

Cellulose nanofiber orientation-induced crystallinity evolution: Enabling ultrahigh strength and toughness in polymer composites

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ABSTRACT: Fiber-reinforced polymer composites (FRPs) are indispensable in modern structural engineering owing to their exceptional specific strength and ultralow density. However, their advancement remains constrained by an intrinsic trade-off between strength and toughness. Herein, an orientation-induced crystallization strategy is proposed to construct lightweight FRPs that simultaneously achieve high strength and toughness. This approach couples bidirectional freezing with hot-press processing to create a cellulose nanofiber (CNF) oriented polyvinyl alcohol (PVA) composite architecture. During bidirectional freezing, CNFs align along the ice crystal growth direction, guiding the ordered arrangement of PVA chains. Subsequent hot pressing enables the oriented CNFs to act as crystallization templates, promoting controlled recrystallization of the PVA matrix and significantly enhancing its molecular alignment and crystallinity. Moreover, robust interfacial hydrogen bonding between CNFs and PVA ensures efficient stress transfer, mitigates local stress concentrations, and facilitates superior energy dissipation during deformation. As a result, the resulting PC-orientation composite exhibits a remarkable combination of high tensile strength (44.42 MPa) and impressive toughness (34.74 MJ·m⁻³) while maintaining an ultralow density (0.75 g·cm⁻³), representing the state-of-the-art in reported FRPs. This work provides a universal pathway to break the long-standing strength-toughness trade-off in FRPs and highlights a promising design paradigm for lightweight structural components.

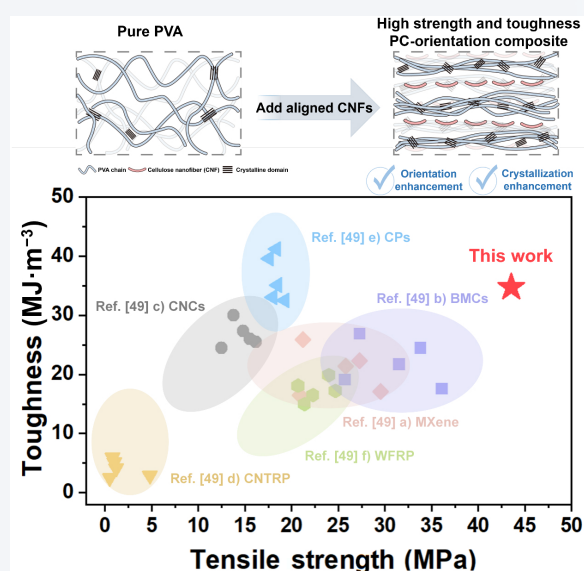
KEYWORDS: cellulose nanofiber, crystallinity, fiber-reinforced polymer composites, mechanical strength, toughness

1 Introduction

Modern engineering demands materials that combine high load-bearing capability with lightweight and versatile mechanical performance to meet the stringent requirements of advanced transportation, energy, and biomedical systems. Fiber-reinforced polymer composites (FRPs), featuring a unique combination of high specific strength, stiffness, and low density, have therefore become indispensable in these fields [1, 2]. However, their development remains constrained by an inherent trade-off between

strength and toughness, as conventional reinforcement strategies typically enhance one property at the expense of the other [3–5]. Achieving a synergistic balance between these competing attributes represents a fundamental challenge in advancing the high-performance FRPs.

Currently, various efforts have been proposed to simultaneously enhance the strength and toughness of FRPs, with interface control and structural design mechanisms being the most effective [6, 7]. Strengthening the interfacial bonding between fibers and the matrix [8] and constructing rational anisotropic architectures [9] can markedly enhance stress-transfer efficiency and homogenize internal stress distribution. Such optimization mitigates local stress concentration, thereby retarding crack initiation and propagation, improving toughness and fatigue resistance, and ultimately enhancing the durability of material [10, 11]. Despite these advances, most of these approaches primarily improve toughness



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and resilience, while their contribution to the enhancement of ultimate strength remains limited [12, 13]. Consequently, realizing the simultaneous achievement of high strength and high toughness continues to pose a formidable challenge for FRPs.

Crystallinity plays a pivotal role in dictating the strength and toughness of polymer-based composites [14, 15]. Polymer-based composites with low crystallinity typically exhibit disordered molecular packing and a high density of structural defects, which readily act as stress concentrators under external loading, promoting crack initiation and propagation and thereby compromising load-bearing capacity [16]. Moreover, the inefficient energy dissipation in such disordered structures hinders the uniform distribution of external stresses, further limiting their mechanical robustness [17]. In contrast, high-crystallinity materials feature well-ordered crystalline domains with fewer defects, which not only suppress stress localization but also enhance energy dissipation efficiency during deformation, leading to superior mechanical stability and toughness [18–20]. Consequently, regulating crystallinity has emerged as a key strategy to achieve a synergistic enhancement of both strength and toughness. Previous studies have demonstrated that template-induced crystallization, strain-induced crystallization, and the incorporation of nanomaterials can effectively promote molecular orientation and crystallization in polymers, thereby improving their mechanical properties [21–23]. However, imperfect structural design [24], or weak interfacial bonding during stress transfer can induce local stress concentration [25], interfacial defects [26], or even fiber pull-out [27], severely undermining the overall performance. Therefore, the rational design of anisotropic architectures combined with the enhancement of interfacial adhesion and crystallinity is essential for developing high-performance FRPs with high strength and toughness.

In this study, we present a crystallinity-regulation strategy that leverages the orientation-induced effects of cellulose nanofibers within the polyvinyl alcohol (PVA) matrix to achieve a synergistic enhancement of strength and toughness through reinforced interfacial interactions and anisotropic structural design. Cellulose nanofibers (CNFs) reinforced PVA composites were fabricated via a bidirectional freezing technique followed by hot pressing, enabling simultaneous control over molecular orientation and interfacial architecture. During bidirectional freezing, CNFs aligned along the ice growth direction within the PVA matrix, while the PVA chains underwent preliminary orientation under the same directional constraint, forming an ordered network that effectively facilitated stress transfer and energy dissipation. Subsequently, during hot pressing, the thermoplastic PVA chains exhibited controlled flow and recrystallization, while the aligned CNFs served as nucleation templates that guided ordered crystallization of the PVA matrix, markedly improving its overall crystallinity and molecular orientation. Furthermore, the strong interfacial interactions between the amorphous PVA regions and crystalline CNFs enhanced load transfer efficiency and mitigated local strain concentration, thereby endowing the composite with superior mechanical robustness. As a result, the resulting PC-orientation composite exhibited remarkable mechanical performance, achieving a tensile strength of 44.42 MPa and a toughness of 34.74 MJ·m⁻³ while maintaining a low density (0.75 g·cm⁻³). This lightweight FRP composite, which combines high specific strength with excellent toughness, holds great potential for practical applications in the fields of aerospace and intelligent

manufacturing, particularly in structural components such as unmanned aerial vehicle (UAVs) shells (Fig. 1(g)).

2 Experimental

2.1 Materials

Cellulose nanofibers (carboxyl content = 1.2 mmol·g⁻¹) were purchased from Tianjin Wood Spirit Biotechnology Co., Ltd. According to the data provided by the supplier, the purchased CNFs have an average diameter of 10–20 nm and an average length of 1–5 μm. Polyvinyl alcohol 1750 ± 50 (> 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2 Preparation of PC-orientation composites

Anisotropic composites were fabricated by bidirectionally freeze-casting CNF/PVA slurry over a polydimethylsiloxane (PDMS) wedge on a cooling platform. First, PVA (5 g) was completely dissolved in deionized water (95 mL) in a 90 °C oil bath, stirring until clear. Various amounts of CNF (CNF/PVA = 0 wt.% to 2 wt.%, mass ratio) were added, followed by vigorous stirring until uniformity was achieved. The resulting slurry was then poured into a PDMS (wedge angle 25°) mold. The entire reaction unit was placed atop a copper cylinder with its bottom surface immersed in a liquid nitrogen reservoir. During freezing, layered ice crystals grew in parallel along a dual temperature gradient. Simultaneously, CNF/PVA from the slurry was ejected from the formed solidification front, aligning parallel between ice layers. The frozen sample was freeze-dried and subsequently hot-pressed at 90 °C under 10 MPa for 30 min to obtain the PC-orientation composites. By varying the CNF/PVA ratio in the slurry (0 wt.%–2 wt.%), PC-orientation composites with different CNF contents were obtained. For clarity, the samples were designated as follows: N-PVA represents the non-oriented pure PVA sample prepared by direct casting and drying, PVA-orientation represents the oriented pure PVA sample prepared using the same bidirectional freeze-casting and hot-pressing procedures as the PC-orientation sample but without the addition of CNFs, N-PC represents the non-oriented PVA/CNF composite, and PC-orientation represents the oriented PVA/CNF composite. Therefore, the PVA-orientation sample serves as a control to distinguish the effect of matrix orientation from the reinforcing and orienting effects introduced by CNFs.

