating fiber modulus under the investigated conditions. The distinct microstructural mechanisms underlying these effects are examined in detail in Section 3.2 through XRD and orientation analyses [27]. These mechanisms are temperature-driven crystallite coarsening versus tension-driven orientation enhancement.

To quantitatively characterize the saturation behavior observed in Figure 4, we fitted all modulus-versus-tension curves using an exponential saturation model: $y = y_0 + A \times [1 - \exp(-x/T_c)]$, where y_0 is the zero-tension modulus, A is the saturation amplitude, and T_c is the critical tension constant. The fitting curves are shown in Figure S4, and the fitting parameters are summarized in Table 1. The zero-tension modulus increases monotonically with increasing graphitization temperature: from 285.61 GPa at 1700 K to 341.86 GPa at 2100 K. This temperature-dependent saturation onset indicates that higher thermal activation energy facilitates earlier saturation of tension-induced crystallite alignment, consistent with the enhanced atomic mobility at elevated temperatures. The saturation amplitude A also increases with temperature (from 65.97 GPa at 1700 K to 114.19 GPa at 2100 K), reflecting the greater achievable modulus increment at higher graphitization temperatures. The excellent goodness-of-fit with $R^2 > 0.98$ for all temperatures confirms the validity of the exponential saturation model for describing the tension–modulus relationship.

Table 1. Exponential saturation fitting parameters for modulus, crystallite size, and orientation as functions of tension at different graphitization temperatures.

Parameter	Temperature/K	y_0 /GPa	A	T_c /N	R^2
Modulus/GPa	1700	285.61	65.97	55.40	0.9872
	1900	308.31	70.04	71.95	0.9941
	2100	341.86	114.19	98.31	0.9859
La/nm	1700	5.13	0.22	14.36	0.9743
	1900	6.33	0.43	14.79	0.9866
	2100	8.11	0.53	32.97	0.9784
Lc/nm	1700	1.91	0.050	16.85	0.9179
	1900	2.17	0.059	18.66	0.9757
	2100	2.55	0.091	23.10	0.9758

Table 1. Cont.

Parameter	Temperature/K	y_0 /GPa	A	Tc/N	R ²
Orientation/%	1700	0.837	0.029	18.85	0.9606
	1900	0.826	0.037	38.68	0.9628
	2100	0.856	0.019	46.98	0.9971

Note: y_0 is the initial value at zero tension; A is the saturation amplitude; Tc is the critical tension constant; R² is the coefficient of determination.

3.2. Microstructural Variations of Carbon Fibers

3.2.1. Graphite Crystallite Size

The in-plane crystallite dimension (La) and stacking height (Lc) calculated from XRD patterns (Figures S1 and S2) are plotted against applied tension under different graphitization temperatures in Figure 5. These two parameters quantitatively reflect the degree of graphitization and crystallite growth in carbon fiber bulk structure. Graphitization temperature plays a dominant role in controlling the final size of graphite crystallites. At the same tension value, both La and Lc increase significantly with rising temperature. When tension is fixed at 40 N, the La value is only 5.51 nm at 1700 K, whereas it reaches 8.48 nm at 2100 K. The same temperature-driven growth trend is observed for Lc. Higher temperature provides sufficient thermal activation energy, accelerating the rearrangement of amorphous carbon and promoting the coalescence of small crystallites into larger graphite domains [28,29]. This is consistent with the well-established graphitization law for PAN-based carbon fibers under high-temperature heat treatment. The interlayer spacing d_{002} , calculated from the (002) peak position in equatorial scans, decreases with increasing graphitization temperature: from 0.345 nm at 1700 K to 0.339 nm at 2100 K (averaged across all tension levels). This reduction approaches the ideal graphite value of 0.335 nm [4], confirming the progressive graphitization of the carbon structure at elevated temperatures. The temperature dependence of d_{002} is consistent with the observed growth of Lc and La, further validating the dominant role of temperature in driving graphitization.

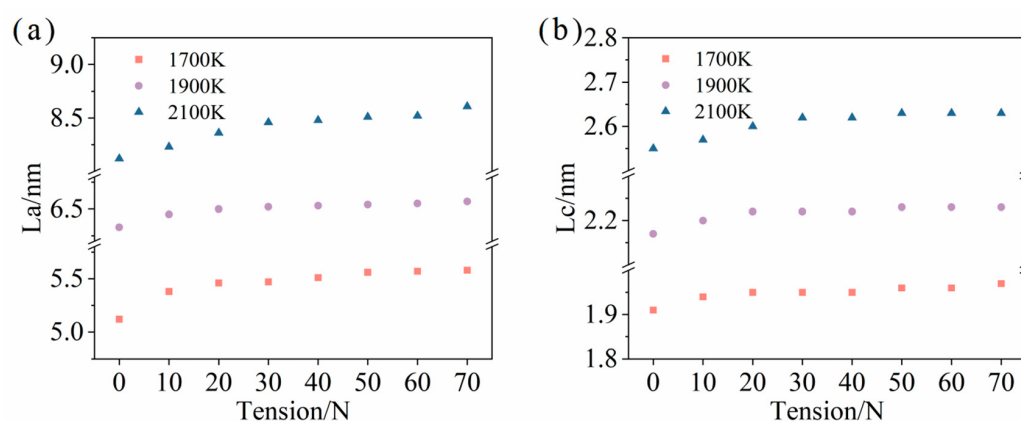


Figure 5. (a) La and (b) Lc of carbon fibers under different tension–temperature.

