

Bioinspired nano-fishnet structural construction for ultra-high dynamic toughness of carbon nanotube composite films

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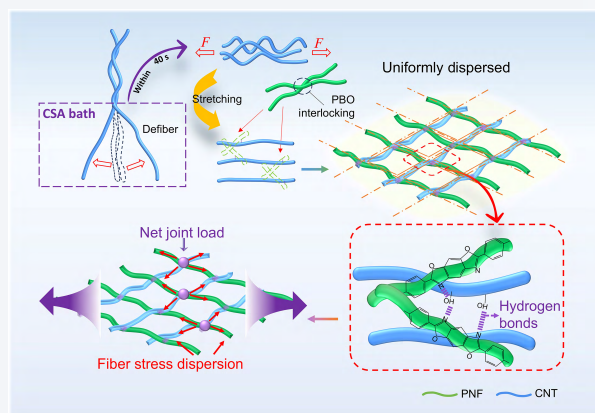
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ABSTRACT: Structure design and interlocking construction are expected to generate desirable mechanical properties of advanced carbon nanotube (CNT) film for their impact protective applications. However, inadequate orientation and weak interlocking network often suffer from the large difference between the measured and theoretical mechanical properties. Here, we introduced a bioinspired nano-fishnet construction strategy to accurately control the alignment and interlocking state of CNT in the film. The strategy creates an aligned and densified structure as well as strong interlocking network via coordinated regulation of stretching and p-phenylene benzobisoxazole (PBO) infiltration. The developed PBO-CNT film shows excellent dynamic mechanical properties with a dynamic tensile strength of 4.92 ± 0.2 GPa and a toughness of 118.96 ± 9.78 MJ·m⁻³ with the ability to support weights up to 166,667 times its own. In addition, the relationship of structural regulation strategies and enhancement mechanisms of composite PBO-CNT film has been further revealed. This work establishes a structural design paradigm for optimizing the dynamic performance of carbon-based materials in protection management.



KEYWORDS: carbon nanotube film, bioinspired nano-fishnet, dynamic strength, toughness, enhancement mechanism

1 Introduction

Carbon nanotube (CNT) films are two-dimensional (2D) advanced nanomaterials composed of densely intertwined CNTs, offering notable advantages in lightness, flexibility, and specific surface area. Their scalable manufacturing and ease of integration make them promising candidates for impact-resistant composite applications [1–3]. However, the widespread application of CNT films is limited by their insufficient mechanical strength. Typical values are below 1 MPa in fracture strength, 5 MPa in modulus, and approximately 500 kJ·m⁻³ in toughness [4–6]. These deficiencies originate from structural shortcomings such as random CNT alignment, abundant entanglements, inter tube gaps, residual catalyst particles, and weak

van der Waals interactions between tubes [7, 8]. Various structural optimization approaches have been explored to enhance alignment and packing density as well as to reduce defects. These approaches include mechanical stretching [9], liquid-induced densification [10], and ultrasonic treatment [11]. Nevertheless, the mechanical improvements achieved are still modest relative to theoretical predictions. This is largely attributed to the inherent structural complexity of CNT films. Single mode processing struggles to control multiple structural factors including orientation, density, interfacial stress transfer, and defect distribution simultaneously [12–14]. For instance, stretching can improve alignment but may also lead to over elongation and fracture [15]. Methods using liquid media rely on specific solvents and lack reproducibility [16–18], while ultrasonic processing may introduce new defects or even fragment CNTs [19, 20]. Thus, conventional post processing techniques struggle to comprehensively optimize the film structure while preserving its integrity [21, 22].

Biological hierarchical architectures, such as those in pangolin scales and silk fibers, have evolved hierarchical microstructures with graded distributions of strength and modulus, achieving a balance

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between strength and toughness [23, 24]. These hierarchical architectures facilitate efficient load transfer and strong interfacial interactions, which are highly desirable in engineered composites [25, 26]. Inspired by the hierarchical architecture of silk fibers, a biomimetic nano-fishnet structural strategy is proposed to construct an interconnected network. Strong interfacial interactions in such a network allow efficient multi path load transfer, excellent damage tolerance, and simultaneous improvement of strength and toughness, thus overcoming the weak van der Waals interfaces in CNT assemblies [27–29]. In addition, previous work on CNT fibers has demonstrated that combining progressive stretching with p-phenylene benzobisoxazole (PBO) infiltration can improve interfacial bonding, alignment, and densification, thereby yielding enhanced mechanical performance [30, 31]. Therefore, PBO nanofibers (PNFs) emerge as a suitable candidate for constructing a chemically cross-linked and network-like reinforcement phase which represents a direct and effective strategy, not only due to their favorable intrinsic strength and modulus but also because they can replicate the critical mechanics of a nano-fishnet.

To date, fundamental understandings of the interface engineering and interfacial reinforcement mechanisms between CNTs and PBO in thin-film structures are still limited. The dynamic mechanical behavior (including stress-strain response and damage evolution) of such composite films is largely uninvestigated. This knowledge gap impedes the development of CNT films for applications requiring high dynamic performance, such as impact protection. By forming a dense and interconnected cross-linking network within the aligned CNTs, PNFs effectively mimic the natural structural design, providing continuous stress redistribution, suppressing crack propagation, and thereby providing a feasible route to improve the strength, toughness, and damage tolerance of CNT based materials.

Herein, we proposed a bioinspired nano-fishnet strategy that integrates precisely controlled stretching with *in-situ* PNF interlocking to fabricate strong and tough PBO-CNT composite films. This approach addresses the key structural limitations of CNT films. (1) A tailored stretching process in chlorosulfonic acid (CSA) reduces entanglements and defects, producing a aligned and densified CNT network (film density increased from 0.56 to 1.19 g·cm⁻³). (2) The stretched and opened structure enables uniform infiltration and distribution of PNFs throughout the film, forming a strong chemically crosslinked nano-fishnet that enhances stress transfer and interfacial cohesion. (3) Synergistic combination of physical alignment and chemical interlocking yields excellent dynamic mechanical properties, with tensile strength reaching 4.92 ± 0.2 GPa and toughness up to 118.96 ± 9.78 MJ·m⁻³, increases of 3954.39% and 1060.59%, respectively, compared to the pristine CNT film. This work elucidates the reinforcement mechanisms of PBO-interlocked CNT films under dynamic loading and provides a scalable and controllable approach toward high-performance protective nanomaterials, paving the way for their potential commercial application in advanced impact-protection systems.

2 Experimental

2.1 Materials

CNT films were supplied by Suzhou Jiedina Nano Technology Co., and PBO fibers were provided by Zhongke Jinqi New Materials Technology Co., Ltd. CSA (99.5%), acetone (ACE, 99.5%),

trifluoroacetic acid (TFA, 99.5%), and isopropanol (IPA, 99.7%) were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Methanesulfonic acid (MSA, 98%) was obtained from Shanghai McLean Biochemical Technology Co., Ltd. Deionized water was prepared in the laboratory.

2.2 Mechanical stretching strategy for CNT films

Precise regulation of stretching cycles and ratio yielded aligned and densified CNT films, with the core goal of synergizing orientation and densification. Multiple stretching cycles promoted gradual nanotube orientation and reduced disordered entanglement, while the stretching ratio controlled packing density to avoid fracture (excessively high ratio) or insufficient orientation (excessively low ratio). Each stretching cycle was completed within 40 s to maintain consistent speed, preventing orientation disorder and stress concentration caused by local speed differences.

The CNT films were immersed in CSA solution for 20 s. Solution infiltration induced a volume expansion effect, which weakened the van der Waals forces between CNTs. After completing stretching within 40 s, the films were immediately cleaned in an acetone coagulation bath and rinsed with deionized water to remove residual CSA. Subsequent post-treatments were performed for structural optimization. The films were stacked on polytetrafluoroethylene (PTFE) sheets and hot pressed at 150 °C and 1 MPa for 2 h, where thermo-mechanical coupling promoted the dense packing of CNTs and enhanced inter tube contact. Thereafter, the pressure of 1 MPa was maintained for 12 h at room temperature to realize slow structural relaxation and stabilization of the films. Ultimately, CNT films with uniform orientation, dense structure, and smooth surface were prepared, and the film was named the CSA-CNT film.

