Combining polymers with small amounts of stiff carbon-based nanofillers such as graphene or graphene oxide is expected to yield low-density nanocomposites with exceptional mechanical properties. However, such nanocomposites have remained elusive because of incompatibilities between fillers and polymers that are further compounded by processing difficulties. Here we report a water-based process to obtain highly reinforced nanocomposite films by simple mixing of two liquid crystalline solutions: a colloidal nematic phase comprised of graphene oxide platelets and a nematic phase formed by a rod-like high-performance aramid. Upon drying the resulting hybrid biaxial nematic phase, we obtain robust, structural nanocomposites reinforced with graphene oxide.
Reinforcing polymers with nano-scale fillers like carbon nanotubes, graphene, and graphene oxide, is often touted as a prescription for fabricating low-density nanocomposites with exceptional mechanical properties. However, property enhancement is critically dependent on stress transfer from the relatively soft polymer matrix to the stiff reinforcement. The efficacy of stress transfer is, in turn, sensitive to the polymer morphology, the distribution of the filler particles, and ill-defined intermolecular interactions between the particle surface and polymer. To date a haphazard Edisonian approach to reinforcing inherently low-modulus polymers has been pursued by adding nano-scale fillers to melts or solutions of polymers with random coil secondary structures. Consequently, strong nanocomposites remain elusive in part because of incompatibilities between amorphous polymer morphology and filler causing the latter to aggregate; composite fabrication is also impacted by processing difficulties. Using a water-based process, we report that highly reinforced nanocomposite films can be obtained by simply mixing two uniaxial liquid crystalline solutions: (i) a colloidal nematic filler phase comprised of a suspension of aligned graphene oxide (GO) platelets and (ii) a nematic solution of rod-like high-performance aramid polymers. The resulting mixture is hybrid biaxial nematic—a mesoscopic lyotropic nematic comprised of GO platelets embedded in a lyotropic polymeric nematic with respective directors orthogonal—with a locally stratified supramolecular organization. On drying, the stratified arrangement in the biaxial fluid is compressed into a uniplanar morphology yielding robust, structural nanocomposite films. The nanocomposite exceeds theoretical estimates—a 20 GPa modulus enhancement of the aramid and a strength enhancement of ~320 MPa without any decrease in the strain-at-break. The hybrid mesophase route employed in this work yields a uniform dispersion of filler and suggests a design strategy for fabricating structural nanocomposites. In short, we present a facile, robust route to overcome processing challenges and achieve well-dispersed nanocomposites that exhibit excellent load transfer between the matrix polymer and the GO reinforcing component.