In sharp contrast, axial tension only induces mild changes in crystallite size within the whole loading range of 0–70 N. For the group treated at 1900 K, La only rises moderately from 6.33 nm to 6.57 nm as tension increases from 0 N to 70 N, and the corresponding variation in Lc is less than 0.06 nm. Even for the 2100 K high-temperature group, the overall fluctuation of La does not exceed 0.49 nm under continuous tension elevation. Axial tensile load mainly restricts thermal shrinkage and aligns graphite layers along the fiber axis; it cannot offer enough energy to drive grain boundary migration and crystallite

coarsening [21]. As a result, tension hardly enlarges graphite crystallites, even though it greatly improves axial orientation and tensile modulus.

A small initial rise in L_a and L_c occurs when tension increases from 0 N to 30 N. This slight growth is attributed to the elimination of structural voids and defects under axial compression, which facilitates local ordering of carbon atoms. After tension exceeds 30 N, the crystallite size tends to plateau and remains nearly stable, with only minor random fluctuations. No obvious continuous crystallite coarsening can be detected under high tension.

The same exponential saturation analysis was applied to the crystallite size data in Figure 5a,b (Table 1), and the fitting curves are shown in Figures S5 and S6. For L_a , the critical tension T_c ranges from 14.36 N at 1700 K to 32.97 N at 2100 K, exhibiting a similar but less pronounced temperature dependence than that observed for modulus. The saturation amplitudes A for L_a are substantially smaller (0.22–0.53 nm) than those for modulus, confirming that tension primarily enhances modulus through orientation improvement rather than crystallite growth. For L_c , the T_c values range from 16.85 N to 23.10 N, with saturation amplitudes below 0.091 nm. The relatively low R^2 values (0.9179–0.9866) for crystallite size fittings reflect the inherent scatter in XRD-derived parameters and the mild response of crystallite dimensions to tension, consistent with our conclusion that tension has only a negligible effect on crystallite coarsening.

3.2.2. Microcrystalline Orientation

The axial orientation factor calculated from azimuthal X-ray diffraction profiles (Figure S3) describes the degree to which graphite basal planes align parallel to the fiber axial direction, and this structural parameter dominates the tensile modulus of PAN-derived carbon fibers [25]. The full width at half maximum values derived from Figure S3 were used to calculate the orientation factor (π) via Equation (3), with higher π values corresponding to better axial alignment of graphite crystallites. Figure 6 summarizes the variation in orientation factor with increasing axial tension under different graphitization temperatures.

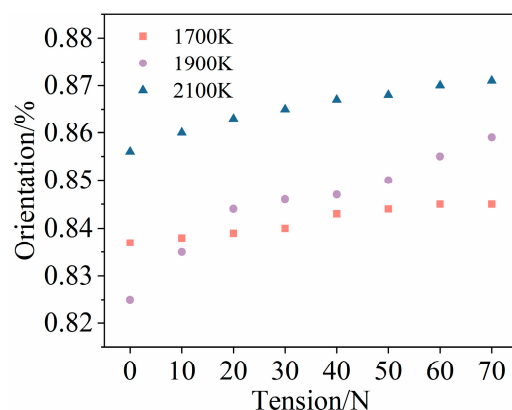


Figure 6. Axial orientation of carbon fibers under different tension–temperature.

Within every fixed thermal treatment condition, the orientation factor rises steadily as tension increases from 0 N to 70 N, and no obvious plateau appears across the whole loading range. At 1900 K, the orientation factor starts from approximately 0.825 under zero tension and gradually climbs to 0.859 at the maximum tension load. Axial tension suppresses the natural thermal contraction of fiber tows during high-temperature heat treatment, and the persistent stretching force drives disordered graphite sheets to rotate toward the fiber axis, continuously improving preferred axial alignment [30]. Compared with crystallite size (L_a , L_c), the microcrystalline orientation is extremely sensitive to tensile load.

Graphitization temperature also exerts a positive influence on graphite alignment. Under identical tension, fibers treated at higher temperature always possess a higher orientation value. At 50 N tension, the orientation factor is 0.844 for samples processed at 1700 K and increases to 0.868 for the 2100 K group. Elevated temperature enhances the mobility of carbon atomic clusters, facilitating the reorientation of graphite lamellae under external tensile stress. The effect of tension on orientation, however, exhibits a clear temperature dependence. Raising tension from 0 N to 70 N increases the orientation factor by approximately 0.034 at 1900 K, whereas the same tension increment yields only 0.008 at 1700 K and 0.015 at 2100 K. This temperature-dependent efficiency suggests that the interplay between thermal mobility and mechanical constraint is most favorable at intermediate temperatures: at 1700 K, limited thermal mobility restricts lamellar rotation even under tension; at 2100 K, extensive crystallite growth and alignment have already occurred during the high-temperature treatment, leaving less room for further tension-induced improvement [27,30]. The effect of tension on orientation becomes comparable to that of temperature variation only up to a tension of approximately 40 N; beyond this threshold, the tension effect continues to increase at 1900 K, while the temperature effect saturates earlier. This indicates an interactive, rather than simply additive, relationship between temperature and tension in controlling orientation.

The orientation factor data in Figure 6 were also fitted using the exponential saturation model (Table 1), and the fitting curves are shown in Figure S7. The critical tension T_c increases from 18.85 N at 1700 K to 46.98 N at 2100 K, closely following the temperature dependence observed for modulus. This parallel behavior confirms that the saturation of modulus enhancement is governed by the saturation of microcrystalline orientation. The saturation amplitudes A for orientation range from 0.019 to 0.037, corresponding to relative improvements over the zero-tension baseline. The high R^2 values (>0.9606) demonstrate that the exponential model effectively captures the orientation–tension relationship across all temperatures.