The total stretching ratio was initially set at 40%, and mechanical stretching experiments were performed for 1, 2, 3, and 4 cycles, with the corresponding stretching ratios of 40%, 20%, 13%, and 10%, respectively. The samples were denoted as 1-40, 2-20, 3-13, and 4-10. Subsequently, the number of stretching cycles with the optimal mechanical properties was selected. On this basis, experiments with different total stretching ratios were designed, specifically 40%, 60%, 80%, 100%, and 120%, and the samples were labeled as 2-40, 2-60, 2-80, 2-100, and 2-120, respectively.

2.3 Preparation of nano-fishnet PBO-CNT composite film

A certain amount of PBO fibers were immersed in acetone for cleaning and then dried, and then dissolved in a mixed solvent of TFA and MSA premixed at a volume ratio of 1:1. The solution was continuously stirred at 25 °C and 600 rpm for 24 h to obtain a homogeneous PNFs solution. Mechanically pre-stretched CNT films were immersed in the PNF solution for a certain period of time, followed by repeated gradient solvent exchange in IPA and thorough rinsing with deionized water. The films were then placed on PTFE sheets, hot pressed at 150 °C and 1 MPa for 2 h, and slowly cooled to room temperature in the furnace at 1 MPa for 12 h, yielding uniform and compact PBO-CNT composite films.

PBO solutions with different concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mg·mL⁻¹) were prepared, with a fixed treatment time of 30 min. The samples were named 0.2P30, 0.4P30, 0.6P30, 0.8P30, and 1.0P30, respectively. The optimal concentration for improving mechanical properties was determined through mechanical testing. To investigate the effect of different treatment time on the mechanical properties of composite film, the treatment time was set

to 20, 25, 30, 35, and 40 min, with the PBO solution concentration fixed at 0.6 mg·mL⁻¹. The corresponding samples were named 0.6P20, 0.6P25, 0.6P30, 0.6P35, and 0.6P40.

2.4 Characterization

The surface morphologies and failure morphologies of the CNT films and PBO-CNT composite films were observed using a scanning electron microscopy (SEM, Hitachi Regulus 8100) at an accelerating voltage of 10 kV. Five distinct regions were selected for observation on each sample. The structural properties of the CNT and PBO-CNT composite films were characterized by a laser confocal Raman spectrometer (LabramHR 800, Horiba Jobin Yvon). Tests were performed in the wavenumber range of 100–3000 cm⁻¹. To ensure the reliability of the results, full-spectrum scans were conducted at five randomly selected positions. Thermal stability of the films was characterized using a thermogravimetric analyzer (TG209 F1, Netzsch). Samples were heated from 30 to 900 °C at a constant heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. X-ray photoelectron spectrometer (K-Alpha, Thermo Fisher Scientific) was employed to analyze the impurities in the CNT films. The chemical structures of CNT and PBO-CNT composite films were characterized by Fourier transform infrared (FTIR) spectroscopy (Nicolet iS5, Hitachi) with a wavenumber range of 1100–1800 cm⁻¹, a resolution of 4 cm⁻¹, and 32 scans. Static tensile mechanical properties were tested using a universal testing machine (UTM, Instron 3365). The CNT films were cut into standard rectangular specimens of 20 mm × 1 mm, with a gauge length of 10 mm and a crosshead speed of 2 mm·min⁻¹. Each sample was tested 10 times repeatedly. The cross-section of the specimen was measured and calculated based on SEM images. Film density was measured using a high-precision analytical balance (XPR2U, Mettler Toledo), calculated as the ratio of film mass to its volume. Electrical conductivity was characterized by a four-point probe system (ST2558B-F01, Suzhou Jingge Electronics Co., Ltd.). Electromagnetic interference shielding effectiveness was measured using a vector network analyzer (N5230A, Agilent Technologies). The dynamic mechanical properties of the CNT films and PBO-CNT composite films were tested with a split Hopkinson pressure bar (SHTB, SN-SHPB-P06, China Dimeitai Precision Technology Co., Ltd.) (Fig. S1 in the Electronic Supplementary Material (ESM)), and the gauge length was set to 5 mm. Tensile tests were performed at various strain rates, and each sample was tested 10 times.

3 Results and discussion

3.1 Bioinspired nano-fishnet structure construction and characterization

Based on the synergistic construction strategy of orientation regulation and uniform PBO interlocking, the as-prepared PBO-CNT composite film achieves notable improvement in dynamic toughness. The optimization of such macroscopic mechanical properties originates from the ordering of multiscale structures and the strong interfacial interactions within the composite film. Aiming at the key issues of CNT films, such as orientation disorder, weak interfacial bonding, and stress concentration, a multiscale synergistic design strategy of precision orientation regulation–interfacial interlocking construction–molecular interaction enhancement is proposed. Through the stepwise regulation of CSA protonation induction, mechanical stretching,

and *in-situ* compounding with PNFs, the directional construction of the nano-fishnet-like dense interlocking structure is successfully achieved (Fig. 1(a)).

The pristine CNT films exhibit an entangled and disordered arrangement, accompanied by numerous structural defects and impurities (Fig. 1(b)(i)). This disordered structure directly accounts for the poor mechanical properties and high susceptibility to stress concentration in CNT films. To address this issue, protonation induction treatment was performed via CSA solution immersion, enabling the gradual disentanglement and dispersion of the originally entangled CNT bundles [32]. On this basis, directional mechanical stretching was applied. Under the synergistic effect of chemical disentanglement and physical stretching, the CNTs transformed from random distribution to an oriented arrangement along the stretching direction, resulting in a distinct improvement in the orientation order inside the film (Fig. 1(b)(ii)). Meanwhile, local defects and stress concentration sites caused by disordered arrangement were effectively reduced, constructing a continuous and aligned “net rope” primitive framework for the nano-fishnet structure.

After immersing the well-aligned CNT films in the PBO solution, PNFs, relying on their good dispersibility and high aspect ratio, uniformly penetrate and fill the gaps and defect regions of the CNT framework, forming an interpenetrating mesoscopic interlocking structure with the CNTs. These structures act as the “node” units of the nano-fishnet, ultimately assembling into a continuous and dense interlocking structure, which is shown as the red lines in Fig. 1(b)(iii). At the molecular scale, hydrogen bonds form between the hydroxyl groups on the CNT surface and the nitrogen (N) atoms in the PNF molecular chains, which enhances the interfacial bonding strength between the two phases and suppresses CNT slippage and local stress concentration.

This composite system achieved cross-scale synergistic optimization of macroscopic ordered orientation, mesoscopic interlocking cross-linking, and molecular interfacial reinforcement, facilitating the stable formation of the nano-fishnet structure. Meanwhile, it leveraged the intrinsic high strength and high modulus advantages of CNTs, and realized the simultaneous improvement of the mechanical properties of the composite films by virtue of PNF filling and interlocking. The tensile strength, Young’s modulus, and toughness of the PBO-CNT composite films reached 1.94 ± 0.08 GPa, 62.71 ± 2.82 GPa, and 71.5 ± 7.9 MJ·m⁻³, which were 27.5, 8.0, and 5.1 times those of the pristine CNT films, respectively (Figs. 1(c) and 1(d)). The electrical conductivity and electromagnetic shielding efficiency of the PBO-CNT composite film reached 3.43×10^5 S·m⁻¹ and 54.2 dB, which were 5.9 and 1.2 times higher than those of the pristine CNT film, respectively (Fig. S2 in the ESM). The performance of the composite films was superior to that of the pristine CNT films in multiple dimensions (Fig. 1(e)).