2.3 Characterization

Prior to observation, the samples were sputter-coated with a thin layer of conductive gold, and their morphologies were characterized using a scanning electron microscope (Tescan XEIA SEM, after palladium sputtering). To analyze the variations in chemical bonding, Fourier transform infrared spectroscopy (FTIR, Nicolet 170SX, reflection absorption mode) was employed. The samples were ground into fine powders and pressed into transparent pellets using a hydraulic press. Spectra were recorded in the wavelength range of 400–4000 cm⁻¹ with a resolution of 0.5 cm⁻¹, and each sample was scanned 64 times. Raman spectroscopy (Renishaw inVia, UK) was conducted using a 532 nm laser with a power of 5 mW to investigate changes in hydrogen bonding. X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer over a 2θ range of 5°–90° at a scanning rate of 5 °·min⁻¹. Using Origin software, the XRD diffraction peaks were fitted with a Gaussian–Lorentzian function to calculate the crystallinity of the material.

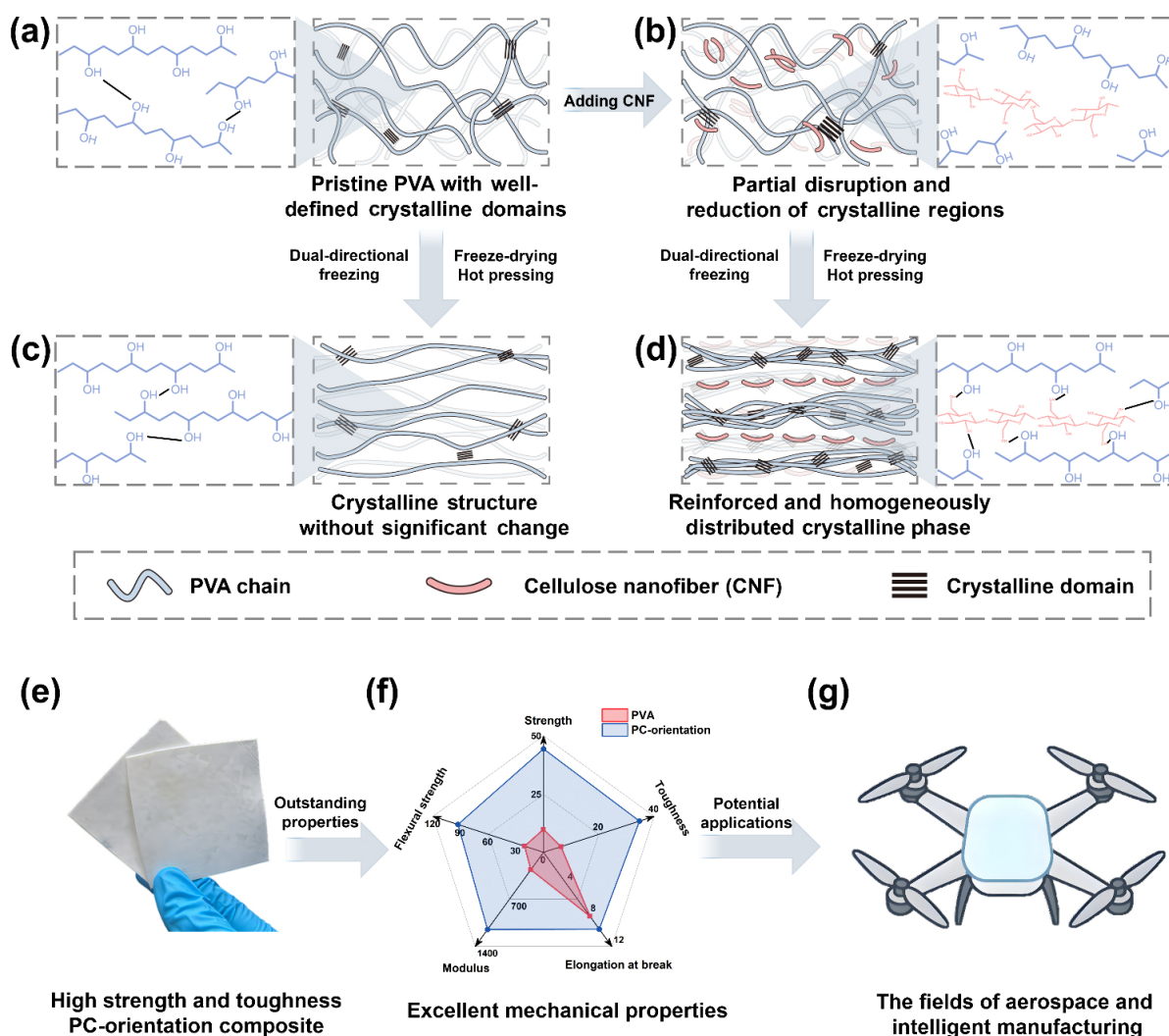


Figure 1 Schematic illustration of the orientation-induced reinforcement strategy for controlling matrix crystallinity. This strategy involves bidirectional freezing to achieve CNF orientation and preliminary PVA chain alignment, followed by hot pressing to induce lattice-matched heterogeneous nucleation and constrained nucleation at the interface ((a) and (d)), resulting in well-defined crystalline morphologies. In contrast, conventional strategies, such as interface engineering and structural design, tend to improve toughness and fatigue life but suffer from insufficient crystallinity and uneven dispersion ((b) and (c)). (e) Lightweight, high-strength, and high-toughness PC-orientation composite. (f) Performance radar chart of the PC-orientation composite. (g) Potential applications of the PC-orientation composite.

The mechanical properties were measured using a universal testing machine under ambient laboratory conditions at room temperature. Prior to testing, all samples were fully dried to minimize the influence of absorbed moisture; therefore, the reported mechanical properties correspond to the dry-state performance of the composites. For the tensile test, the procedure followed the GB/T 1040 standard. The gauge length was set to 20 mm, and the tensile rate was 10 mm·min⁻¹. Each reported value represents the average of five specimens. For the flexural test, the procedure was conducted according to the GB/T 9341-2008 standard. The span between the supports was fixed at 20 mm, with a crosshead speed of 5 mm·min⁻¹. The diameters of the loading nose and the supporting rollers were both 4 mm. Each measurement was based on the average of five specimens.

The density of the composites was determined using the geometric method by measuring the mass and physical dimensions of the specimens.

Thermogravimetric (TG) analysis was performed using a TAQ500 instrument (TA Instruments, USA). The samples were

heated from 30 to 700 °C at a rate of 10 °C·min⁻¹ under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was heated from 20 to 200 °C at a ramping rate of 10 °C·min⁻¹ under a nitrogen atmosphere.