Figure 7 presents a schematic illustration of internal graphite stacking evolution in PAN-based carbon fibers subjected to axial tension during high-temperature graphitization. Without applied tension, graphitic domains are randomly distributed throughout the filament, with lamellae adopting diverse angular orientations relative to the fiber axis. When sustained axial tension F is imposed, thermally activated fiber shrinkage generates uniform radial compressive stress f across the cross-section. This radial stress acts as the key driving force for graphite lamella rearrangement. Under the combined thermal and mechanical fields, graphitic fragments rotate toward the radial direction of the fiber cross-section.

Such structural transformation yields two competing effects that jointly govern Sac content. On one hand, tensile constraint promotes moderate crystallite growth, which reduces the number of edge carbon sites within graphite domains. On the other hand, radial reorientation pushes more lamellar boundaries toward the fiber outer surface, exposing additional unsaturated edge carbon atoms [25]. These counteracting structural changes explain the experimental observation that Sac remains nearly constant across a broad tension range at fixed graphitization temperature. Although axial tension effectively improves the preferred orientation of graphitic crystallites and enhances tensile modulus, it does not continuously elevate or deplete Sac concentration.

Figures S8–S10 show the Raman spectra of skin and core for HMCfS treated at different temperature under various tension. The R value (I_D/I_G) serves as a direct indicator of local graphitization level. Figure 8 presents the evolution of R value under different tensions and different temperatures.

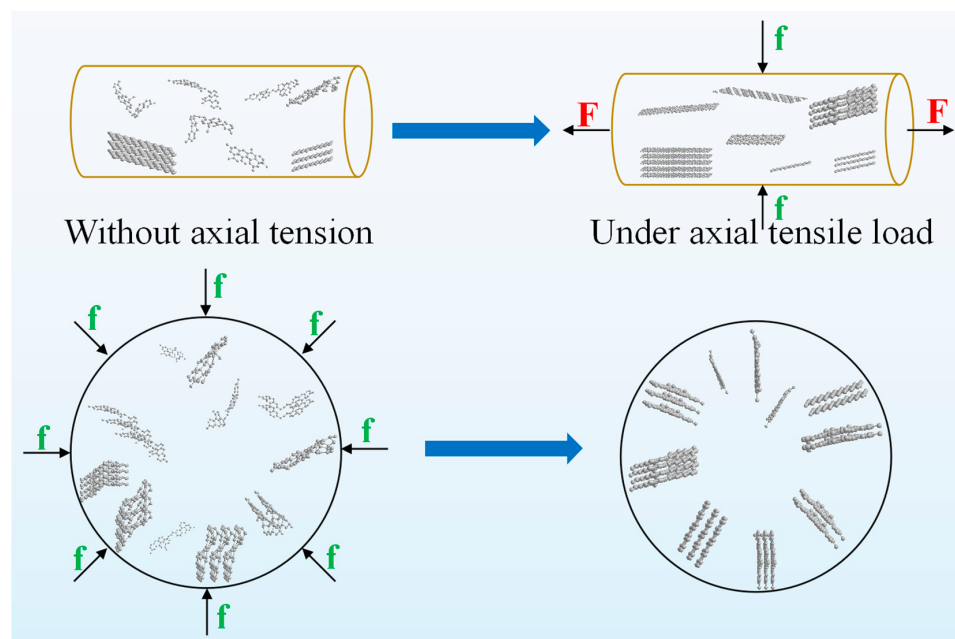


Figure 7. Schematic diagram of microcrystalline orientation carbon fibers under axial tension.

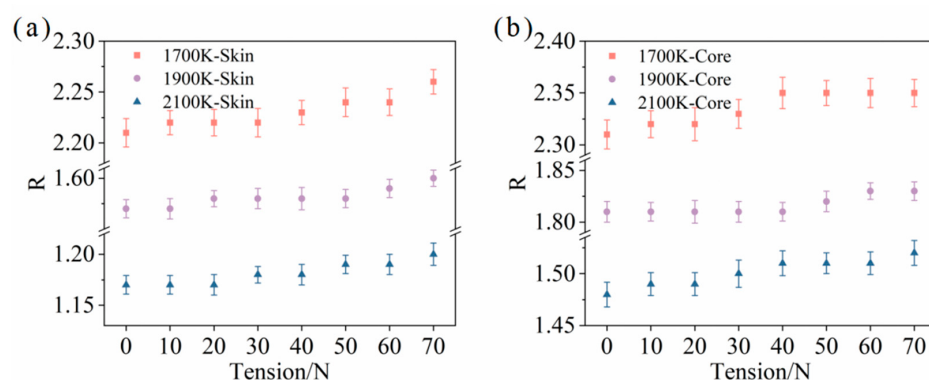


Figure 8. Evolution of R value for HMCs under different tension–temperature: (a) R values of the fiber skin region; (b) R values of the fiber core region.

At each fixed heat treatment temperature, the R-skin value only fluctuates mildly when axial tension increases continuously from 0 N to 70 N, without showing any obvious rising or falling trend. At 1700 K, the R-skin value remains stable between 2.21 and 2.26 throughout the whole tension gradient, and no systematic decline caused by crystallite growth can be observed. As discussed in the previous XRD analysis, tension only induces slight coarsening of graphite crystallites. This minor grain growth would theoretically reduce the number of boundary carbon atoms and lower the R value. However, axial tension produces radial compressive stress during fiber shrinkage, which forces graphite basal planes to rotate toward the fiber radial direction and expose more edge sites on the outer surface. These two competing structural changes counteract each other, so the surface defect density stays nearly constant regardless of tensile load.