Results

Hybrid biaxial nematics. Poly(2,2′-disulfonyl-4,4′-benzidine terethalalimide) (PBDT; Fig. 1a) is an all-aromatic, rodlike polyelectrolyte related to the high performance aramid, Kevlar. PBDT forms a uniaxial nematic phase (N) above 1.9 wt.% in water with its local director—the axis of alignment of quasi-parallel, high-performance-softness (rodlike) PBDT polymers, specified by n_p; the + sign indicates that the largest refractive index is parallel to n_p. The PBDT solutions are biphase between 1.9 and 12 wt.%, and fully nematic above the latter concentration (Supplementary Fig. 1). In the Onsager excluded-volume picture of lyotropic liquid crystal formation, a low onset concentration suggests a high aspect ratio. This results because the rod-like PBDT double helix aggregates into prlate particles—with an axial persistence length of ~260 nm (see Supplementary Note 1) and an aspect ratio of ~330–10^4. Graphene oxide (GO), a precursor to “synthetic graphene”, has a lower modulus (~250 GPa) than G, but the heterogeneity of the GO primary structure enables formation of a stable aqueous colloidal nematic phase above a critical concentration (with its director n_GO specifying the average direction of platelet normals; the largest refractive index is perpendicular to n_GO, hence the negative sign in the phase designation, N). Micron-size GO platelets with (ideally) the thickness of a single carbon atom implies a very high aspect ratio (>10^4) and correspondingly a much lower liquid crystal onset concentration (~0.018 wt.% and smaller biphase range (0.018–0.9 wt.%); see Supplementary Figs. 1 and 2. The size selected GO platelets ~3.6 μm in diameter...
mixtures i.e. when adjacent to the beam-stop. The non-uniform azimuthal intensity in the sediment on mild centrifugation (Fig. 1c). In nematic hybrid directors resulting in a hybrid phase with the two respective nematic maximizes the interactions between PBDT rods and GO platelets. In our case tangential anchoring of PBDT on the GO surfaces the particle surfaces resulting in two orthogonal nematic directors. In the latter, mesoscopic rodlike particles were added to a thermotropic molecular nematic, which adopted normal anchoring relative to the particle surfaces resulting in two orthogonal nematic directors. In our case tangential anchoring of PBDT on the GO surfaces maximizes the interactions between PBDT rods and GO platelets resulting in a hybrid phase with the two respective nematic directors \( n_P \) and \( n_{GO} \) orthogonal to one another. Hybrid PBDT + GO phases were prepared by mixing aqueous solutions of PBDT and GO (Fig. 1b and Methods) such that the mass fraction \( (F_{GO}) \) is held constant \( (F_{GO} = GO/(PBDT + GO) = 0.0244) \) in both the fluid mixtures (Supplementary Table 1) and in the solid films prepared by drying those mixtures. However, in order to create stable fluid dispersions of GO in solution it is essential to have the PBDT component in its liquid crystalline phase (Fig. 1c); when the total solids content, \( C_{total} \) (the concentration of GO + PBDT), is less than 2.0 wt.%, the mixture is a simple isotropic solution and PBDT acts as a follocculant causing the GO to aggregate and sediment on mild centrifugation (Fig. 1c). In nematic hybrid mixtures i.e. when \( C_{total} > 2.0 \) wt.%, GO exceeds its critical overlap concentration \( (\theta_{GO}) \) (see Supplementary Table 2 and associated calculations in Supplementary Information) resulting in orientational correlation between GO platelet normals. Furthermore, the effective volume per GO platelet \( (V_{eff,GO}) \) which is a measure of the accessible volume for GO platelets reduces below the corresponding GO overlap volume (Supplementary Table 2). Dispersions of GO in the \( N^+ \) phase of PBDT are stable even when the PBDT component is biphasic; for \( C_{total} > 3.6 \) wt.%, the entire solution appears as a uniform stable \( hN_b \) phase. The detailed phase behavior of PBDT rods mixed with GO platelets is complex: For example, a 4.75 wt.% PBDT in water is biphasic \( (I + N^+) \), as is a 0.0120 wt.% GO suspension in water \( (I + N^-) \) (Supplementary Table 1). But the mixture of the two solutions \( (C_{total} = 4.9 \) wt.%) is a homogeneous \( hN_b \) phase that does not phase separate on centrifugation. The aspect ratio of the GO in mixtures is also a critical variable (Supplementary Figs. 3a and 4). Despite long-standing theoretical predictions\(^{19,21}\), we are unaware of prior reports of stable rod + plate biaxial mesophases as de-mixing occurs spontaneously.\(^{24}\)

In contrast, the random coil polymer, poly(2,2’-disulfonylbenzidine isophthalimide) (PBDI; Fig. 1a) does not form a liquid crystalline phase and merely acts as a polyelectrolyte flocculating agent for GO (Fig. 1c). As a result, contrasting the behavior of PBDI with the rodlike PBDT gives insights into how nanocomposite precursor phases impact mechanical properties.

Transmission small angle X-ray diffraction measurements were performed on the PBDT + GO mixtures with the geometries shown in Fig. 2a, at normal \( \alpha = 90^\circ \) and ”edge-on” \( \alpha = 15^\circ \) incidence with respect to the containing cell surface.

At normal incidence, the scattering is essentially isotropic over the investigated concentration range (apart from the weak anisotropy from shear-induced orientation introduced during sample loading) (Supplementary Fig. 5a). In the edge-on geometry, the small-angle (low \( q \)) GO-dominated scattering transforms from a circular pattern to an anisotropic azimuthal intensity distribution in the fully nematic mixtures (Fig. 2a and Supplementary Fig. 5a). The anisotropy appears to be generated from two sources: (i) shear-induced order on filling the cell with liquid crystalline fluids; (ii) anchoring preferences, i.e., the PBDT nematic adopts a homogeneous texture (random in-plane tangential anchoring) while the GO nematic favors homeotropic alignment (normal anchoring). The random alignment of \( n_P \) in the plane of the cell results in a two-dimensional mosaic structure of biaxial domains, which accounts for the isotropic scattering in the \( hN_b \) phase for \( \alpha = 90^\circ \). To reiterate, in the \( hN_b \) phases there is a preference for \( n_P \) to adopt tangential anchoring to surfaces (the cell and the GO) hence \( n_{GO} \) adopts orthogonal ordering (Fig. 2b). This interpretation is reinforced by the