Wide-angle X-ray scattering measurements were performed on a Xenocs Xeuss small-angle X-ray scattering (SAXS)/wide-angle X-ray scattering (WAXS) system, using an incident Cu K α radiation beam ($\lambda = 0.154$ nm) perpendicular to the fiber axis. The distance between the sample and the detector was fixed at 80 mm. The WAXS patterns were analyzed using Foxtrot software. The degree of orientation is an important indicator for evaluating fiber alignment, and is calculated based on the ordered crystals of specific crystal planes within the fiber [28–30]. It was determined by integrating the azimuthal intensity distribution of the WAXS patterns. Two diffraction peaks were fitted using a Lorentzian function in Origin software, and the full width at half maximum (FWHM) was obtained from the fitted curve. The degree of orientation was then calculated using the following formula

$$S = \frac{180\text{-FWHM}}{180} \quad (1)$$

SAXS measurements were performed on a Xenocs Xeuss SAXS/WAXS system using an incident Cu K α radiation beam ($\lambda = 0.154$ nm) perpendicular to the fiber axis. The sample-to-detector distance was set to 1188 mm. The SAXS patterns were analyzed using the FIT two-dimensional (2D) software. SAXS was employed to investigate the scattering behavior in the small-angle region, enabling analysis of the internal microstructural features of the fibers, such as the misorientation angle [31]. The angle between the microfibrils and the fiber axis was defined as the misorientation angle (B_ϕ). The value of B_ϕ was determined from the equatorial streaks in the SAXS pattern using the Ruland streak method, which is expressed as follows

$$B_{\text{obs}} = \frac{1}{s l_f} + B_\phi \quad (2)$$

where s is the scattering vector, B_{obs} represents the FWHM of the azimuthal intensity distribution, and l_f is the length of the elementary fibril. The scattering vector s can be determined according to the following equation

$$s = \frac{2 \sin \theta}{\lambda} \quad (3)$$

where θ is half of the scattering angle, and λ is the wavelength of the incident X-rays. All azimuthal intensity distributions were fitted using a Lorentzian function.

2.4 Molecular dynamics (MD) simulation

All-atom MD simulations were performed using the COMPASS III force field implemented in the Materials Studio software package [32]. The COMPASS III force field has been extensively validated for condensed-phase polymer systems and has demonstrated reliable performance in describing hydrogen-bonding interactions in PVA-, cellulose-, and polysaccharide-based materials [33]. Therefore, it is particularly suitable for accurately capturing the intermolecular interactions and structural evolution in the PVA/CNF composite system. The molecular models of PVA chains and CNFs were first constructed using the Visualizer module. All initial configurations were geometrically optimized under the Born–Oppenheimer approximation to obtain energy-minimized structures. The CNF model was built based on XRD analysis, with an interplanar spacing of approximately 4 Å. Four CNF chains were placed in a simulation box of 71 Å $\times$ 60 Å $\times$ 50 Å to construct two configurations: an ordered arrangement (PC-orientation) and a randomly disordered arrangement (N-PC). Subsequently, PVA chains were inserted into both PC-orientation and N-PC systems using the Packing function in the amorphous cell module to form two composite models [34]. All initial structures were subjected to geometry optimization followed by five annealing cycles between 300 and 500 K to eliminate unfavorable conformations. The systems were then pre-equilibrated for 1 ns under the NPT ensemble at 298 K (Nosé thermostat, coupling constant $\tau = 0.1$ ps) and 1 atm (Berendsen barostat) [35]. Production runs of 10 ns were carried out under the NVT ensemble at 298 K. A cutoff radius of 12 Å was applied for non-bonded interactions, and long-range electrostatic interactions were computed using the particle-mesh Ewald (PME) method [36]. The time step was set to 2 fs, and the neighbor list was updated every 10 steps with periodic boundary conditions applied in all three dimensions. Structural and dynamic

properties were analyzed based on the equilibrated trajectories. The spatial correlations between PVA and CNFs were characterized by the radial distribution function (RDF), which is defined as

$$g(r) = \frac{1}{4\pi r^2 \rho N} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta(r - r_{ij}) \quad (4)$$

where ρ is the number density and r_{ij} is the distance between atoms. The adsorption behavior and local ordering of PVA on the CNF surface were evaluated based on the peak positions and intensities in the RDF. The diffusion behavior of PVA chains was further analyzed using the mean square displacement (MSD), defined as

$$\text{MSD}(t) = \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle \quad (5)$$

The self-diffusion coefficients of PVA in the ordered and disordered CNF structures were estimated from the slope of the MSD curves within the diffusive regime. Additionally, the root-mean-square deviation (RMSD) of PVA chains was calculated using a custom Perl script to evaluate the conformational stability of PVA within the composite systems. All analyses were performed based on the 10 ns equilibrated trajectories, and averaging over multiple time intervals was employed to improve statistical reliability. The equilibration of the systems was confirmed by the stabilization of key thermodynamic parameters, including the total energy, temperature, and density, which exhibited only minor fluctuations during the final stage of the simulation. Therefore, the 10 ns simulation time was considered sufficient to obtain reliable equilibrium configurations for subsequent analyses.

3 Results and discussion

3.1 Synthesis and design of PC-orientation composite materials

To achieve fiber-reinforced polymer composites with simultaneous ultrahigh toughness and mechanical strength, a dual-freezing-assisted hot-pressing strategy was developed to fabricate high-performance CNFs reinforced PVA composites (PC-orientation) (Figs. 1(a)–1(e)). The dual-freezing process effectively prevents CNFs agglomeration during thermal processing, thereby preserving their oriented alignment within the PVA matrix [37]. Subsequent hot pressing enables lattice-matching-induced heterogeneous nucleation and restricted crystal growth to occur synergistically without disrupting the pre-established orientation architecture [38, 39]. In the PC-orientation, the aligned CNFs act not only as a reinforcing scaffold but also as efficient nucleation templates, guiding the ordered rearrangement of PVA molecular chains and markedly enhancing the crystallinity and molecular orientation of the PVA matrix. Moreover, unlike conventional inorganic fibers that suffer from poor compatibility and interfacial repulsion with polymer matrices, CNFs exhibit exceptional interfacial affinity and reinforcing potential [40]. The abundant surface hydroxyl and CNFs' abundant surface hydroxyl and oxygen-containing groups hydrogen-bond strongly with PVA's polar hydroxyls, forming stable interfaces that enable efficient stress transfer and ordered polymer stacking [41, 42]. This orientation-assisted, phase-induced crystallization strategy thus offers a powerful route to regulate polymer crystallization at the molecular level while enhancing the strength, toughness, and structural integrity of PC-orientation. As a result, the obtained PC-orientation exhibits ultrahigh strength and

unprecedented toughness at a low density (Fig. 1(f)), indicating their great promise for lightweight and high-performance fiber-reinforced polymers (Fig. 1(g)).

The internal microstructures of the PC-orientation were characterized by scanning electron microscopy. The bidirectionally frozen PVA materials and PC-orientation composites exhibited well-defined oriented architectures, in sharp contrast to those prepared by direct freezing without directional control (Fig. 2(a)). Notably, clear morphological differences were observed between the ordered PVA (PVA-orientation) and PC-orientation (Fig. 2(a)(iii)

and Fig. S1 in the Electronic Supplementary Material (ESM)), which can be ascribed to distinct interfacial interactions and crystallization behaviors. During bidirectional freeze-induced orientation, the incorporation of CNFs promotes the directional alignment of PVA molecular chains, while the CNFs themselves participate in forming the anisotropic framework. Acting as nanoscale scaffolds, CNFs guide PVA chain arrangement and enhance the regularity of the crystalline domains through interfacial hydrogen bonding. Furthermore, CNFs serve as heterogeneous nucleation centers, inducing localized and ordered crystallization of