Graphitization temperature still dominates the final R-skin value. Under identical tension, fibers treated at lower temperature always deliver a much higher R value. When tension is fixed at 40 N, the R-skin reaches 2.23 at 1700 K, whereas it falls to only 1.18 for the 2100 K group. High-temperature graphitization drastically accelerates the growth of graphite crystallites and eliminates boundary defects, which makes the fiber surface chemically inert and weakens interfacial bonding with epoxy resin [31]. Unlike tension, elevated temperature cannot bring about radial lamella rearrangement to compensate for

the loss of edge carbon sites. This explains why the surface polarity inevitably declines if we only rely on high-temperature treatment to improve fiber modulus.

It is worth noting that the skin-core structural difference does not expand or shrink significantly under varying tension. Axial tensile stress acts uniformly along the fiber axial direction and only causes overall radial compression. It cannot alter the radial temperature gradient inside the fiber furnace zone or change the difference in graphitization degree between the fiber skin and core regions [32]. As a result, tension will not aggravate the radial structural heterogeneity, which is another advantage of the tension–temperature synergistic processing route.

3.3. Temperature-Dominated Surface Polarity and Interfacial Properties

Figure 9 presents the surface polarity and interfacial properties of HMCFs as a function of graphitization temperature, with each data point averaged across all tension levels (0–70 N). This representation is justified by the tension independence of these parameters, as confirmed by linear fits of the individual tension-dependent curves, yielding slopes approximately equal to zero (Figure S11). This tension-independence results from the offsetting effects of two concurrent structural changes: mild crystallite coarsening and radial lamella exposure. Their competition keeps the surface-active carbon content stable under varying tensile load [25,33].

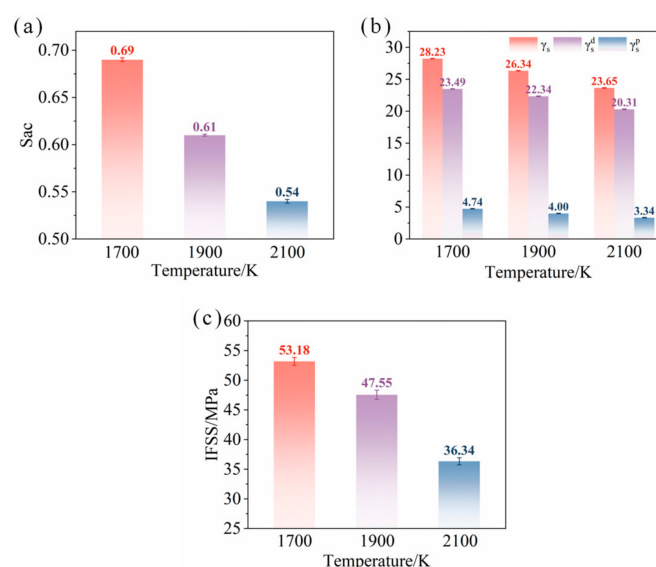


Figure 9. Surface polarity and interfacial properties as a function of graphitization temperature: (a) Sac; (b) surface energy component (γ_s , γ_s^d , γ_s^p); (c) IFSS.

Figure 9a shows the evolution of the Sac parameter with graphitization temperature. The Sac value decreases markedly from 0.692 ± 0.002 at 1700 K to 0.542 ± 0.002 at 2100 K with a reduction of approximately 22%. This temperature-driven decline reflects the accelerated coalescence of graphite crystallites at elevated temperatures, which eliminates edge-active carbon sites on the fiber surface [34]. The strong negative temperature dependence (linear regression slope: $-1.50 \times 10^{-4} \text{ K}^{-1}$, $R^2 = 0.999$) confirms that temperature is the decisive factor governing the intrinsic surface polarity of HMCFs.

Figure 9b presents the surface energy components as functions of temperature. The total surface energy (γ_s) decreases from $28.23 \pm 0.05 \text{ mN}\cdot\text{m}^{-1}$ at 1700 K to $23.65 \pm 0.05 \text{ mN}\cdot\text{m}^{-1}$ at 2100 K. This decrease is primarily attributed to the dispersive component (γ_s^d), which drops from $23.49 \pm 0.04 \text{ mN}\cdot\text{m}^{-1}$ to $20.31 \pm 0.06 \text{ mN}\cdot\text{m}^{-1}$ over the same temperature range, while the polar component (γ_s^p) exhibits a more modest decline

from $4.74 \pm 0.05 \text{ mN}\cdot\text{m}^{-1}$ to $3.34 \pm 0.05 \text{ mN}\cdot\text{m}^{-1}$. Well-stacked sp^2 carbon lattices give rise to stable non-polar dispersion forces that show sensitivity to processing temperature. Their abundance is directly reflected by the Sac parameter. Unsaturated sp^2 edge carbon sites and residual heteroatom groups on the fiber surface serve as polar interaction sites for epoxy matrices [35].

Figure 9c illustrates the IFSS values averaged across all tension levels at each temperature. IFSS decreases from $53.18 \pm 0.66 \text{ MPa}$ at 1700 K to $36.34 \pm 0.60 \text{ MPa}$ at 2100 K, following a linear trend with temperature (slope: $-0.028 \text{ MPa}\cdot\text{K}^{-1}$, $R^2 = 0.999$). The strong positive correlation between IFSS and Sac confirms that the surface-active carbon content is the primary determinant of fiber–matrix adhesion [31].

Collectively, these results demonstrate that graphitization temperature plays the dominant role in regulating both the surface polarity and interfacial bonding strength of HMCs, while tension effectively enhances bulk modulus without sacrificing surface polarity.

3.4. Response Surface Analysis of Coupled Processing, Surface and Interfacial Performance Parameters

Figure 10 presents four three-dimensional response surfaces constructed to decouple the independent and synergistic effects of temperature and tension on modulus, IFSS, and surface energy. The fitted quadratic regression models all yield adjusted determination coefficients above 0.93, confirming reliable predictive capability.