The notable enhancement in the mechanical properties of the PBO-CNT composite films was essentially the result of precise regulation of the microstructure. In the pristine CNT films, the CNT bundles exhibited a random and disordered network structure with numerous voids and impurities between the tubular structures, resulting in a relatively loose arrangement. The CNT bundles were entangled with each other, forming a typical “network-like” morphology (Figs. 2(a) and 2(d)). Following CSA treatment and mechanical stretching, the CNTs were aligned directionally along the stretching direction (Fig. 2(b)). The disordered cross

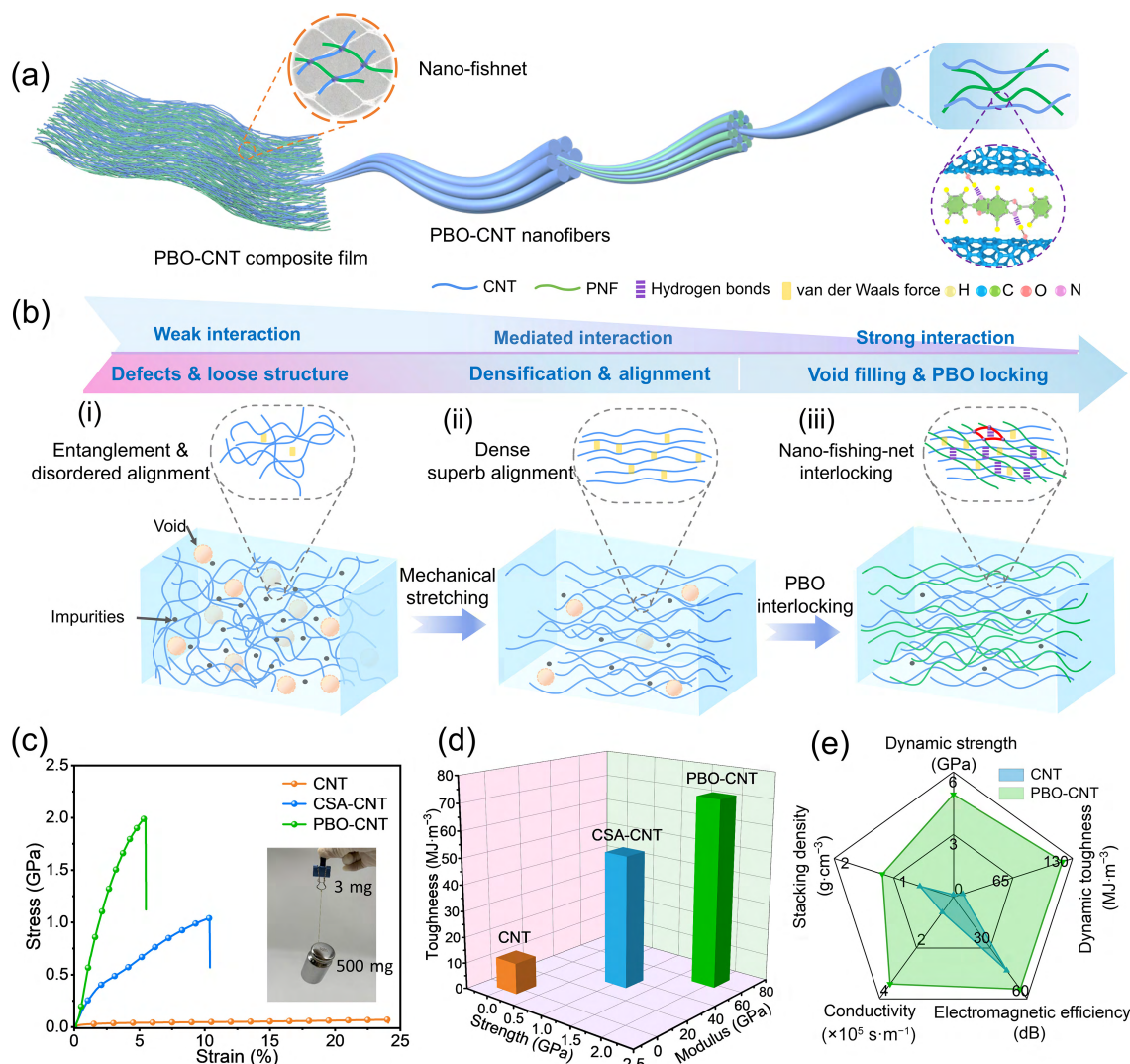


Figure 1 Design of PBO-CNT composite films using mechanical stretching and PBO crosslinking strategies. (a) Schematic diagram of multiscale structure reinforcement. (b) Schematic diagrams of fiber structures during sample preparation: (i) entangled and disordered arrangement, (ii) dense and ordered arrangement, and (iii) nano-fishing-net structured crosslinking. (c) Static stress-strain curve. (d) Comparison of quasistatic tensile strength, Young's modulus, and toughness. (e) Comprehensive performance enhancement plot.

points and voids were effectively compressed, achieving improved densification (Fig. 2(e)). The film density increased from 0.56 to 0.94 g·cm⁻³, thus forming a regular and dense CNT framework (Fig. 2(g)). The I_G/I_D ratio of the CSA-PBO film reached 8.33, higher than that of the pristine film (Fig. 2(i)). This indicates that CSA treatment and stretching reduce the structural defect density of the CNT film.

PBO fibers were protonated in an acidic mixed solution to obtain nanofibers (Fig. S3 in the ESM) [33–35]. These nanofibers, with diameters ranging from 6 to 18 nm, were composited with nanoscale CNTs. The X-ray photoelectron spectroscopy (XPS) spectrum of the PBO-CNT composite films exhibited new peaks at 287.1 (–C–N) and 289.1 eV (–C=N), confirming the successful incorporation of PNFs into the CNT network (Fig. 2(j)). The PNFs uniformly penetrated and filled the remaining voids in the CNT framework (Fig. 2(c)). The cross-sectional morphology of the PBO-CNT film shown in Fig. 2(f) is denser than that of the CSA-CNT film in Fig. 2(e), confirming that PNFs penetrated into the interior of the film. The density of the composite film increased from 0.94

to 1.19 g·cm⁻³ (Fig. 2(g)), with PNF loading of approximately 21%. The evolutionary process of the film from random disorder to densification can be directly observed in Fig. 2(h). During the stretching process, the pores within the CNT films were further compressed, while residual impurities in the pristine material were effectively removed and structural defect sites were reduced. After cross-linking with the composited PNFs, uniform and compact PBO-CNT composite films were formed. The I_G/I_D ratio of the film was close to 0 (Fig. 2(i)), which may be attributed to the opaque surface of the composite film after PBO incorporation, indicating that PNFs have been uniformly attached to the surface of the CNT film [36]. Furthermore, the characteristic vibrational peak of hydroxyl groups in the FTIR spectrum underwent a red shift from 3408 cm⁻¹ for pristine CNT films to 3385 cm⁻¹ for the composite films (Fig. 2(k)). This phenomenon demonstrates the formation of hydrogen bonding interactions between hydroxyl groups on the CNT surface and the molecular chains of PBO. PNFs form a dense coating on the CNT surface, achieving effective interfacial bonding through hydrogen bonds, π – π interactions, and physical