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**Fig. 2 Characterization of PBDT + GO hybrid nematics.** a Small angle X-ray scattering from fluid PBDT + GO mixture contained in a transmission cell (parallel mica windows separated by a 750 \( \mu \)m spacer) for \( \alpha \simeq 15^\circ \) (“edge-on”) and \( \alpha = 90^\circ \) (normal incidence). In the hybrid phases the scattering from the PBDT is easily distinguished from scattering due to GO platelets; the former is at larger scattering angles\(^{8}\) and the latter, dominated by GO scattering, is adjacent to the beam-stop. The uniform azimuthal intensity in the \( \alpha \simeq 15^\circ \) scattering from the \( hN_b \) phase \( (C_{total} = 4.9, 7.1, \text{and } 14.4 \text{ wt.}%) \) derives from a combination of flow-induced orientation on preparing the cell and preferential anchoring of both components of the \( hN_b \) phase. The inter-rod spacing \( d_{P} \) for PBDT in the (biphasic) \( hN_b \) phase appears to be well behaved exhibiting a \( d_{P} = C_{P}^{-1/2} \) scaling relationship; the unstable GO dispersion in the isotropic mixture \( (C_{total} = 1.7 \text{ wt.}%) \) deviates from the scaling relationship. b A schematic diagram of the stratified supramolecular arrangement in a single monodomain of the \( hN_b \) phase wherein the directors \( n_{GO} \) and \( n_P \) are orthogonal.
angular dependence of the scattering (Supplementary Fig. 5a) where the inter-PBDT rod scattering and inter GO platelet scattering intensity is concentrated along the meridian for the edge-on diffraction patterns (Fig. 2a). The anisotropic, coaxial, meridional scattering from PBDT and GO along with the well behaved $d_0 = C P^{-1/2}$ scaling relationship (Fig. 2a and Supplementary Fig. 5b) is evidence of a biaxial hybrid nematic showing the superposition of orthogonal PBDT rod and GO platelet directors, $n_P$ and $n_{GO}$ respectively (Fig. 2b). The stratified supramolecular arrangement of PBDT rods between GO platelets is reminiscent of the stratified morphology observed in a system comprising DNA rods adsorbed between 2D lipid membranes.25

**Nanostructure of nanocomposite films.** Nanocomposite films with thickness $\approx 20 \mu m$ were prepared by a casting process (doctor blade, gap $= 1 \text{ mm}$, casting velocity $= 1 \text{ mm s}^{-1}$) using thoroughly blended mixtures of separately prepared solutions of PBDT and colloidal GO in water. Polymer baseline properties are determined by preparing neat PBDT films; at some point during drying of neat (isotropic or biphasic) PBDT solutions, the critical concentration for lyotropic N$^\ast$ mesophase formation is exceeded. Since the N$^\ast$ phase adopts tangential anchoring on the flat casting substrate (untreated glass), $n_P$ is parallel to the substrate interface, but the direction of $n_{GO}$ is not uniform throughout the fluid film (Supplementary Fig. 6 and Supplementary Fig. 7a). Unless the fluid is deliberately sheared while drying there is an absence of long-range order of $n_P$. Typically, dimensionally stable, neat PBDT films exhibit a poly-domain mosaic morphology with the PBDT rods adopting a uniplanar orientation relative to the casting substrate. With the incident X-ray beam at $\alpha = 90^\circ$ (normal incidence), neat PBDT films and all PBDT + GO nanocomposite films SAXS data associated with intramolecular and intermolecular periodicities in PBDT (Supplementary Fig. 7a) have a nearly uniform intensity distribution, indicating a random arrangement of PBDT directors in the plane of the films (Supplementary Fig. 7a). The parallelism of $n_P$ to the substrate i.e. the degree of uniplanar alignment of PBDT in the film can be evaluated by comparing an order parameter $(P_2 = (3 \cos^2 \beta - 1)/2)^{26}$, where $\beta$ is the out-of-plane deviation of PBDT rods for edge-on incident beam data ($\alpha = 0^\circ$, Fig. 3). The order parameter $(P_2)$ may be calculated from the azimuthal intensity distribution of the diffraction at $d_0 = 3.8 \AA$ i.e. the inter-rod spacing in the dry films.26,27