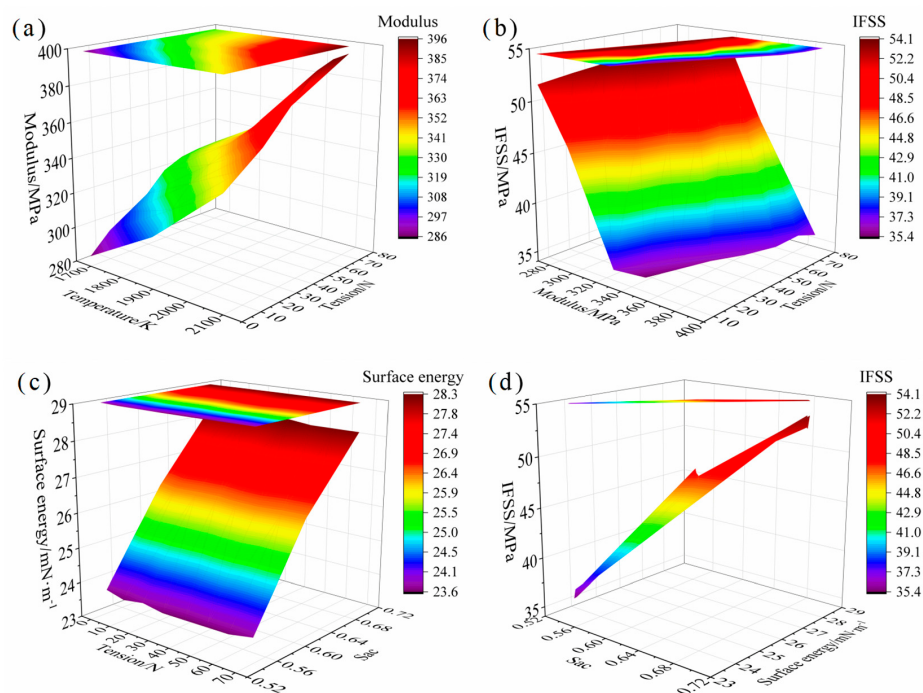


Figure 10. Three-dimensional response surfaces: (a) tensile modulus as functions of temperature and tension; (b) IFSS as functions of modulus and tension; (c) surface energy as functions of tension and Sac; (d) IFSS as functions of Sac and surface energy.

Figure 10a shows the 3D surface for tensile modulus, which exhibits a consistent upward incline along both temperature and tension axes. The surface gradient along the tension coordinate is steeper, confirming that axial hot-stretching contributes more substantially to modulus elevation. Most notably, multiple coordinate points on the same modulus isoline indicate that different temperature–tension combinations can yield identical modulus values, enabling modulus preservation while tuning surface polarity.

Figure 10b shows the IFSS response surface plotted against modulus and tension. IFSS changes drastically along the modulus axis but remains constant across the tension range at any fixed modulus, confirming that tension does not affect interfacial performance. Fibers with identical modulus produced via low-temperature high-tension processing exhibit significantly higher IFSS than their high-temperature low-tension counterparts.

Figure 10c presents the surface energy response as a function of tension and Sac. Total surface energy increases monotonically with Sac but shows no systematic shift with tension at a fixed Sac, confirming that tension does not alter the intrinsic Sac-surface-energy relationship.

Figure 10d shows the IFSS response as a function of Sac and surface energy. IFSS rises continuously with both parameters in a near-linear manner, indicating additive effects without mutual interference. Combined with the dual-factor processing surfaces, these correlations establish a complete logic chain: temperature dominates Sac and surface energy, tension independently controls axial orientation and modulus, and IFSS is determined by surface polarity rather than bulk mechanical properties.

3.5. Tension–Temperature Coupling Strategy for High-Modulus High-Polarity Carbon Fibers

Table 2 compares two processing routes that yield equivalent modulus (~350 GPa): high-temperature low-tension (2100 K, 10 N) and low-temperature high-tension (1900 K, 60 N). The high-temperature route produces larger crystallites ($L_a = 8.23$ nm, $L_c = 2.57$ nm) with lower surface polarity (Sac = 0.539), while the low-temperature high-tension route retains finer crystallites ($L_a = 6.55$ nm, $L_c = 2.23$ nm) with significantly higher Sac (0.612) and IFSS (48.8 MPa vs. 35.4 MPa). The nearly identical moduli (351 GPa vs. 350 GPa) confirm that tension fully offsets the modulus loss from reduced temperature through enhanced axial orientation.

Table 2. Sample parameters with modulus approximately 350 GPa.

Temperature /K	Tension /N	Modulus /GPa	L_a /nm	L_c /nm	Orientation	Sac	Surface Energy /mN·m ^{−1}	IFSS /MPa
2100	10	351	8.23	2.57	0.860	0.539	23.6	35.4
1900	60	350	6.55	2.23	0.855	0.612	26.3	48.8

Figure 11 schematically contrasts the two microstructural states. High-temperature low-tension processing (Figure 11a) yields large, thick-stacked crystallites with random orientation and scarce edge sites. Low-temperature high-tension processing (Figure 11b) produces smaller crystallites with abundant edge carbon defects and superior axial alignment. The synergy of fine crystallites that retain surface-active sites and high tension that promotes axial orientation enables equivalent modulus with enhanced interfacial performance, thereby overcoming the conventional modulus–polarity trade-off.