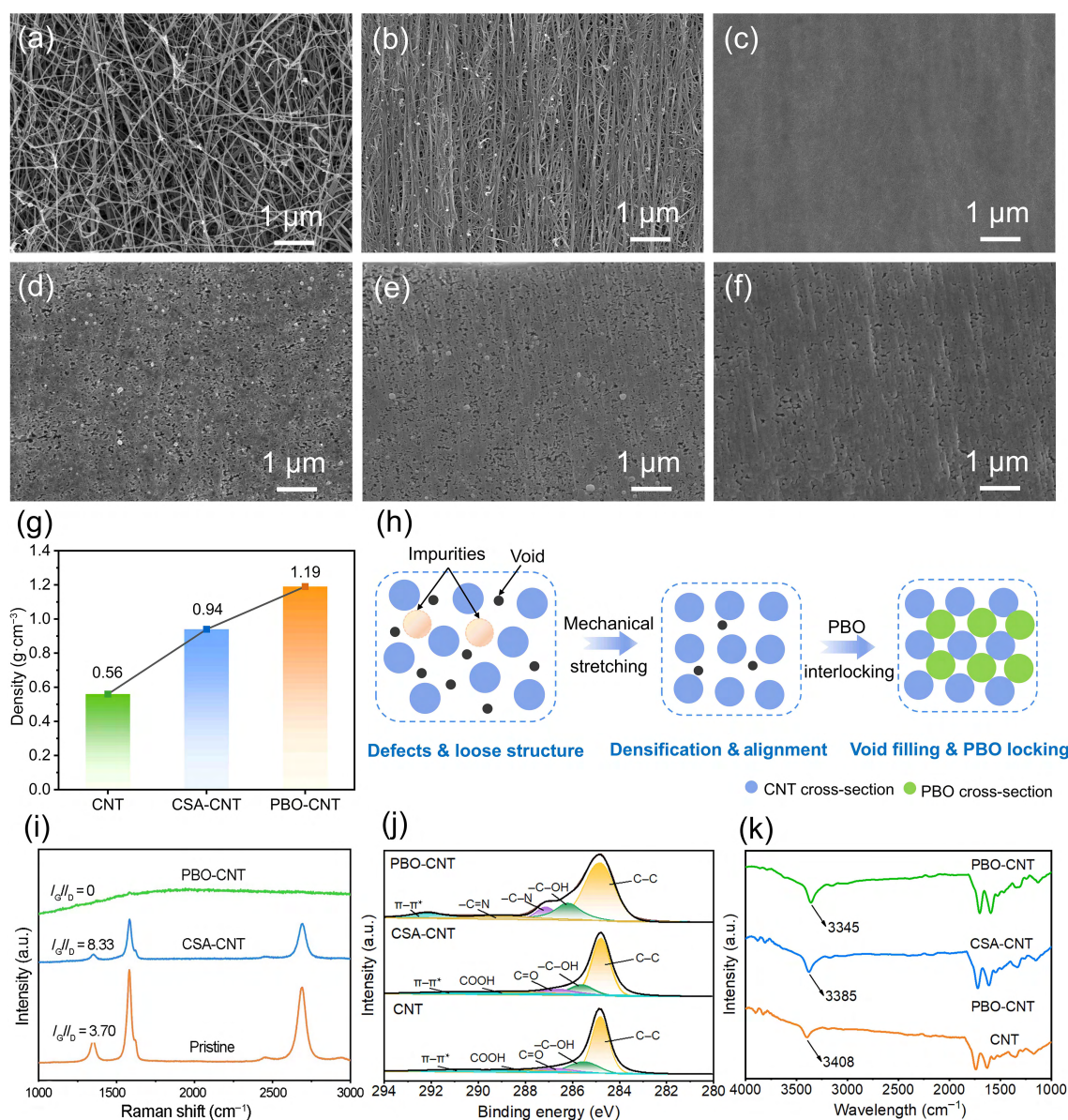


Figure 2 Structural characterization and properties of CNT films with different treatments. ((a)–(c)) Surface morphologies of different CNT films. ((d)–(f)) Cross-sectional morphologies of different CNT films. (g) Density variation. (h) Schematic diagram of film cross-sectional variation. (i) Raman spectra. (j) XPS spectra. (k) FTIR spectra.

interlocking [37], providing a chemical guarantee for efficient load transfer and structural stability.

3.2 Mechanical stretching-induced alignment and densification

Mechanical stretching, as one of the key strategies for structural regulation, directly determines the orientation arrangement, densification degree, and defect state of CNTs inside the film, thereby governing their macroscopic mechanical behavior. By tuning the stretching cycles and stretching ratio, the randomly entangled and disorderly oriented CNT bundles in the original film were disentangled and aligned, achieving an ordered orientation, forming a continuous, dense, and defect-free interconnected network with improved uniformity of surface morphology (Figs. 3(a)–3(c)).

Raman spectroscopy results quantitatively reveal the evolution of

this structure. The $I_G/I_{G\perp}$ ratio of the CNT films increased from 1.02 to 1.48 (Fig. 3(d)), and the I_G/I_D ratio rose from 3.02 to 9.41 (Fig. 3(e)), confirming a notable improvement in the alignment degree of the film and a reduction in disordered carbon bond defects. The intensity of the I_D peak in the Raman spectra (Fig. S5 in the ESM) further indicates a reduction in defects in the sp^2 carbon structure of the CNTs [36], while the I_G peak, corresponding to the ordered vibrational mode of sp^2 -hybridized carbon, became more distinct. XPS analysis was performed in the S 2p and Cl 2p regions of the films. Strong peaks corresponding to S and Cl appeared in the films after CSA treatment (Figs. S4(a) and S4(b) in the ESM), and the C/O ratio of the films decreased from 26.72 to 9.43 (Fig. S6(a) in the ESM). These results indicate that the wetting effect of CSA altered the surface chemical environment of the CNT films, weakened bundle agglomeration, and provided a chemical basis for the stretching-induced rearrangement of CNTs [32]. The intensity of the Fe 2p signal decreased (Fig. S6(b) in the ESM). Combined

with the TGA results (Fig. 3(f)), the content of amorphous carbon and iron-based catalyst impurities decreased from 8.2 wt.% to 5.3 wt.%, confirming that the stretching process contributed to impurity removal and defect purification.

This finding was further supported by energy dispersive X-ray

spectroscopy (EDS) elemental mapping (Fig. S7 in the ESM). Such impurity removal facilitated interactions between CNTs and promoted the densification of the films. In addition, the X-ray diffraction patterns of CNT films subjected to different mechanical stretching treatments (Fig. S8 in the ESM) showed a consistent

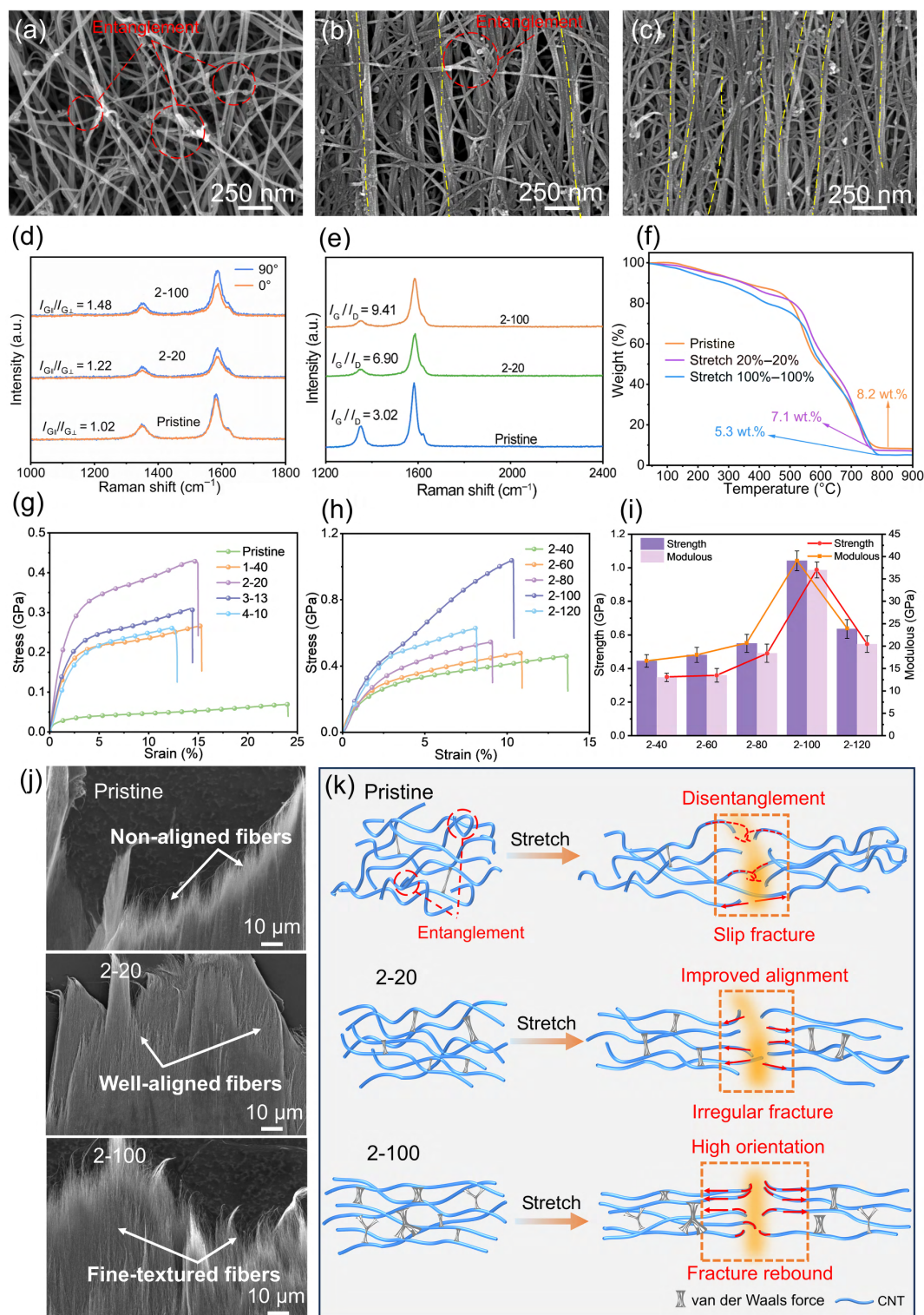


Figure 3 Structural characterization and properties of CNT films with different mechanical stretching treatments. (a) Surface morphology of untreated CNT films. (b) Surface morphology of 2-20 CNT films. (c) Surface morphology of 2-100 CNT films. (d) Polarized Raman spectra. (e) Raman spectra. (f) TGA curves. (g) Stress-strain curves at different stretching cycles. (h) Stress-strain curves at different stretching ratios. (i) Histograms of fracture strength and modulus at different stretching ratios. (j) Static mechanical fracture morphologies of CNT films. (k) Fracture mechanisms of CNT films under static loading.

characteristic peak at $2\theta = 26.5^\circ$ (0.334 nm) [38], corresponding to the (111) reflection of CNTs. No new functional groups were observed in the FTIR spectra of the films after different treatments (Fig. S9 in the ESM), indicating that CSA mainly densified and aligned CNTs through the synergy of its excellent dispersibility and mechanical stretching, without altering the types of surface functional groups of CNTs.