For neat PBDT films, $(P_2) \approx 0.6$ and is independent of the PBDT concentration in the casting solution. However, in the PBDT + GO mixtures, the $C_{total}$ has a pronounced influence on PBDT organization within the nanocomposite films. Casting and drying from stable, hybrid nematic phases (e.g., $C_{total} > 4.9$ wt.% results in stratified supramolecular organization i.e. narrower distributions of the inter-rod scattering intensity (higher in-plane alignment) with a higher $(P_2)$ value $>0.8$). By contrast, diffuse inter-rod (Fig. 3 and Supplementary Fig. 7a) scattering patterns with lower $(P_2)$ values are obtained in composite films cast from the metastable PBDT + GO mixtures (e.g., $(P_2) \approx 0.25$ and $= 0.4$ for $C_{total} = 1.7$ and 2.9 wt.% respectively). In nanocomposite films cast from $h_{GO}$ mixtures, the meridional scattering for the nanocomposite SAXS measurements (Fig. 3 and Supplementary Fig. 7a) and the well-defined isotropic scattering at $\alpha = 90^\circ$ suggests the presence of relatively well-defined aggregates (PBDT fibrils)7 separating GO platelets with high in-plane orientational order $(P_2) > 0.9$) (Supplementary Fig. 7b). We do note that the prohibitively high viscosity of $C_{total} = 14.4$ wt.% prevents the preparation of uniform nanocomposite films using a doctor blade. PBDI + GO nanocomposite films are brittle with isotropic scattering exhibiting no significant change in PBDI morphology by adding the GO filler (Supplementary Fig. 8).

(Thermo) Mechanical properties. The casting solution concentration $C_{total}$, which controls the perfection/homogeneity of the hybrid mesophase, strongly affects the nanocomposite stiffness determined from storage modulus ($E$) values using dynamic mechanical thermal analysis (DMTA) (Supplementary Fig. 9). Pure PBDT films have $E$ values of 10 GPa, and for this high-performance polymer, $E$ is invariant with temperature up to 400 °C (Supplementary Fig. 9). The magnitude of the mechanical enhancement of PBDT with GO depends on the phase of the casting solution—isotropic or (hybrid) liquid crystalline—which in turn affects the dispersion quality (Fig. 4a and Supplementary Fig. 10).

Films cast from the unstable isotropic or biphasic hybrid mixtures (e.g., $C_{total} = 1.7$ wt.% ($I$) or 2.8 wt.% ($I + h_{GO}$) exhibit visible GO aggregation on a length scale of several hundred of microns, (Supplementary Fig. 10). Additionally, the low in-plane alignment of the polymer $(P_2) = 0.25$ in films prepared from the isotropic hybrid mixture $(C_{total} = 1.7$ wt.%) results in nanocomposite $E'_{NC}$ values marginally lower $(E'_{NC} = 8.3$ GPa $< E'_{PM} = 10$ GPa) than that of pure PBDT. Nanocomposite films derived from the biphasic hybrid mixture $(C_{total} = 2.8$ wt.%$)$ exhibit a modest $E$ enhancement $(\Delta E = E'_{NC} - E'_{PM} = 1.7$ GPa)$^8$ despite GO aggregation (Supplementary Fig. 10a) and polymer alignment $(P_2) = 0.4$ lower than that of neat PBDT $(P_2) = 0.6$. This observed $\Delta E$ lies within the range of values commonly obtained for commodity plastics modified with GO (Fig. 4a) and indicates that the contribution is primarily from stress-transfer to the mechanical reinforcement. The stratified morphology of nanocomposite films cast from monophasic $h_{GO}$ mixtures $(C_{total} = 4.9$ and 7.1 wt.%) results in large $E$ values of 25.5 and 33.2 GPa i.e. $\Delta E = 15.5$ GPa and 23.2 GPa respectively that are greater than all.
previously reported glassy polymer + GO nanocomposites (Fig. 4 and Supplementary Data 1). The simple fabrication of the nanocomposite films described herein yields $\Delta E$ values that are comparable to polymer + GO nanocomposite fibers. The lack of modulus enhancement in nanocomposites cast from unstable PBDT + (small GO) or the isotropic PBDI + GO precursor mixtures ($C_{total} = 4.9$ wt.% in both) (Supplementary Fig. 9) further highlights the importance of preparing nanocomposites from stable, hybrid biaxial nematic mixtures.