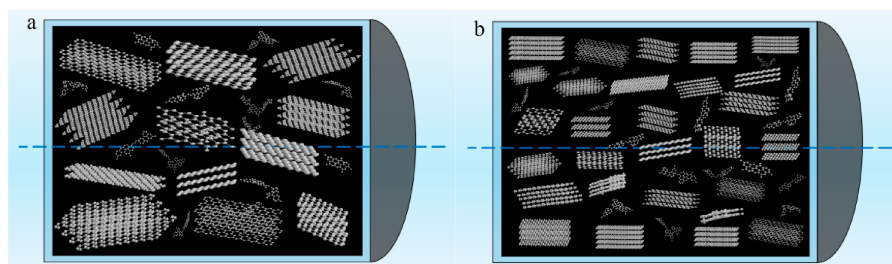


Figure 11. Schematic diagram of carbon fiber structure prepared with different temperature–tension combinations: (a) high-temperature low-tension combination; (b) low-temperature high-tension combination.

4. Conclusions

This paper systematically decouples the regulatory effects of graphitization temperature and axial tension on the microstructure, surface polarity, and interfacial bonding of PAN-based HMCs. Combined XRD, Raman, contact angle and microdroplet debond characterizations of samples prepared at 1700–2100 K under 0–70 N tension confirm that temperature governs graphite crystallite growth and surface-active carbon content, while tension primarily enhances axial lamellar orientation with negligible influence on crystallite dimensions. A competitive balance between mild crystallite coarsening and radial graphite lamella exposure induced by tensile shrinkage keeps the Sac value, surface energy, and IFSS nearly unchanged across the entire tension range. The Sac parameter exhibits strong linear correlations with total surface energy ($R^2 > 0.95$) and IFSS ($R^2 > 0.93$), validating its reliability as a quantitative polarity indicator.

Based on the experimental results, the recommended processing condition for achieving balanced modulus and enhanced interfacial performance is 1900 K graphitization temperature combined with 60 N axial tension. This combination yields a tensile modulus of ~350 GPa, a Sac of 0.612, and an IFSS of 48.8 MPa. For applications requiring different modulus targets, the response surface analysis indicates that a processing window of 1850–1950 K with 50–70 N tension can achieve comparable modulus while maintaining elevated surface polarity. Comparative analysis of two representative routes confirms that this low-temperature high-tension synergistic route fully compensates for modulus loss from moderate temperature reduction through enhanced axial orientation, achieving a 13.5% higher Sac and a 37.9% improvement in IFSS relative to the conventional high-temperature low-tension scheme. This one-step in situ processing strategy eliminates the need for ultrahigh-temperature graphitization and additional post-surface modification, offering a scalable industrial pathway for producing HMCs with superior intrinsic fiber–matrix interfacial performance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma19163514/s1>, Table S1: The physical properties of HMCs with different temperatures and tensions; Table S2: Thermodynamic parameters of test liquids at 25 °C; Figure S1: The equatorial XRD patterns of HMCs treated at various tension with different temperature (1700 K, 1900 K, 2100 K), The equatorial scan for d002 and Lc from the (002) peak; Figure S2: The meridional XRD patterns of HMCs treated at various tension with different temperature (1700 K, 1900 K, 2100 K), the meridional scan for La from the (100) peak; Figure S3: The azimuthal XRD patterns of HMCs treated at various tension with different temperature (1700 K, 1900 K, 2100 K), The azimuthal scan for orientation factor π from the (002) azimuthal intensity distribution; Figure S4: Exponential saturation fitting of tensile modulus as functions of applied tension at three graphitization temperatures (1700 K, 1900 K, and 2100 K); Figure S5: Exponential saturation fitting of La as functions of applied tension at three graphitization temperatures (1700 K, 1900 K, and 2100 K); Figure S6: Exponential saturation fitting of Lc as functions of applied tension at three graphitization temperatures (1700 K, 1900 K, and 2100 K); Figure S7: Exponential saturation fitting of axial orientation as functions of applied tension at three graphitization temperatures (1700 K, 1900 K, and 2100 K); Figure S8: The Raman spectra of skin and core for HMCs treated at 1700 K under various tension; Figure S9: The Raman spectra of skin and core for HMCs treated at 1900 K under various tension; Figure S10: The Raman spectra of skin and core for HMCs treated at 2100 K under various tension; Figure S11: Variations of (a) Sac, (b) total surface energy- γ_s , (c) polar component- γ_s^p , (d) dispersive component- γ_s^d , and (e) IFSS as a function of tension for carbon fibers graphitized at 1700 K, 1900 K and 2100 K.

Author Contributions: Conceptualization, A.G. and H.Z.; Methodology, T.F. and A.G.; Software, T.F.; Formal Analysis, W.T. and H.Z.; Investigation, T.F. and P.X.; Resources, A.G. and P.X.; Data Curation, W.T. and H.Z.; Writing—Original Draft Preparation, A.G. and H.Z.; Writing—Review and