A single high-strain cycle (1-40) induced a pronounced lag between network rearrangement kinetics and the applied deformation rate, leading to localized structural instability and premature crack initiation, which ultimately constrains the mechanical performance. Sequential low-strain stretching (3-13 and 4-10) mitigate instantaneous damage but lack the driving force necessary to overcome intertube interactions and entanglements, thus failing to trigger effective network rearrangement. The newly formed intertube contacts under such mild conditions remain metastable after repeated stretching, resulting in insufficient densification and compromised mechanical properties [10, 39]. In optimal contrast, a two-step stretching strategy employing 20% strain per cycle provides sufficient driving force for structural rearrangement in each step while allowing intermediate structural relaxation. This dynamic balance between orientation enhancement and defect healing positions the two-step 20% strain protocol as the most effective route for maximizing overall mechanical performance (Fig. 3(g)).

Under the condition that the number of stretching steps is fixed at two, the stretching ratio is gradually increased. Continuous stretching improves the orientation of CNTs along the loading direction, enhances the densification degree of the film, and strengthens intertube interactions, thus effectively improving the load transfer efficiency. The optimal mechanical properties are achieved under 100% double stretching, with the fracture strength and modulus reaching 1.04 ± 0.06 and 36.99 ± 1.80 GPa, which are increased by 149.28% and 5420.90% compared with the sample under 20% stretching, respectively. When the stretching ratio exceeded 100%, the excessive force field induced the destruction of the CNT network structure, resulting in a decline in mechanical properties (Figs. 3(h) and 3(i)). This confirms that precise regulation is crucial for structural optimization, and excessive manipulation will lead to structural failure.

The evolution of fracture morphology and fracture mode intuitively reveals the intrinsic correlation between structure and mechanical behavior. From the fracture morphology (Fig. 3(j)) and fracture mechanism (Fig. 3(k)) of the films under static mechanical failure, it can be observed that the pristine CNT film exhibits a fracture mode dominated by the untangling and sliding of entangled bundle structures. The CNTs are disorderly arranged with weak intertube interactions. Under external loading, interbundle sliding readily occurs accompanied by the unraveling of entangled structures, ultimately leading to film fracture. In the 2-20 film subjected to low-ratio secondary stretching, the CNT orientation is improved, yet local inhomogeneity still exists in bundle arrangement, resulting in a transition to an irregular fracture mode. During fracture, sliding of some incompletely oriented bundles occurs, and the overall fracture behavior is heterogeneous due to the variation in orientation. For the 2-100 film with high-ratio secondary stretching, the CNT bundles achieve highly ordered alignment, with dense packing and enhanced intertube interactions. Obvious fiber rebound occurs after film fracture, and load can be efficiently transferred along the oriented pathways, fully exerting the mechanical properties of CNTs.

3.3 Nano-fishnet structure enhancement of the mechanical performance

Based on the aligned and dense CNT films, PNFs were introduced, and the dispersion concentration and treatment time were synergistically regulated to construct an interfacial interlocked nano-fishnet composite structure (Fig. 4(a)). PNFs can evenly penetrate into the pores and defect areas of the CNT skeleton, and form a bridging structure between adjacent CNT bundles, thereby constructing connecting nodes. Similar to the network system composed of network cables, nodes, and mesh holes in the macroscopic fishing net structure, the oriented CNT bundles are the main bearing unit, and the nodes induced by PNFs are used as the connection units, which are jointly assembled to form a continuous interlocking network structure. The resulting PBO-CNT composite films exhibited a uniform and dense surface (Fig. 4(b)). The EDS analysis was performed on the surface and cross-section of the PBO-CNT composite films, where the presence of N element confirmed the successful compositing of PBO and CNT films (Figs. 4(c) and 4(d)).

The PBO-CNT composite films exhibited optimal mechanical properties when the PBO concentration was $0.6 \text{ mg}\cdot\text{mL}^{-1}$ (Fig. 4(e)). At this concentration, PNFs can penetrate the gaps between CNTs and form efficient hydrogen bonding interactions with CNTs. Excessively high concentration leads to greater PNF loading, which triggers agglomeration of PNFs between CNTs, disrupts the original oriented arrangement, and consequently reduces the interfacial bonding efficiency and tensile strength. The tensile strength of the composite films reached the optimal value after 30 min of treatment (Figs. 4(f) and 4(g)), at which point PNFs can penetrate and uniformly cover the surface of the CNT films, constructing a strong synergistic interface through physical interlocking and molecular hydrogen bonding. Prolonging the treatment time caused excessive deposition of PNFs in local areas, damaging the continuity of the nano-fishnet structure and the load transfer pathways. After regulating at a PBO concentration of $0.6 \text{ mg}\cdot\text{mL}^{-1}$ and a treatment time of 30 min, the tensile strength and Young's modulus of the composite film reach 1.94 ± 0.08 and 62.71 ± 2.82 GPa, respectively, achieving a secondary leap in mechanical properties.

To further clarify the strengthening effect of structural modification on the mechanical properties of CNT composite films, a split Hopkinson pressure bar was employed to investigate the dynamic mechanical properties of CNT films with different treatments under high strain rates, and the dynamic mechanical properties of the CNT films were evaluated using typical stress wave curves (Fig. S1 in the ESM). The samples fractured when the dynamic stress reached the peak value, and the strain rate was maintained constant during fracture. Under high strain rate loading conditions, a linear positive correlation exists between strain rate and impact velocity (Fig. 4(k)).

There were differences in the stress-strain curves of the CNT films under high strain rate and quasi-static loading conditions. Under high strain rate conditions, no sudden stress drop occurred after reaching the peak (Figs. 4(h) and 4(i)). This was attributed to the insufficient time for the CNT film to undergo rate-sensitive conformational adjustments, such as unravelling, reorientation, and sliding of CNTs, which triggered a cascading fracture mechanism of individual CNTs. As a result, the modulus was enhanced, and the slope was also increased compared with the quasi-static stress-strain curve [40]. Under quasi-static loading, the carbon