The stress-strain analysis of nanocomposite films having a “compressed” unipolar $^1$GO morphology exhibits enhanced mechanical properties (e.g., Young’s modulus, tensile strength, and strain-at-break) relative to the unipolar morphology of pure PBDT films (Supplementary Fig. 10c, $C_{total} = 4.9$ wt.% and Supplementary Table 3). We observe a tensile strength enhancement of 320 MPa (Fig. 4b) without any decrease in the strain at break—contrary to the commonly reported propensity for brittle fracture that accompanies an increase in nanocomposite stiffness. A comparison of the largest (and the average) strain-at-break values for PBDT and PBDT + GO (Supplementary Table 3) indicates that the strain-at-break is improved in the nanocomposite films. Generally, mechanical properties, such as modulus, strength, and strain at break of rigid-rod polymers such as Kevlar® increase with polymer orientation. In PBDT + GO nanocomposite films, the enhancements in modulus, strength, and strain at break result from the increased PBDT + GO orientation; this is in turn derived from the unique supramolecular organization of the rodlike polymer and plateletlike filler—a stable, stratified morphology obtained from drying the hybrid biaxial nematic solutions.

Discussion

The striking enhancements in modulus and strength for nanocomposites prepared from hybrid biaxial nematic mixtures clearly demonstrates that rigid-rod high-performance polymers are excellent matrix materials for GO-based nanocomposites. The phase stability of the aqueous mixtures provides a variable for control of the morphological organization in GO-reinforced films. Our observations provide design and optimization strategies for preparing nanocomposite materials from anisotropic precursors, thus enabling polymer nanocomposites with properties that have remained elusive despite decades of effort. Blending liquid crystalline phases of mesoscale reinforcements with liquid crystalline phases of high-performance polymers may provide a pathway for overcoming the putative Achilles heel of structural nanocomposites—processing a wide range of filler loadings to generate large mechanical enhancements.

Methods

Materials.

The monomers terephthaloyl chloride (TC) and isophthaloyl chloride (IPC) were purchased from Sigma Aldrich. Only freshly sublimed terephthaloyl chloride and isophthaloyl chloride were utilized for the polymerization reactions. The diamine monomer, 4,4′-diaminobiphenyl-2,2′-disulfonic acid hydrate (95%) (BDSA) was purchased from Alfa Aesar and purified before use. Polyethylene glycol 300 (PEG-300) was purchased from Sigma Aldrich. Natural graphite flakes from Sigma Aldrich were used to make graphene oxide. SpectraPor 1 dialysis membranes were purchased from Sigma Aldrich.

Methods. Polymer synthesis.