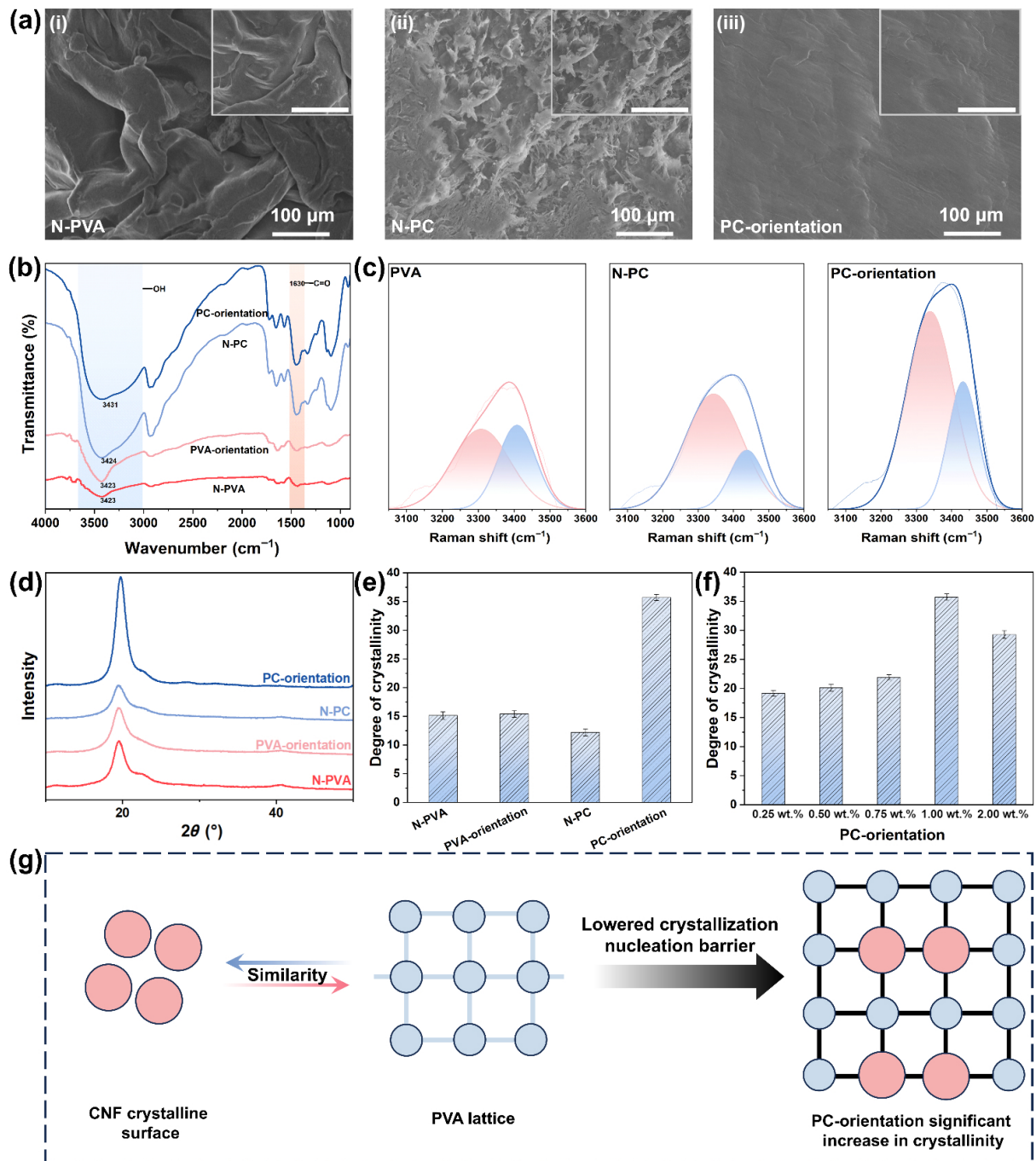


Figure 2 Physicochemical characterization of PC-orientation composites. (a) Schematic illustration of the internal microstructure of different PVA-based composites (inset scale bar: 50 nm). (b) FTIR spectra of different PVA composites and (c) their Raman spectra. (d) XRD patterns of the PVA composites and (e) corresponding crystallinity calculations. (f) Crystallinity of PC-orientation composites with varying CNF contents. (g) Schematic illustration of lattice-matched heterogeneous nucleation and constrained nucleation at the interface in PC-orientation composites.

PVA chains around their surfaces. As a result, the PC-orientation exhibits a more compact and uniformly aligned fibrous crystalline network compared to the relatively loose and irregular morphology observed in pure PVA-orientation sample.

To elucidate the effect of CNFs orientation on interfacial interactions within PC-orientation, four types of samples were prepared: unordered PVA (N-PVA), PVA-orientation, randomly mixed PVA/CNF (N-PC), and PC-orientation. The interfacial bonding mechanisms were examined using FT-IR and Raman spectroscopy. As shown in Fig. 2(b) and Fig. S2 in the ESM, all composites exhibited characteristic O–H stretching vibrations near 3423 cm^{-1} . Compared with N-PVA, both PC-orientation and N-PC showed noticeable changes in O–H vibration, confirming the formation of hydrogen bonds between PVA and CNFs. The orientation of the PVA matrix alone had negligible influence on the hydroxyl peak. Interestingly, the O–H band of the PC-orientation composite shifted from 3423 to 3431 cm^{-1} , corresponding to an increase of 8 cm^{-1} in peak position. Such a change indicates a reconstruction of the hydrogen-bonding environment induced by CNFs alignment, resulting in enhanced interfacial interactions between CNFs and PVA chains [43]. However, excessive CNFs alignment (e.g., 2 wt.%) induced aggregation, reducing the effective interfacial area and causing a red shift of the O–H band to 3427 cm^{-1} . Raman spectra further corroborated these results. The broad bands between $3000\text{--}3800\text{ cm}^{-1}$ correspond to O–H stretching vibrations [44], where the peak near 3200 cm^{-1} is generally assigned to strongly hydrogen-bonded hydroxyl groups [45], while the peak near 3400 cm^{-1} is attributed to weakly hydrogen-bonded or relatively free hydroxyl groups [46]. As shown in Fig. 2(c), the Raman spectra of PVA, N-PC, and PC-orientation all display characteristic O–H stretching vibration peaks within the range of $3050\text{--}3600\text{ cm}^{-1}$. Compared with pure PVA, the O–H region in the N-PC composite exhibits slight peak broadening, with only minimal changes in the relative peak areas corresponding to strong and weak hydrogen bonds, indicating that randomly dispersed CNFs induce only limited perturbation to the hydrogen-bonding network. In contrast, the PC-orientation composite shows pronounced changes in the O–H stretching band. The relative area of the strong hydrogen-bond component ($\sim 3200\text{ cm}^{-1}$) increases substantially, whereas that of the weak hydrogen-bond component ($\sim 3400\text{ cm}^{-1}$) decreases accordingly, resulting in a significant increase in the strong-to-weak hydrogen bond intensity ratio ($I_{\text{strong}}/I_{\text{weak}}$). This observation indicates that CNFs alignment reinforces the strong hydrogen-bond interactions within the composite matrix, thereby enhancing interfacial coupling between CNFs and PVA chains in PC-orientation.

The crystallization behavior of the PC-orientation was evaluated by XRD (Fig. 2(d) and Fig. S3 in the ESM). As shown in Fig. 2(e), the negligible difference between PVA-orientation and N-PVA indicates that orientation alone does not alter the crystallinity of the PVA matrix. In contrast, the crystallinity of N-PC decreases relative to N-PVA, suggesting that the direct incorporation of unoriented CNFs inhibits PVA crystallization. This phenomenon is attributed to the steric obstruction generated by randomly dispersed CNFs and their occasional agglomeration, which collectively disrupt the structural integrity of the PVA network during hot pressing [47, 48]. Strikingly, the PC-orientation sample exhibits the highest diffraction peak intensity. Such pronounced crystallization originates from the incorporation of aligned CNFs, which act as crystal-surface-assisted heterogeneous nucleation sites while

simultaneously imposing spatial confinement that restricts nucleation pathways, thereby synergistically accelerating PVA crystallization (Fig. 2(g)). During bidirectional freezing, temperature gradients induce directional ice crystal growth, creating confined spaces that guide the ordered alignment of CNFs between dendritic branches. Within these confined regions, a robust hydrogen-bond network between CNFs and PVA restricts chain mobility, promoting regular alignment and ordered stacking of PVA segments. Simultaneously, compressive and shear forces associated with ice crystal growth induce directional migration of CNFs, stretching and aligning PVA chains along their surfaces [49]. Furthermore, the highly crystalline and rigid CNFs provide abundant stable heterogeneous interfaces [50, 51]. The regularly arranged hydroxyl groups and ordered crystalline surfaces of CNFs facilitate hydrogen-bond-mediated adsorption and alignment of PVA chains, thereby reducing the interfacial energy barrier for crystallization and serving as effective heterogeneous nucleation sites. In addition, the surface topography and chemically active groups further promote preferential PVA chain alignment and subsequent crystal growth [52]. The combined effect of restricted nucleation and crystal-surface-assisted interfacial heterogeneous nucleation substantially accelerates crystallization, yielding a highly ordered polymer network with enhanced interfacial stability, which directly contributes to the improved strength and toughness of the PC-orientation. XRD analysis (Fig. 2(f)) shows that increasing oriented CNFs content up to 1 wt.% progressively enhances the (101) reflection at 19.5° .