Editing, A.G. and H.Z.; Visualization, H.Z.; Supervision, A.G.; Project Administration, A.G. and P.X.; Funding Acquisition, A.G. and H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Frontier Technologies R&D Program of Jiangsu (BF2025051), the Key Technology Research and Development of Henan Province (252102231081), and the Key Research Project of Higher Education of Henan Province (23A430004).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Author Panpan Xu was employed by the company Jiangsu Hengshen Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Qiu, B.W.; Zou, Q.; Sun, T.; Ling, Y.Q.; Zhou, S.T.; Chen, Y.; Xia, S.; Heng, Z.G.; Zou, H.W.; Liang, M. Environmentally friendly water-soluble epoxy emulsions nano sphere improved the interfacial performance of high modulus carbon fiber reinforced epoxy composites based on robust van der Waals force. *Compos. Part B Eng.* **2022**, *243*, 110141. [\[CrossRef\]](#)
2. Gao, A.J.; Wang, T.H.; Liu, P.H.; Tian, W.Z.; Zhan, C.Y.; Zhang, H.L. Time-temperature synergy driven kinetic compensation: Source-active regulation to break modulus-polarity trade-off for high-modulus carbon fibers. *Polym. Compos.* **2026**, *47*, 14179–14190. [\[CrossRef\]](#)
3. Zhang, Y.Y.; Yang, P.W.; Sun, Y.H.; Li, G.; Yang, X.P. Optimization of interfacial properties of different high modulus carbon fiber composites by tailored interphase stiffness with MWNT-EP/epoxy sizing. *Surf. Interfaces* **2023**, *39*, 102977. [\[CrossRef\]](#)
4. Jeon, C.; Hwang, S.; Han, M.J.; Lee, S.; Gwak, H.J.; Won, J.S.; Bin Bae, S.; Chae, H.G. Unveiling the graphitization behaviors of highly stiff and thermally conductive graphitic carbon fibers. *Carbon* **2025**, *245*, 120791. [\[CrossRef\]](#)
5. Gao, D.X.; Wang, M.F.; Hou, W.L.; Gao, A.J.; Cao, W.Y. Superior interfacial properties of high modulus carbon fiber reinforced epoxy composites achieved based on efficient electrochemical deposition of polydopamine layer. *Compos. Part B Eng.* **2026**, *316*, 113566. [\[CrossRef\]](#)
6. Huang, C.Y.; Zhang, P.; Liu, Z.W.; Sun, M.C.; Liu, H.S.; Sun, J.S.; Li, B.; Zhao, Y.; Bao, J.W. Effect of electrochemical anodic oxidation modification on the interfacial properties of carbon fiber reinforced polyimide composites. *Polym. Compos.* **2025**, *46*, 2390–2403. [\[CrossRef\]](#)
7. Li, Z.R.; Wang, J.B.; Tong, Y.J.; Xu, L.H. Anodic Oxidation on structural evolution and tensile properties of polyacrylonitrile based carbon fibers with different surface morphology. *J. Mater. Sci. Technol.* **2012**, *28*, 1123–1129. [\[CrossRef\]](#)
8. Zang, Z.L.; Tang, G.; Wei, G.F.; Wang, D.M.; Chang, D.F.; Huang, J.H.; Yan, W. The mechanical and tribological properties of anodic oxidation treatment carbon fiber-filled PU composite. *Polym.-Plast. Technol.* **2012**, *51*, 1501–1504. [\[CrossRef\]](#)
9. Li, Y.R.; Liu, Q.C.; Shao, W.; Tan, Z.; Wu, Y.; He, D.Y. Effects of low-pressure plasma surface modification on the surface properties of carbon fibers. *J. Mater. Res. Technol.* **2026**, *42*, 6368–6378. [\[CrossRef\]](#)
10. Wang, J.; Yu, Z.Y.; Yang, S.; Wang, Z.H.; Ren, R.; Xiong, X.H. Effects of argon plasma treatment on carbon fiber surface characteristic and its reinforcing polyimide composites interfacial properties at room and elevated temperatures. *Diam. Relat. Mater.* **2025**, *151*, 111765. [\[CrossRef\]](#)
11. Liu, X.D.; Wang, Z.H.; Zhen, G.Q.; Chen, B.H.; Xiong, X.H.; Chen, P. Influence of argon plasma treatment on interfacial performance of CFRP at high temperature. *Compos. Interfaces* **2025**, *32*, 95–106. [\[CrossRef\]](#)
12. Zia, A.W.; Wang, Y.Q.; Lee, S. Effect of physical and chemical plasma etching on surface wettability of carbon fiber-reinforced polymer composites for bone plate applications. *Adv. Polym. Technol.* **2015**, *34*, 21480. [\[CrossRef\]](#)
13. Liu, H.L.; Liu, J.X.; Wu, G.S. Facile preparation of hyperbranched polysiloxane-grafted carbon fibers with improved interfacial strength of silicone resin composites. *Polym. Compos.* **2019**, *40*, 4257–4265. [\[CrossRef\]](#)
14. Hu, M.Q.; Leng, C.Y.; Zhang, B.; Ma, X.L.; Xu, M.J.; Guo, N.N.; Ai, L.L.; Ma, Q.T.; Yuan, D.T.; Zhang, S.S.; et al. Electrochemical graft of polymer molecules on carbon fibers surfaces to construct high-performance carbon fiber/epoxy composites with micrometer-scale interphases. *Compos. Part B Eng.* **2025**, *304*, 112630. [\[CrossRef\]](#)
15. Xiao, J.Y.; Li, H.G.; Lu, M.N.; Wang, Y.Q.; Jiang, J.; Yang, W.G.; Qu, S.X.; Lu, W.B. Enhancing the interfacial shear strength and tensile strength of carbon fibers through chemical grafting of chitosan and carbon nanotubes. *Polymers* **2023**, *15*, 2147. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Liu, J.X.; Liu, H.L.; Wu, G.S. Chemical grafting of salicylaldehyde onto carbon fiber for enhancing interfacial strength of silicone resin composites. *Polym. Compos.* **2020**, *41*, 911–919. [\[CrossRef\]](#)