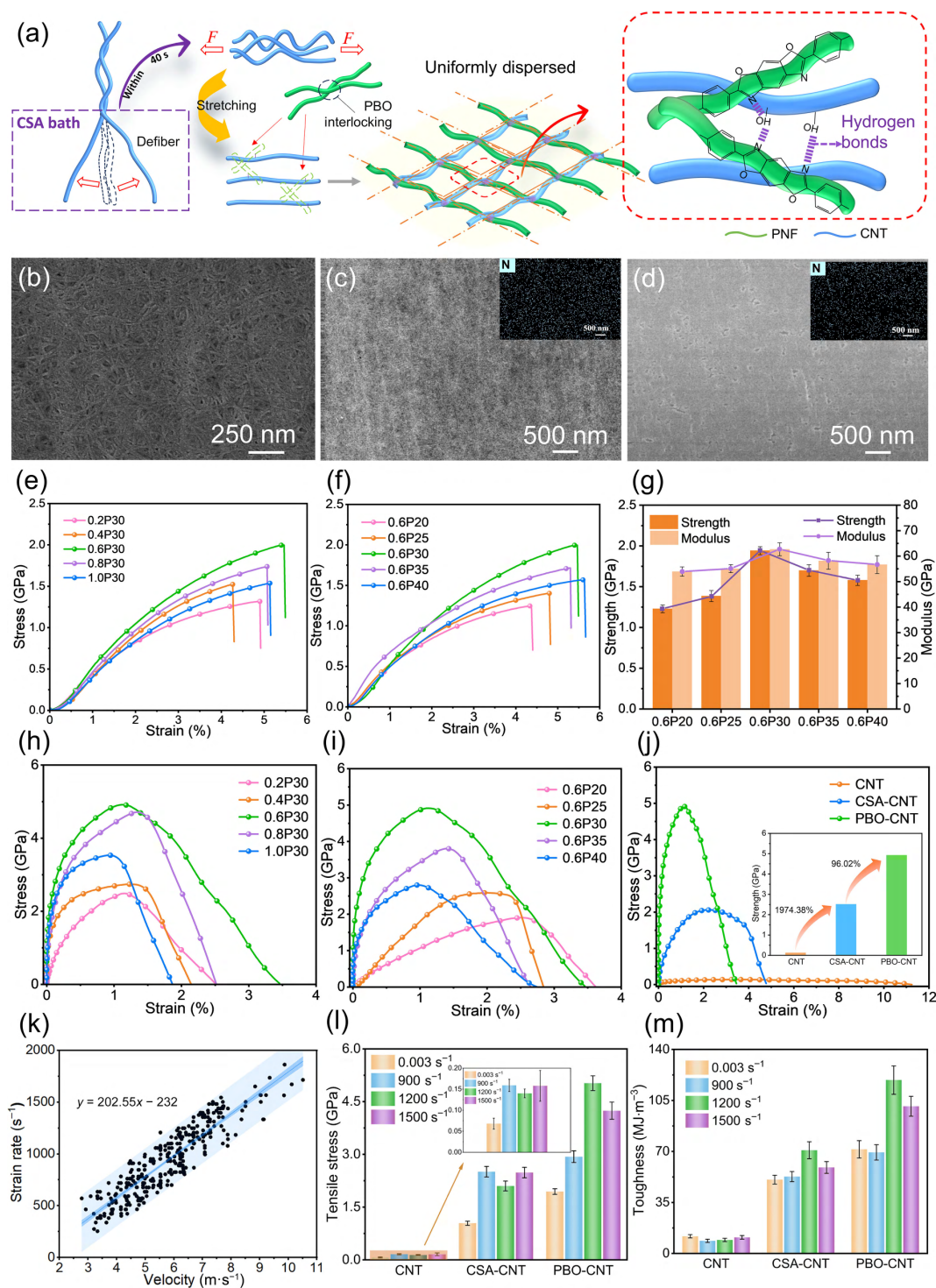


Figure 4 Structural characterization and properties of PBO-CNT films. (a) Schematic diagram of PBO cross-linking mechanism. (b) High-magnification surface morphology of PBO-CNT films. (c) and (d) Morphology and full-area energy dispersive spectroscopy of PBO-CNT films: (c) surface morphology and (d) cross-sectional morphology. (e) and (f) Static stress-strain curves of PBO-CNT films: (e) different PBO concentrations and (f) different PBO treatment durations. (g) Fracture strength and modulus of PBO-CNT films with different PBO treatment durations. (h)–(j) Dynamic stress-strain curves of PBO-CNT films: (h) different PBO concentrations, (i) different PBO treatment durations, and (j) comparison of tensile strength. (k) Impact velocity versus strain rate curve. (l) Comparison of tensile strength of CNT films at different strain rates. (m) Comparison of dynamic toughness of CNT films at different strain rates.

nanotube film has sufficient time for conformational adjustment. This process dissipates a large amount of energy, resulting in a relatively low modulus and a gentle slope of the curve. Meanwhile, after infiltrating into the pores of the CNT network, PNFs form physical crosslinking points, which greatly restrict the relative

sliding between CNTs. The failure mechanism of the CNT film changes from intertube sliding to fiber fracture, resulting in a decrease in the elongation at break of the film. The synergistic structural optimization strategy combining CSA mechanical stretching and PBO compositing enabled a remarkable cascading

improvement in the dynamic mechanical properties of the CNT films (Fig. 4(j)). The dynamic strength of the CNT films after CSA stretching treatment reached 2.51 ± 0.14 GPa at a strain rate of approximately 900 s^{-1} (Fig. S10 in the ESM). The dynamic strength of the CNT films cross-linked with PNFs was increased to 4.92 ± 0.2 GPa (Fig. S11 in the ESM). At a strain rate of 1200 s^{-1} , its dynamic strength was 40.5 times that of the pristine CNT films and 1.96 times that of the CSA-CNT films (Fig. 4(l)), with a dynamic toughness as high as $118.96 \pm 9.78 \text{ MJ}\cdot\text{m}^{-3}$ (Fig. 4(m)). This comparison was a direct demonstration of the critical role of PBO in enhancing strength, toughness, and structural stability. Under impact at a high strain rate of 1500 s^{-1} , the sliding between CNTs was suppressed, and stress cannot be effectively dissipated via sliding. Consequently, a large number of molecular chains and CNTs reached their fracture limit almost simultaneously, triggering brittle overall fracture, which led to the degradation of the material's mechanical properties under such circumstances [41, 42].

The composite films exhibited excellent structural stability and load-bearing potential. No cracks or delamination were observed after deformation treatments such as winding and folding (Fig. S12 in the ESM). A film weighing only 3 mg could bear a 500 g of object (166,667 times its own weight) (Fig. 1(c)), which fully demonstrates its outstanding mechanical properties.

Under dynamic tensile loading, relative sliding and disordered misalignment of fibers were observed on the fracture surface of the pristine CNT films (Fig. 5(a)). Finite element simulation results indicate that the material failure was dominated by inter fiber sliding (Fig. 5(e)(i)), where stress was dispersed and could not be effectively transferred, resulting in low mechanical properties. The establishment of the relevant finite element model and the simulated mechanical response curves were detailed in the ESM (Figs. S13–S15 in the ESM). For the films subjected to CSA stretching treatment, the fibers on the fracture surface were densely and orderly arranged with a rebound phenomenon (Fig. 5(b)). Correspondingly, the finite element simulation results also showed that the film fracture was characterized by fiber bundle breakage (Fig. 5(e)(ii)). The inter fiber sliding behavior was suppressed, but stress was concentrated within individual fiber bundles, and the damage was still confined to the fiber bundle units. Thus, the improvement of mechanical properties was limited by the inherent strength of the fiber bundles themselves.

The introduction of PNFs constructs a nano-fishnet structure via hydrogen bonding and spatial interlocking, further evolving the fracture mechanism into a layered interlocking fracture mode. The fracture surface presents a dense layered morphology (Fig. 5(c)). PNFs enhance the synergistic chemical and physical inter fiber bonding to form a nano-fishnet structure. Under dynamic loading, interlaminar local damage dominates, with load dispersed through network nodes to avoid stress concentration and induce serrated fractures (Fig. 5(d)). The finite element simulation reveals stress partitioning, and the fibers at the fracture surface still maintain a compact arrangement (Fig. 5(e)(iii)). During the fracture process, more energy is dissipated through interlayer interlocking rather than the rapid failure of individual fibers.

Synergistic mechanical stretching orientation regulation and PBO cross-linking modification effectively improve the dynamic mechanical properties of CNT films (Fig. 5(f)). Comparing the static and dynamic mechanical properties of the film with the existing high-performance films, its comprehensive mechanical indexes have distinct advantages (Figs. 5(g) and 5(h)). This not only verifies the effectiveness of the structural regulation strategy, but

also reflects the practical application potential of composite films in high-performance flexible structures and functional devices. This fully demonstrates the efficient optimization effect of the process strategy on the mechanical properties of carbon nanotube-based films.

4 Conclusions

PBO-CNT films with excellent dynamic mechanical performance were obtained in this work via mechanical regulation to realize aligned CNTs and the formation of a cross-linked and interlocked nano-fishnet structure with PBO. The resulting PBO-CNT composite films exhibited a packing density twice that of the pristine films, with a dynamic tensile strength of 4.92 ± 0.2 GPa and a toughness of $118.96 \pm 9.78 \text{ MJ}\cdot\text{m}^{-3}$, which were 3954.39% and 1060.59% higher than those of the untreated CNT films, respectively. Detailed analysis of the static and dynamic tensile fracture morphologies revealed the key roles of stretching and PBO composite modification. The high orientation and densification of the structure, as well as the nano-fishnet structure constructed by PBO cross-linking and interlocking, enabled effective fracture energy absorption. Future work will focus on exploring the potential applications of these high-performance composite films in advanced protective fields, and extending the proposed design philosophy to other carbon-based nanocomposite systems for broader engineering applications.

Electronic Supplementary Material: Supplementary material (split Hopkinson rod test method, tensile test at high strain rate, conductive and electromagnetic interference shielding properties of CNT films and PBO-CNT films, TEM image of PBO nanofibers at a concentration, XPS elemental spectra of CNT films, enlarged Raman spectra of CNT films, XPS spectra and Fe 2p spectrum of CNT films, EDS multi-element mapping of CNT films, XRD patterns of CNT films, FTIR spectra of CNT films, dynamic tensile properties of CNT films, dynamic tensile properties of PBO-CNT films, and images of winding and folding behaviors of PBO-CNT composite films) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908843>.

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

All the contributing authors report no conflict of interests in this work.