However, beyond 2 wt.%, excessive CNFs lead to the formation of CNF-rich aggregated regions, as confirmed by SEM observations (Fig. S4 in the ESM), which ultimately inhibits PVA crystallization. This phenomenon is attributed to the tendency of excessive CNFs to form aggregated domains due to strong interfibrillar hydrogen-bonding interactions, which reduce the effective interfacial area available for heterogeneous nucleation [53]. In addition, the CNF-rich regions hinder the diffusion and ordered arrangement of PVA molecular chains and act as physical crosslinking domains that restrict chain mobility [54, 55]. Consequently, the synergistic effect of heterogeneous nucleation and ordered crystal growth becomes weakened, leading to a decrease in the crystallinity of the composite.

To further quantitatively analyze the crystallization behavior, DSC heating scans were performed, and the results are shown in Fig. S5 in the ESM. The measured melting enthalpies (ΔH_m) of N-PVA, N-PC, PVA-orientation, and PC-orientation were 119.59, 110.11, 120.35, and $146.43\text{ J}\cdot\text{g}^{-1}$, respectively. Using the theoretical melting enthalpy of fully crystalline PVA ($138.6\text{ J}\cdot\text{g}^{-1}$) as a reference [56], the corresponding crystallinity values were calculated to be 86.28%, 79.44%, 86.83%, and 105.64%, respectively. The apparent crystallinity of PC-orientation slightly exceeded 100%, suggesting an exceptionally high degree of molecular ordering, which may arise from the highly ordered interfacial regions formed between oriented CNFs and PVA chains. Notably, the crystallinity of PVA-orientation was nearly identical to that of N-PVA, whereas the crystallinity of N-PC was slightly lower. In contrast, PC-orientation exhibited a significantly higher apparent crystallinity, consistent with the XRD results. These findings further confirm that the enhancement in matrix crystallinity primarily originates from the orientation-induced templating effect of CNFs.

3.2 Mechanical performance of PC-orientation

Tensile testing revealed that the optimal CNFs loading for achieving

superior mechanical performance is 1 wt.% (Fig. 3(a)). As the content of oriented CNFs increased from 0 to 0.75 wt.%, a trade-off between strength and elongation was observed that the tensile strength gradually increased, whereas elongation at break declined. Interestingly, at a CNF loading of 1 wt.%, both tensile strength and elongation improved simultaneously. The PC-oriented composite achieved a maximum tensile strength of 44.42 MPa and a toughness of 34.74 MJ·m⁻³, markedly outperforming composites containing other oriented CNF loadings (Fig. 3(c)). This enhancement can be attributed to the dominant orientation-induced crystallization effect of CNFs at this loading, which promotes regular alignment and ordered stacking of PVA molecular chains while maintaining robust interfacial interactions. Consequently, the combination of orientation-reinforced matrix crystallinity and strong PVA/CNF interfacial bonding enables the

simultaneous attainment of high strength and exceptional toughness. However, further increasing the oriented CNFs content to 2 wt.% led to a pronounced decline in mechanical performance. This deterioration arises primarily from CNFs aggregation, which introduces structural defects and diminishes effective interfacial interactions with the PVA matrix [57, 58]. In addition, agglomerated CNFs are less effective in inducing PVA chain orientation and crystallization, thereby reducing the reinforcing efficiency of the oriented network. These results highlight the critical importance of optimizing CNFs content to balance orientation-induced crystallization, interfacial interactions, and structural integrity in high-performance PC-orientation composites.

We also investigated the effect of ambient humidity on the mechanical properties of PC-orientation composites (Fig. S6 in the

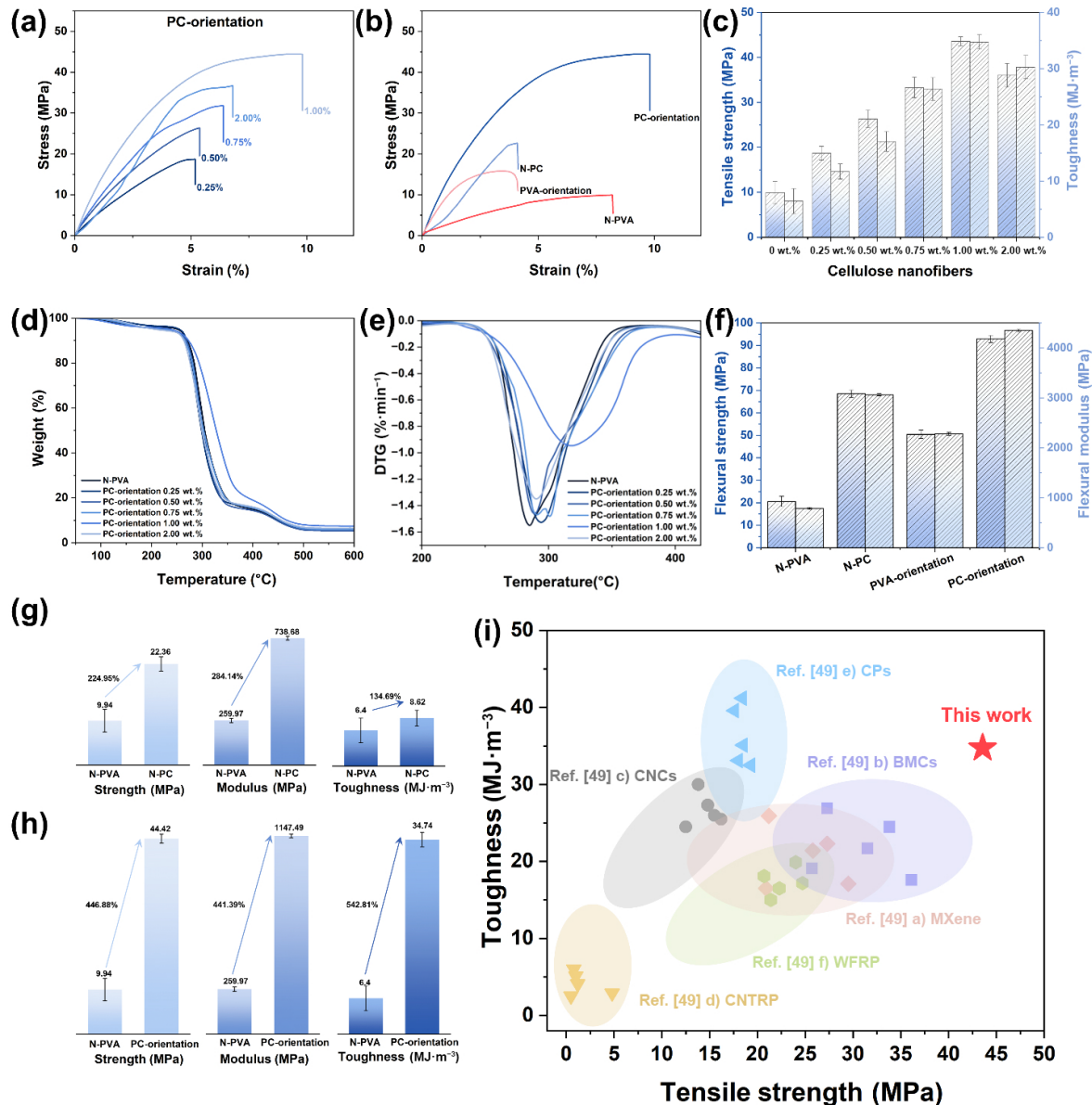


Figure 3 Mechanical properties of PC-orientation composites. (a) Stress–strain curves of PC-orientation composites with varying CNF contents. (b) Stress–strain curves of different PVA-based composites. (c) Mechanical strength of the prepared PC-orientation composites. (d) TGA curves of PC-orientation composites with different CNF contents. (e) DTG curves of PC-orientation composites with different CNF contents. (f) Bending strength of different PVA-based composites. (g) Comparison of mechanical properties between N-PVA and N-PC 1 wt.% composites. (h) Comparison of mechanical properties between N-PVA and PC-orientation 1 wt.% composites. (i) Mechanical strength and toughness of various lightweight fiber-reinforced polymer composites.