17. Xu, P.; Yu, Y.H.; Guo, Z.J.; Zhang, X.R.; Li, G.; Yang, X.P. Evaluation of composite interfacial properties based on carbon fiber surface chemistry and topography: Nanometer-scale wetting analysis using molecular dynamics simulation. *Compos. Sci. Technol.* **2019**, *171*, 252–260. [[CrossRef](#)]
18. Qiu, B.W.; Qiu, B.L.; Sun, T.; Zou, Q.; Yuan, M.S.; Zhou, S.T.; Chen, Y.; Xia, S.; Heng, Z.G.; Zou, H.W.; et al. Constructing a multiscale rigid-flexible interfacial structure at the interphase by hydrogen bonding to improve the interfacial performance of high modulus carbon fiber reinforced polymer composites. *Compos. Sci. Technol.* **2022**, *229*, 109672. [[CrossRef](#)]
19. Behr, M.; Rix, J.; Landes, B.; Barton, B.; Billovits, G.; Hukkanen, E.; Patton, J.; Wang, W.J.; Keane, D.; Weigand, S. High-temperature tensile cell for real-time investigation of carbon fibre carbonization and graphitization processes. *J. Synchrotron Radiat.* **2016**, *23*, 1379–1389. [[CrossRef](#)] [[PubMed](#)]
20. Yu, S.; Cho, H.J.; Ko, T.H.; Kim, H.Y.; Chung, Y.S.; Kim, B.S. Draw-induced structural optimization of PAN-based carbon fibers during high-temperature carbonization. *Nanomaterials* **2025**, *15*, 1335. [[CrossRef](#)] [[PubMed](#)]
21. Ye, C.; Wu, H.; Huang, D.; Li, B.L.; Shen, K.; Yang, J.X.; Liu, J.S.; Li, X.K. The microstructures and mechanical properties of ultra-high-strength PAN-based carbon fibers during graphitization under a constant stretching. *Carbon Lett.* **2019**, *29*, 497–504. [[CrossRef](#)]
22. Wang, Y.; Yan, T.; Wu, S.; Tong, Y.J.; Gao, A.J.; Xu, L.H. Stretching deformation mechanism of polyacrylonitrile-based carbon fiber structure at high temperatures. *Fiber. Polym.* **2018**, *19*, 751–759. [[CrossRef](#)]
23. Jiang, Z.Y.; Chen, Q.F.; Fan, B.L.; He, J.; Malik, H.; Zhang, H.; Liu, Y.; Yu, J.Y. Microstructure and properties of PAN-based carbon fiber with different graphitization temperature (up to 3000 °C). *Diam. Relat. Mater.* **2025**, *152*, 111953. [[CrossRef](#)]
24. GB/T 3362-2017; Test Methods for Tensile Properties of Carbon Fiber Multifilament. Standards Press of China: Beijing, China, 2017.
25. Li, D.; Wang, H.; Wang, X. Effect of microstructure on the modulus of PAN-based carbon fibers during high temperature treatment and hot stretching graphitization. *J. Mater. Sci.* **2007**, *42*, 4642–4649. [[CrossRef](#)]
26. Chawla, S.; Cai, J.Z.; Naraghi, M. Mechanical tests on individual carbon nanofibers reveals the strong effect of graphitic alignment achieved via precursor hot-drawing. *Carbon* **2017**, *117*, 208–219. [[CrossRef](#)]
27. Newcomb, B.A. Processing, structure, and properties of carbon fibers. *Compos. Part A Appl. S.* **2016**, *91*, 262–282. [[CrossRef](#)]
28. Qian, X.; Zhi, J.H.; Chen, L.Q.; Zhong, J.J.; Wang, X.F.; Zhang, Y.G.; Song, S.L. Evolution of microstructure and electrical property in the conversion of high strength carbon fiber to high modulus and ultrahigh modulus carbon fiber. *Compos. Part A Appl. S.* **2018**, *112*, 111–118. [[CrossRef](#)]
29. Yang, F.H.; Liu, W.; Yi, M.Z.; Ran, L.P.; Ge, Y.C.; Peng, K. Effect of high temperature treatment on the microstructure and elastoplastic properties of polyacrylonitrile-based carbon fibers. *Carbon* **2020**, *158*, 783–794. [[CrossRef](#)]
30. Love-Baker, C.; Harrell, T.M.; Vautard, F.; Klett, J.; Li, X.D. Analysis of the turbostratic structures in PAN-based carbon fibers with wide-angle x-ray diffraction. *Carbon* **2024**, *224*, 119037. [[CrossRef](#)]
31. Sharma, M.; Gao, S.L.; Mäder, E.; Sharma, H.; Wei, L.Y.; Bijwe, J. Carbon fiber surfaces and composite interphases. *Compos. Sci. Technol.* **2014**, *102*, 35–50. [[CrossRef](#)]
32. Sha, Y.; Liu, W.; Li, Y.; Cao, W.Y. Formation mechanism of skin-core chemical structure within stabilized polyacrylonitrile monofilaments. *Nanoscale Res. Lett.* **2019**, *14*, 93. [[CrossRef](#)] [[PubMed](#)]
33. Li, S.; Cui, D.; Wang, Y.; Gao, A.J.; Tong, Y.J. Effect of multiple stretching on microstructure and mechanical properties of PAN-based carbon fibers. *Carbon Lett.* **2025**, *35*, 907–916. [[CrossRef](#)]
34. Xiao, J.; Tian, S.Y.; Zhou, H.; Gao, A.J.; Xu, L.H. Construction of polar functional groups on the surface of a high-modulus carbon fiber and its effect on the interfacial properties of composites. *ACS Omega* **2023**, *8*, 29262–29269. [[CrossRef](#)] [[PubMed](#)]
35. Wu, Q.; Jin, D.; Ma, Q.S.; Xiao, B.L.; Li, Y.T.; Zhang, Y.D.; Zhu, J.F. Two geometries of polydopamine synergistically enhance carbon fiber-epoxy interfacial adhesion. *Compos. Part B Eng.* **2025**, *305*, 112768. [[CrossRef](#)]

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