Author contribution statement

C. Y. D.: Data curation, validation, writing manuscript, experimental design. Y. Y. L.: Project administration, validation,

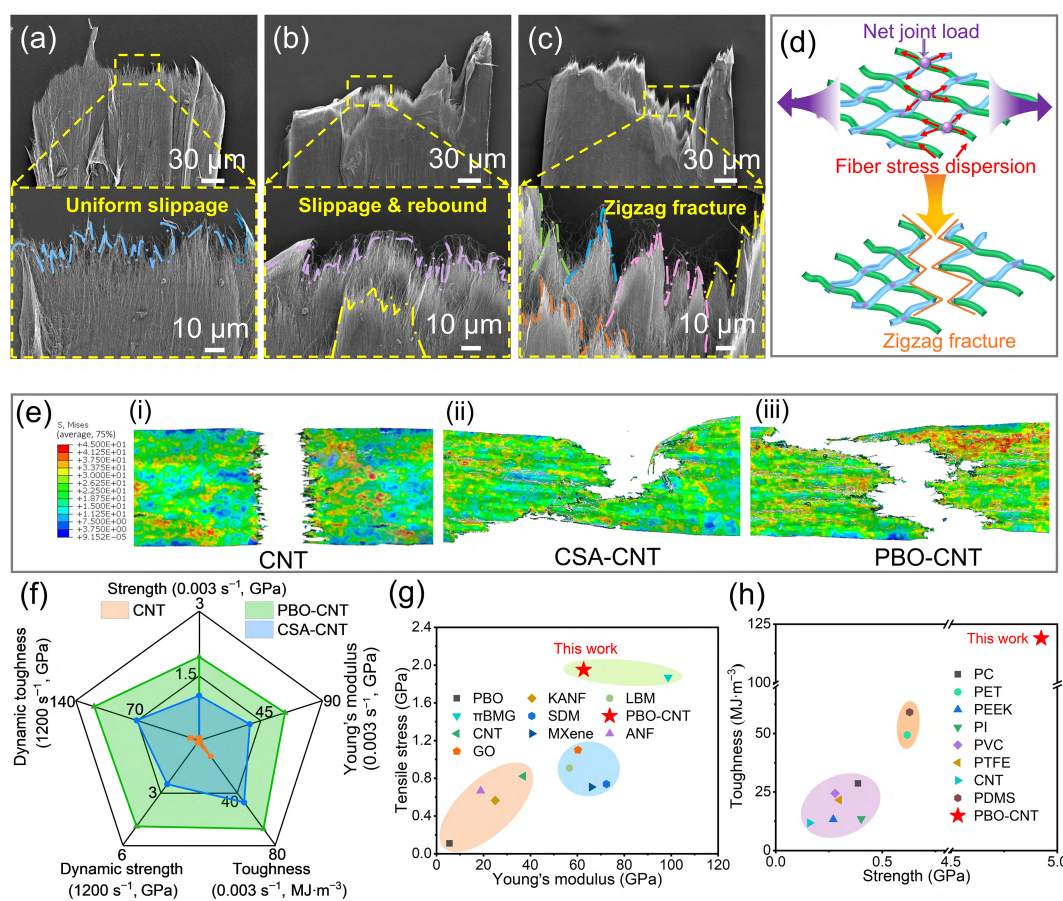


Figure 5 ((a)–(c)) Dynamic mechanical fracture morphology of CNT films with different treatments: (a) pristine CNT film, (b) CSA-CNT film, and (c) PBO-CNT composite film. (d) Fracture mechanisms of PBO-CNT composite films under dynamic loading. (e) Finite element simulation of dynamic mechanics for CNT films with different treatments. (f) Comparison of dynamic tensile properties of different types of films. (g) Comparison of static tensile properties of different films. (h) Comparison of tensile strength and toughness of different film materials at a strain rate of 1200 s^{-1} .

experimental design, writing manuscript, funding acquisition. L. W.: Data curation, experimental design and conduction, result analysis. W. Z.: Data curation, writing manuscript. Z. Q. L.: Experimental design. D. M. H.: Project administration, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Yu, W.; Liu, C. H.; Fan, S. S. Advances of CNT-based systems in thermal management. *Nano Res.* **2021**, *14*, 2471–2490.
- [2] Wu, K. J.; Wang, B.; Niu, Y. T.; Wang, W. J.; Wu, C.; Zhou, T.; Chen, L.; Zhan, X. H.; Wan, Z. Y.; Wang, S. et al. Carbon nanotube fibers with excellent mechanical and electrical properties by structural realigning and densification. *Nano Res.* **2023**, *16*, 12762–12771.
- [3] Zhu, Y. K.; Wei, Y. B.; Zhu, Z. X.; Yue, H. J.; He, Z. Y.; Zhang, Q.; Zhang, S. J.; Wei, F. Preparation of carbon nanotube films towards mechanical and electrochemical energy storage. *Nano Res.* **2023**, *16*, 12411–12429.
- [4] Zhang, S. L.; Ma, Y.; Suresh, L.; Hao, A. Y.; Bick, M.; Tan, S. C.; Chen, J. Carbon nanotube reinforced strong carbon matrix composites. *ACS Nano* **2020**, *14*, 9282–9319.
- [5] Kinloch, I. A.; Suhr, J.; Lou, J.; Young, R. J.; Ajayan, P. M. Composites with carbon nanotubes and graphene: An outlook. *Science* **2018**, *362*, 547–553.
- [6] Fang, B.; Chang, D.; Xu, Z.; Gao, C. A review on graphene fibers: Expectations, advances, and prospects. *Adv. Mater.* **2020**, *32*, 1902664.
- [7] Wang, S. K.; Liu, Q. L.; Li, M.; Li, T. S.; Gu, Y. Z.; Li, Q. W.; Zhang, Z. G. Property improvements of CNT films induced by wet-stretching and tension-heating post treatments. *Compos. Part A: Appl. Sci. Manuf.* **2017**, *103*, 106–112.
- [8] Gao, C. Q.; Guo, M. Y.; Liu, Y. K.; Zhang, D. Y.; Gao, F.; Sun, L.; Li, J. S.; Chen, X. C.; Terrones, M.; Wang, Y. Q. Surface modification methods and mechanisms in carbon nanotubes dispersion. *Carbon* **2023**, *212*, 118133.
- [9] Lee, D. M.; Park, J.; Lee, J.; Lee, S. H.; Kim, S. H.; Kim, S. M.; Jeong, H. S. Improving mechanical and physical properties of ultra-thick carbon nanotube fiber by fast swelling and stretching process. *Carbon* **2021**, *172*, 733–741.
- [10] Zhang, X.; De Volder, M.; Zhou, W. B.; Issman, L.; Wei, X. J.; Kaniyoor, A.; Terrones Portas, J.; Smail, F.; Wang, Z. B.; Wang, Y. C. et al. Simultaneously enhanced tenacity, rupture work, and thermal conductivity of carbon nanotube fibers by raising effective tube portion. *Sci. Adv.* **2022**, *8*, eabq3515.
- [11] Liu, Y. M.; Shi, X. L.; Wu, T.; Wu, H.; Mao, Y. Q.; Cao, T. Y.; Wang, D. Z.; Liu, W. D.; Li, M.; Liu, Q. F. et al. Boosting thermoelectric performance of single-walled carbon nanotubes-based films through rational triple treatments. *Nat. Commun.* **2024**, *15*, 3426.
- [12] De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon nanotubes: Present and future commercial applications. *Science* **2013**, *339*, 535–539.