ESM). The results reveal a pronounced humidity-dependent mechanical response. Under low relative humidity conditions (RH 30%), the composite exhibited the highest tensile strength but relatively limited elongation at break, owing to the strong intermolecular hydrogen-bonding network and restricted mobility of PVA molecular chains. As the relative humidity increased to RH 60%, the tensile strength gradually decreased, whereas the elongation and toughness increased, indicating a moderate plasticization effect induced by absorbed water molecules. Under high humidity conditions (RH 90%), the composite displayed substantially enhanced stretchability accompanied by reduced tensile strength, which can be attributed to the weakening of intermolecular hydrogen-bonding interactions and the increased chain-segment mobility of the PVA matrix [59]. Nevertheless, the PC-orientation composites maintained continuous deformation capability without catastrophic brittle failure even at high humidity, demonstrating that the oriented CNF framework and orientation-induced crystalline network still effectively preserved the structural integrity of the composite. These results suggest that environmental humidity can regulate the balance between rigidity and ductility of the composite while retaining the stability of the anisotropic reinforcing architecture.

To elucidate the impact of orientation-enhanced matrix crystallization on the mechanical performance of PC-orientation composites, four sample groups, including N-PVA, PVA-orientation, N-PC 1 wt.%, and PC-orientation 1 wt.%, were systematically compared. Tensile testing demonstrated that the orientation-induced crystallinity strategy markedly improves mechanical properties (Fig. 3(b)). Specifically, compared with N-PVA (Fig. 3(g)), the tensile strength, modulus, and toughness of N-PC 1 wt.% increased by 2.25, 2.84, and 1.34-fold, respectively. In contrast, the PVA-orientation sample exhibited 1.82, 1.30, and 1.92-fold enhancements in these properties relative to N-PVA (Fig. S7 in the ESM). Furthermore, compared with N-PVA (Fig. 3(h)), the PC-orientation 1 wt.% composite showed further increases of 4.47, 4.42, and 5.43-fold in tensile strength, modulus, and toughness, respectively. Scanning electron microscopy of the fracture surfaces revealed distinct differences in failure behavior (Fig. S8 in the ESM). PC-orientation composites displayed irregular, tortuous fracture surfaces, which facilitate effective stress dissipation and uniform stress distribution. In contrast, non-oriented samples (N-PC) exhibited smooth, regular fracture morphologies, indicating limited energy dissipation around crack tips [60]. These observations highlight that while both orientation and CNFs reinforcement enhance strength and stiffness, sufficient crystallinity is essential to optimize toughness. Remarkably, PC-orientation 1 wt.% achieved a low density of $0.75 \text{ g}\cdot\text{cm}^{-3}$, combining light weight with superior tensile strength and toughness, outperforming many reported polymer composites of similar composition (Fig. 3(i)) [61–66].

To understand the origin of the low-density characteristic, the porosity of the composites was analyzed (Fig. S9 in the ESM). The N-PVA sample exhibited a porosity of 26.34%, whereas the porosity of the PC-orientation composite decreased to 14.82%. The reduced porosity is mainly attributed to the orientation structural densification and hot-pressing process, which effectively compressed the internal voids while improving the packing efficiency between PVA molecular chains and aligned CNFs. These results indicate that the PC-orientation composite achieves an optimized balance between lightweight characteristics and structural compactness.

Meanwhile, the flexural tests further confirmed the reinforcing effect of orientation-induced crystallization on the macroscopic mechanical response. As the content of CNFs increased, the flexural performance of the composites first increased and then decreased, with the PC-orientation 1 wt.% sample exhibiting the most optimal mechanical properties (Fig. S10 in the ESM). Compared with N-PVA, its flexural strength and modulus increased by approximately 4.51 and 5.54-fold, respectively; relative to N-PC 1 wt.%, the corresponding enhancements were 1.36 and 1.42-fold (Fig. 3(f)). When the content of CNFs was further increased to 2 wt.%, both the flexural strength and modulus decreased to some extent, suggesting that excessive CNFs loading led to local aggregation, which weakened the degree of orientation and consequently reduced the reinforcing effect. Notably, the PC-orientation 1 wt.% sample maintained high toughness and low density while exhibiting excellent stress transfer and energy dissipation capabilities, indicating that the material can achieve dynamic equilibrium between uniform stress transfer and energy dissipation under external bending deformation. These findings further confirm the critical role of CNFs orientation-induced crystallization and strong interfacial interactions in enhancing the overall mechanical synergy of the composites.

In addition, the oriented CNFs significantly enhanced the interfacial adhesion and matrix crystallinity, which translated into improved thermal stability. The thermal degradation behavior of composites with different CNF contents was evaluated by thermogravimetric analysis (Fig. 3(d)). In the temperature range of 250–350 °C, the weight loss curves of the pure PVA material and the CNF-containing composites largely overlapped, exhibiting similar degradation behavior. Among them, the PC-orientation 1 wt.% sample displayed a weight loss rate plateau in this temperature range comparable to that of pure PVA. Notably, with the introduction of CNFs, the residual mass of the composites at higher temperatures increased. Differential thermogravimetric analysis further confirmed that the decomposition temperature increased with the increasing content of oriented CNFs (Fig. 3(e)). This phenomenon is attributed to the formation of a dense, highly crystalline network structure and strong interfacial bonding between CNFs and the PVA matrix, which together acted as an additional thermal barrier, suppressing molecular motion and hindering the release of thermal degradation products [67]. At an oriented CNF content of 1 wt.%, the degradation rate of the composite decreased significantly, indicating that the synergistic effect of enhanced crystallinity and interfacial interactions effectively stabilized the composite against thermal decomposition.

3.3 Mechanism of orientation-enhanced crystallinity of the matrix

To elucidate the mechanism by which cellulose nanofiber orientation induces an increase in the crystallinity of PC-orientation, wide-angle X-ray scattering was employed to quantitatively analyze the structural orientation and crystallization characteristics. The crystalline orientation degree of the PC-orientation composite was calculated by azimuthal integration of the WAXS patterns, yielding a value of 0.567, which was significantly higher than that of N-PC (0.263) (Figs. 4(a) and 4(b)). These results indicate that the orientation degree of the PC-orientation composite is higher than that of N-PC, as the oriented CNFs effectively promoted the alignment of PVA molecular chains and enhanced the overall polymer ordering. Meanwhile, analysis of

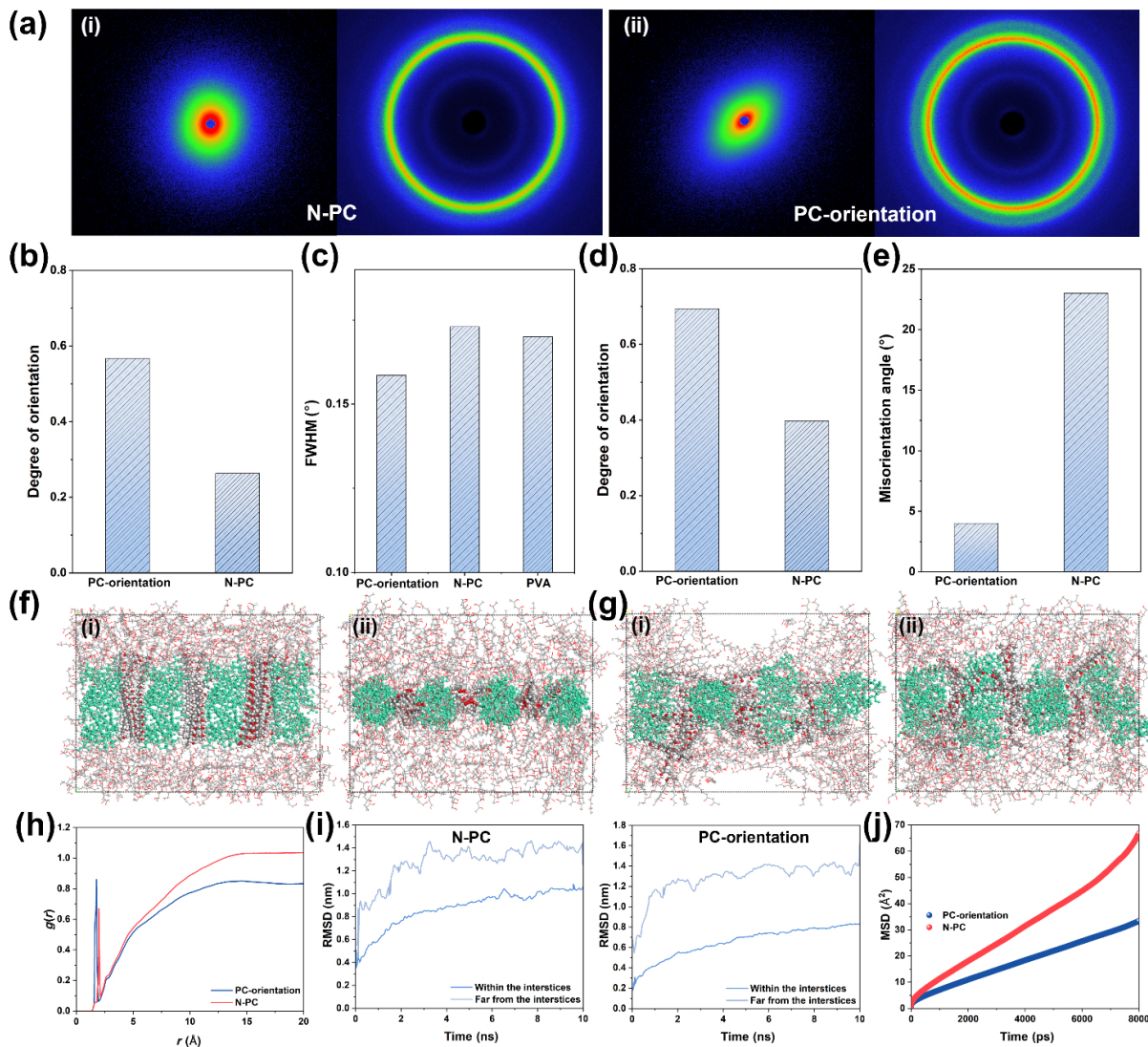


Figure 4 Analysis of the crystallization process. (a) SAXS (left) and WAXS (right) patterns of (i) N-PC and (ii) PC-orientation composites. (b) Comparison of the orientation degree of different PVA composites obtained from WAXS analysis. (c) Comparison of FWHM values from 1D-WAXS curves of different PVA composites. (d) Orientation degree of different PVA composites obtained from SAXS analysis. (e) Microfibril misalignment angles of different PVA composites derived from SAXS patterns. (f) Equilibrated configurations of PC-orientation composites after molecular dynamics relaxation: (i) side view, (ii) top view. (g) Equilibrated configurations of N-PC composites after molecular dynamics relaxation: (i) side view and (ii) top view. (h) RDF of PVA relative to CNFs in PC-orientation and N-PC models. (i) RMSD curves of two types of PVA chains in PC-orientation and N-PC models. (j) MSD curves of PVA chains in PC-orientation and N-PC models.

the FWHM of the equatorial radial integration curves of the WAXS patterns (Fig. 4(c) and Fig. S11 in the ESM) revealed that the FWHM decreased from 0.171 for PVA to 0.158 for PC-orientation, reflecting a significant improvement in crystallinity due to the introduction of oriented CNFs. In contrast, the FWHM of N-PC increased slightly to 0.173, which is consistent with the trend of reduced crystallinity relative to PC-orientation. This behavior can be attributed to the tendency of disordered CNFs to aggregate, which limits their effective interaction with PVA molecular chains and consequently hinders efficient nucleation. Thus, the effect of disordered CNFs on the structural crystallinity of the PVA matrix is relatively weak.

The anisotropic structure of the PC-orientation was further probed using SAXS. N-PC exhibited circular scattering spots, indicative of an isotropic, orientation-independent structure (Fig. 4(a)). In contrast, PC-orientation displayed distinctly elliptical scattering patterns, reflecting the formation of an oriented

crystalline network. This orientation was achieved via a bidirectional freezing strategy, which establishes vertical and parallel temperature gradients that direct ice crystal growth in two orthogonal directions. Vertical ice growth constrains cellulose nanofibers and polyvinyl alcohol chains to occupy the interstitial spaces between ice lamellae, while parallel growth aligns PVA/CNF assemblies along the temperature gradient, promoting macroscopic chain orientation. Quantitative analysis using the Hermann orientation parameter (f_c) derived from azimuthal integration of SAXS intensity confirmed the structural anisotropy. N-PC exhibited a low f_c of 0.390, consistent with its isotropic character, whereas PC-orientation achieved a significantly higher f_c of 0.721 (Fig. 4(d)), corroborating the high degree of molecular alignment induced by the oriented CNFs. In addition, the microfibril misalignment angles derived from SAXS patterns can be used to probe the orientation of microstructures within the fibers. Compared with N-PC (23°), the microfibril orientation angle of PC-

orientation is lower (4°), indicating a more ordered arrangement of microfibrils in the PC-orientation sample (Fig. 4(e)). These results demonstrate that the oriented CNFs act as effective crystallization templates, promoting controlled recrystallization of the PVA matrix and substantially enhancing its crystallinity and molecular alignment.

To further validate the mechanism of cellulose nanofiber orientation-induced crystallinity of PC-orientation, classical all-atom MD simulations were performed using the Forcite module with the COMPASS III force field. Comparison of the initial and equilibrated configurations of PVA chains in systems containing either oriented or disordered CNFs (Figs. 4(f) and 4(g) and Fig. S12 in the ESM) reveals that PVA molecules preferentially adopt an ordered arrangement between regularly spaced oriented CNFs, whereas PVA in the presence of disordered CNFs remains randomly packed even after extended MD relaxation. This behavior arises from the regular arrangement of hydroxyl groups on the CNFs surface, which provides a crystallization template for PVA chains. Hydrogen bonding between PVA hydroxyl groups and those on CNFs drives chain extension along the nanofiber axis, promoting ordered stacking and reducing conformational entropy. Moreover, the confined interstitial spaces between oriented CNFs impose physical constraints that suppress coiled, disordered states, favoring alignment parallel to the fiber axis and facilitating crystallization. RDF analysis further elucidates nearest-neighbor interactions (Fig. 4(h)). The first RDF peak of PVA adjacent to ordered CNFs occurs at a smaller interatomic distance, indicating tighter local packing and enhanced nucleation propensity. In contrast, PVA molecules within disordered CNFs voids exhibit a broader distribution and increased nearest-neighbor distances, reflecting delayed and less efficient crystallization due to the absence of orientation constraints.

RMSD analysis quantifies the freedom of PVA chain motion (Fig. 4(i)). PVA in the oriented CNFs system shows a marked RMSD reduction from 1.34 to 0.73 nm, whereas in the disordered CNFs system, the decrease is smaller (1.32 to 0.98 nm). This difference arises from the ordered CNFs template providing abundant hydrogen-bonding sites and strong orientational constraints, which stabilize PVA packing and suppress conformational fluctuations. MSD analysis further confirms the confinement effect (Fig. 4(j)). In disordered CNFs pores, PVA chains exhibit rapid MSD growth over time, indicating partial freedom of migration constrained primarily by spatial barriers. Conversely, in the oriented CNFs system, MSD growth is substantially slower, reflecting strong confinement due to synergistic effects of interfacial hydrogen bonding and orientation-induced local ordering. These findings collectively corroborate the RDF and RMSD results, demonstrating that ordered CNFs significantly restrict PVA segment mobility through combined effects of interfacial interactions and spatial confinement. Finally, Einstein diffusion analysis shows that the diffusion coefficient of PVA within the oriented CNFs system is $8.503 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$, markedly lower than $1.607 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ observed in the disordered CNFs system, quantitatively confirming the enhanced mobility suppression induced by CNFs orientation.