- [13] Lim, Y. D.; Kong, Q. Y.; Wang, S. M.; Tan, C. W.; Tay, B. K.; Aditya, S. Enhanced field emission properties of carbon nanotube films using densification technique. *Appl. Surf. Sci.* **2019**, *477*, 211–219.
- [14] Gupta, N.; Alred, J. M.; Penev, E. S.; Yakobson, B. I. Universal strength scaling in carbon nanotube bundles with frictional load transfer. *ACS Nano* **2021**, *15*, 1342–1350.
- [15] Wang, Z. Y.; Wu, J. H.; Wei, X. X.; Saleemi, S.; Liu, W.; Li, W.; Marriam, I.; Xu, F. J. Bioinspired microstructure-reorganized behavior of carbon nanotube yarn induced by cyclic stretching training. *J. Mater. Chem. C* **2020**, *8*, 117–123.
- [16] Lee, H. D.; Yoo, B. M.; Lee, T. H.; Park, H. B. Defect-free surface modification methods for solubility-tunable carbon nanotubes. *J. Colloid Interface Sci.* **2018**, *509*, 307–317.
- [17] Lee, J.; Lee, D. M.; Jung, Y.; Park, J.; Lee, H. S.; Kim, Y. K.; Park, C. R.; Jeong, H. S.; Kim, S. M. Direct spinning and densification method for high-performance carbon nanotube fibers. *Nat. Commun.* **2019**, *10*, 2962.
- [18] Bulmer, J. S.; Mizen, J. E.; Gspann, T. S.; Kaniyoor, A.; Ryley, J. B.; Kiley, P. J.; Sparkes, M. R.; O'Neill, B.; Elliott, J. A. Extreme stretching of high G/D ratio carbon nanotube fibers using super-acid. *Carbon* **2019**, *153*, 725–736.
- [19] Zhang, X. H.; Li, Q. W. Enhancement of friction between carbon nanotubes: An efficient strategy to strengthen fibers. *ACS Nano* **2010**, *4*, 312–316.
- [20] Cai, Y. M.; Zhang, L.; Fang, R. L.; Wang, Y.; Wang, J. X. Maximized ion accessibility in the binder-free layer-by-layer MXene/CNT film prepared by the electrophoretic deposition for rapid hybrid capacitive deionization. *Sep. Purif. Technol.* **2022**, *292*, 121019.
- [21] Wu, Y. D.; Ma, Q. Q.; Liang, T.; Yao, Y. M.; Li, J. H.; Zeng, X. L.; Xu, J. B.; Sun, R. A facile strategy to densify aligned CNT films with significantly enhanced thermal conductivity and mechanical strength. *Adv. Mater. Technol.* **2022**, *7*, 2200623.
- [22] Yang, F.; Ma, S. C.; Khor, C. M.; Su, Y. M.; Barani, Z.; Xu, Z. P.; Boyko, A.; Iddya, A.; Segev-Mark, N.; Zheng, X. Y. et al. One-step method for the fabrication of pure and metal-decorated densified CNT films for effective electromagnetic interference shielding. *Carbon* **2023**, *214*, 118370.
- [23] Lyu, Z.; Zhang, W.; Wang, P.; Xu, Q.; Xie, H. P.; Li, C. W.; Dong, S. X.; Hu, D. M.; Li, Q. W. Biomimetic gradient architecture enables superior impact resistance in CA/PBO hybrid composites for protective applications. *Compos. Part B: Eng.* **2026**, *311*, 113225.
- [24] Zhu, M. Q.; Xiao, K. L.; Zhang, W.; Lei, X. D.; Bai, Y. X.; Wang, S. J.; Zhang, P.; Gao, F.; Wang, C. Y.; Xu, W. Q. et al. Fabricating bio-inspired high impact resistance carbon nanotube network films for multi-protection under an extreme environment. *Nano Res.* **2024**, *17*, 7793–7802.
- [25] Kim, Y.; Chang, H.; Yoon, T.; Park, W.; Choi, H.; Na, S. Nano-fishnet formation of silk controlled by Arginine density. *Acta Biomater.* **2021**, *128*, 201–208.
- [26] Liu, R. C.; Deng, Q. Q.; Yang, Z.; Yang, D. W.; Han, M. Y.; Liu, X. Y. “Nano-fishnet” structure making silk fibers tougher. *Adv. Funct. Mater.* **2016**, *26*, 5534–5541.
- [27] Li, B.; Yang, Y. F.; Wu, N.; Zhao, S. Y.; Jin, H.; Wang, G. L.; Li, X. Y.; Liu, W.; Liu, J. R.; Zeng, Z. H. Bicontinuous, high-strength, and multifunctional chemical-cross-linked MXene/superaligned carbon nanotube film. *ACS Nano* **2022**, *16*, 19293–19304.
- [28] Wang, S. Y.; Zhao, J.; Wang, Q. F.; Zhang, D. H. Preparation and recycling of high-performance carbon nanotube films. *ACS Sustain. Chem. Eng.* **2022**, *10*, 3851–3861.
- [29] Zhang, Q.; Zhou, W. Y.; Xia, X. G.; Li, K. W.; Zhang, N.; Wang, Y. C.; Xiao, Z. J.; Fan, Q. X.; Kauppinen, E. I.; Xie, S. S. Transparent and freestanding single-walled carbon nanotube films synthesized directly and continuously via a blown aerosol technique. *Adv. Mater.* **2020**, *32*, 2004277.
- [30] Wang, H.; Sun, X.; Wang, Y. Z.; Li, K. C.; Wang, J.; Dai, X.; Chen, B.; Chong, D. T.; Zhang, L. Y.; Yan, J. J. Acid enhanced zipping effect to densify MWCNT packing for multifunctional MWCNT films with ultra-high electrical conductivity. *Nat. Commun.* **2023**, *14*, 380.
- [31] Zhang, X. S.; Lei, X. D.; Jia, X. Z.; Sun, T. Z.; Luo, J. J.; Xu, S. C.; Li, L. J.; Yan, D.; Shao, Y. L.; Yong, Z. Z. et al. Carbon nanotube fibers with dynamic strength up to 14 GPa. *Science* **2024**, *384*, 1318–1323.
- [32] Parra-Vasquez, A. N. G.; Behabtu, N.; Green, M. J.; Pint, C. L.; Young, C. C.; Schmidt, J.; Kesselman, E.; Goyal, A.; Ajayan, P. M.; Cohen, Y. et al. Spontaneous dissolution of ultralong single- and multiwalled carbon nanotubes. *ACS Nano* **2010**, *4*, 3969–3978.
- [33] Liu, Y.; Zou, W. Z.; Zhao, N.; Xu, J. Electrically insulating PBO/MXene film with superior thermal conductivity, mechanical properties, thermal stability, and flame retardancy. *Nat. Commun.* **2023**, *14*, 5342.
- [34] Meng, Z. R.; Zhong, W. H.; Zhang, D. B.; Liu, Q.; Wang, Z. S.; Ma, Y. D.; Lu, S. C.; Hu, X.; Sun, T. Y. Ultra strong, tough and extreme environments resistant PBO papers with a nacre-like structure constructed by synergistic electrostatic interaction and interlayer entanglement. *Chem. Eng. J.* **2024**, *495*, 153599.
- [35] Gong, K. J.; Peng, Y. M.; Liu, A.; Qi, S. H.; Qiu, H. Ultrathin carbon layer coated MXene/PBO nanofiber films for excellent electromagnetic interference shielding and thermal stability. *Compos. Part A: Appl. Sci. Manuf.* **2024**, *176*, 107857.
- [36] Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cuniff, P.; Sennett, M.; Windle, A. High-performance carbon nanotube fiber. *Science* **2007**, *318*, 1892–1895.
- [37] Shi, X. L.; Sun, B. L.; Zhang, J. Polymer-carbon nanotube composite fibers with ultrahigh dynamic strength. *Adv. Fiber Mater.* **2025**, *7*, 4–6.
- [38] Singh, A. P.; Mishra, M.; Hashim, D. P.; Narayanan, T. N.; Hahm, M. G.; Kumar, P.; Dwivedi, J.; Kedawat, G.; Gupta, A.; Singh, B. P. et al. Probing the engineered sandwich network of vertically aligned carbon nanotube-reduced graphene oxide composites for high performance electromagnetic interference shielding applications. *Carbon* **2015**, *85*, 79–88.
- [39] Smail, F.; Boies, A.; Windle, A. Direct spinning of CNT fibres: Past, present and future scale up. *Carbon* **2019**, *152*, 218–232.
- [40] Zhang, Y. N.; Zheng, L. X.; Sun, G. Z.; Zhan, Z. Y.; Liao, K. Failure mechanisms of carbon nanotube fibers under different strain rates. *Carbon* **2012**, *50*, 2887–2893.
- [41] Wu, A. S.; Nie, X.; Hudspeth, M. C.; Chen, W. W.; Chou, T. W.; Lashmore, D. S.; Schauer, M. W.; Tolle, E.; Rioux, J. Strain rate-dependent tensile properties and dynamic electromechanical response of carbon nanotube fibers. *Carbon* **2012**, *50*, 3876–3881.
- [42] Wang, D. Y.; Wang, P. F.; Wu, Y. F.; Bu, L. H.; Tian, J.; Liu, M.; Sun, G. Z.; Mei, L.; Xu, S. L. Temperature and rate-dependent plastic deformation mechanism of carbon nanotube fiber: Experiments and modeling. *J. Mech. Phys. Solids* **2023**, *173*, 105241.



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