To verify the universality of the orientation-induced crystallization reinforcement strategy, cellulose nanocrystals (CNCs) and reduced graphene oxide (rGO) were selected as additional reinforcing phases to fabricate PVA-based composites, and their crystallization behavior and mechanical properties were

systematically examined. As shown in the XRD patterns (Fig. S13(a) in the ESM), both CNC/PVA and rGO/PVA composites exhibit stronger characteristic diffraction peaks than pure PVA, indicating that the incorporation of these fillers enhances the crystallization of the PVA matrix to some extent. However, in comparison with CNC and rGO, the CNF-reinforced composite displays markedly sharper and more intense diffraction peaks, reflecting a higher degree of crystallinity and a more ordered crystal orientation. This superior crystallization capability arises from the higher aspect ratio and abundant surface hydroxyl groups of CNFs, which strengthen hydrogen-bonding interactions and more effectively direct the ordered alignment of PVA chains, thereby facilitating the formation of well-defined crystalline domains.

The corresponding tensile stress-strain curves further substantiate these observations (Fig. S13(b) in the ESM). While pure PVA (N-PVA) exhibits relatively low strength and elongation, the addition of rGO or CNC significantly improves tensile strength, confirming that interfacial interactions and localized chain alignment contribute to mechanical reinforcement. Notably, the PC-orientation composite achieves a tensile strength of 44.42 MPa, surpassing that of both CNC/PVA (43.21 MPa) and rGO/PVA (39.02 MPa), while still retaining a high fracture strain. These results demonstrate that CNFs provide a superior synergistic effect in promoting matrix orientation-induced crystallization and enabling efficient stress transfer, thereby validating both the universality and the effectiveness of the proposed reinforcement strategy across different filler systems.

3.4 Potential applications

The deployment of UAVs is rapidly expanding across diverse sectors, including agricultural monitoring, logistics delivery, disaster relief, and infrastructure inspection. In these applications, the structural casing not only protects critical components but also directly governs flight endurance, impact resistance, and environmental adaptability (Fig. 5(a)). A fundamental challenge in UAVs design is achieving an optimal balance between lightweight construction and structural integrity. Reducing casing mass improves energy efficiency, extends flight duration, and increases payload capacity; however, insufficient strength or toughness may lead to cracking or damage under aerodynamic forces, drops, or collisions, ultimately compromising reliability and operational safety. PC-orientation composites, with their exceptional strength-to-weight ratio and low density, emerge as a promising candidate for UAVs casings and structural components. To demonstrate this potential, drone prototypes were fabricated using PC-orientation composites (Fig. 5(b)). Compared to conventional UAVs casings made from standard materials, the PC-orientation-based casings exhibit significantly enhanced specific strength and toughness, directly translating to improved take-off performance and extended flight endurance. Specifically, conventional UAVs casings (PA66 or ABS) display a specific strength and toughness of merely $38.1\text{--}43.5 \text{ MPa} \cdot \text{cm}^3 \cdot \text{g}^{-1}$ and $12\text{--}30 \text{ MJ} \cdot \text{m}^{-3}$, whereas PC-orientation composites achieve markedly higher values of $59.3 \text{ MPa} \cdot \text{cm}^3 \cdot \text{g}^{-1}$ and $34.74 \text{ MJ} \cdot \text{m}^{-3}$ (Fig. 5(c)). Importantly, UAVs employing PC-orientation casings outperform counterparts constructed from ABS materials in both take-off acceleration and sustained flight duration (Figs. 5(d) and 5(e)). These results demonstrate the potential of PC-orientation composites as lightweight structural materials for UAV applications. By combining reduced mass with superior mechanical performance, the developed composites exhibit clear advantages in terms of specific strength, toughness, and flight performance. However, considering the inherent moisture sensitivity of PVA-

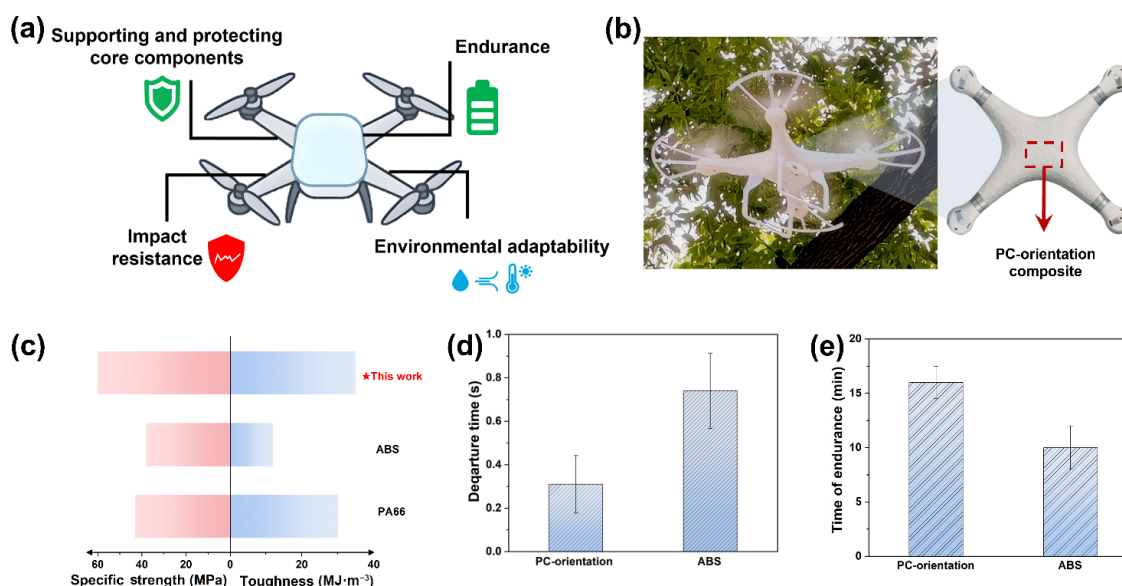


Figure 5 Potential applications of PC-orientation composites. (a) Wide-ranging applications of commercial UAVs. (b) UAV shell fabricated from PC-orientation composites. (c) Comparison of mechanical properties between PC-orientation composite shells and commercial UAV shell materials (ABS, PA66). (d) Comparison of take-off time with ABS material. (e) Comparison of sustained flight time with ABS material.

based materials, further studies on environmental durability, moisture resistance, and protective surface treatments are required before practical outdoor deployment.

4 Conclusions

In summary, we present a strategy for regulating matrix crystallinity via cellulose nanofiber orientation-induced crystallinity within the PVA matrix, yielding a lightweight FRPs with high mechanical strength and unprecedented toughness. Detailed structural characterization and theoretical calculations reveal that oriented cellulose nanofibers act as potent crystallization inducers. By forming crystalline surfaces compatible with the PVA lattice, they provide ordered nucleation sites, lower the crystallization barrier, and substantially increase matrix crystallinity, thereby dramatically enhancing toughness. Moreover, the internal anisotropic architecture of the composite effectively dissipates stress, endowing the material with extraordinary mechanical performance. Consequently, the resulting polymer-cellulose composite exhibits exceptional mechanical strength (44.42 MPa) and ultra-high toughness (34.74 MJ·m⁻³) at an ultralow density (0.75 g·cm⁻³), establishing a new benchmark for fiber-reinforced polymer composites. This work offers valuable insights for designing lightweight FRPs with synergistically enhanced strength and toughness, paving the way for broad practical applications.

Electronic Supplementary Material: Supplementary material (Figs. S1–S9) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908990>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing 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.

Author contribution statement

J. H. L.: Methodology, investigation, formal analysis, writing an original draft. X. Z. W.: Methodology, investigation, formal analysis, validation, visualization. Z. J. Y.: Methodology, investigation, validation. Z. H. L.: Methodology, investigation, writing – review & editing, supervision. S. L.: Data curation, formal analysis, visualization. Y. Q. W.: Investigation, writing – review & editing, supervision. Y. Q.: Methodology, investigation, writing –review & editing, supervision, funding acquisition.

Use of AI statement

None.

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