The PBDT and PBDI polymers with Na+ counter ions were synthesized according to the interfacial procedure reported by Sarkar et al. PBDT synthesis is as follows: A 2 L three-neck round-bottom flask equipped with a mechanical stirrer was charged with sodium carbonate 1.59 g (15 mmol), dry BDSA (2.58 g, 7.5 mmol), PEG 300 (2.4 g) and 500 mL deionized water. This mixture was stirred at 1000 RPM for ~15 min. After 15 min, TPC (1.52 g, 7.5 mmol) dissolved in 100 mL of chloroform was added to the reaction mixture and polymerized for 15 min. A rotary evaporator enabled removal of chloroform from the mixture and the polymer was obtained by precipitation of the aqueous solution in 2 L of acetone. The precipitate thus collected was redissolved in ~200 mL water and precipitated and filtered from 2 L of acetone. This procedure was repeated thrice—until pH of the aqueous solution was 7. PBDI was synthesized
A similar procedure; instead of TPC, IPC dissolved in dichloromethane was used as the diacid chloride solution. Both polymers were dried at 150 °C for 1 h in a vacuum oven. The measured inherent viscosity of PBDT and PBDT in N,N-dimethylformamide at a concentration of 0.5 mg/mL was 0.2 mm in a 0.1% solution in N,N-dimethylacetamide was determined to be 0.9 wt-% and the nanocomposite film is as follows: 300 mg of pre-dried PBDT polymer is dissolved in 3 mL deionized water. This is added dropwise (over ~15 min) to a bottle containing 3 mL 0.25 wt.% LC solution of GO while continuously mixing to homogenize the mixture. The solution was then diluted by a factor of 100. The diluted samples were deposited on to a Au@Si wafer was dipped into this solution by immersing it carefully and later dried in an oven at 60 °C overnight resulting in a nanocomposite film. The film was removed from the glass plate by immersing the plate in an acetone bath. A High-resolution JEOL scanning electron microscope (HR-SEM) was utilized to measure GO flake dimensions and study the cross-sections of the films. For statistical analysis of the GO flake dimensions, the graphene oxide flakes were first deposited on a Si wafer using a rudimentary Langmuir–Blodgett approach based on the work by Cote et al. Graphene oxide samples were mixed with methanol in a 1:5 (water/methanol) ratio. This was done to obtain well-dispersed GO flakes at the air-water interface. This solution was carefully pipetted on to a water trough. A Si wafer was dipped into this solution by immersing it carefully and later dried in a vacuum oven at 0 °C overnight. This enabled us to avoid imaging artifacts due to deposition of the GO on top of each other that makes dimension analysis difficult. The operating conditions of the SEM are as follows: working distance of 8 mm, anode voltage of 1 kV, probe current = 20 μA, and imaging mode utilized was the lower secondary electron image. Transmission electron microscopy (TEM) imaging was performed using a FEI Tecnai TF20 electron microscope operating at 200 kV. The GO aqueous solution was diluted by a factor of 100. The diluted samples were deposited on to a Quantifoil holey carbon grid with Cu-200 mesh using a pipette. The carbon grids were then dried in air at 25 °C for ~30 min. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. The measurements were performed at room temperature and at a chamber pressure of 10−9 mbar. The GO was deposited onto Au/Si substrates prior to analysis. The binding energy corrections were within ±0.1 eV. The C/O ratio of GO was measured by dividing the atom percentage of carbon by the atom percent of oxygen. The nematic phase fraction (%) of PBDT solutions and PBDT + GO hybrid mixtures were analyzed by filling 5 mm NMR tubes and centrifuging them for 2 h at 600 RPM. For GO solutions, the filled NMR tubes were centrifuged at 8000 RPM for 2 h—similar results are achieved by leaving the tubes undisturbed at ambient conditions for ~3.5 days. The nematic phase fraction (%) is calculated based on dividing the height of the nematic phase by the total solution height. The centrifuged NMR tubes were placed between crossed polarizers on a white light background and imaged using an iPhone 8 camera. A Leica DM-LM optical microscope equipped with crossed polarizers was used to image liquid crystal samples. The samples were first transported in to a rectangular Vitruber® capillary (I.D. = 0.2 mm) by capillary action. Transmission small angle X-ray scattering measurements on hybrid mixtures were carried out at the Life Science X-ray Scattering (LIX) beamline of NSLS-II. The X-ray energy was set to 0.918 keV (0.22 Å). This was 3.23 m. The sample holder consisted of two mica plates (~20 micron thick) separated by a 0.75 mm acrylic spacer with a central aperture of 4.6 mm diameter. One of the mica plates was first glued to the spacer. The second mica plate was then placed onto the other side of the spacer (like a microscope cover slip), after the sample was pipetted into the aperture in the spacer. The angle between the incident X-rays and the mica plates was set at 20° (edge-on) in order to analyze the orientation of PBDT + GO composite precursor solutions. In order to ensure that the beam cleared the spacer when the sample was rotated (up to 13°), the X-ray beam was focused to a spot size of ~5 micron. The detector gaps were filled using centro-symmetry.

X-ray scattering studies of nanocomposite films were performed at room temperature both in-house, using a Bruker AXS D8 Discover diffractometer in transmission mode with a CuKa-radiation source, and at the BM28 DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. For every nanocomposite, four layers of the thin films were mounted on a support film that was edge-on. The X-ray beam was then filtered through a 1.5 mm thick slit, and the sample was placed at a distance of 6 cm between the sample and the detector and an exposure time of 5 min. In-house SAXS was performed by placing the samples at a distance of 6.6 cm from the detector for time period of 10 min. Synchrotron measurements of the composite films were performed using a beam wavelength of 0.827 Å/1.033 Å and a sample-to-detector distance of 0.173 m/0.468 m for WAXS/SAXS, respectively. A vacuum chamber was placed between the sample and detector in SAXS measurements to reduce the scattering due to air. For 2D WAXS synchrotron patterns, the experimental semi-circular 2D WAXS patterns were mirrored along the equator for easier visualization.

Stress-strain analysis were performed using a RSA-G2 Solids Analyzer (TA Instrument) with a 32 N load cell. Free-standing films were cut into rectangular strips of approximate cross-sectional area 1.5 x 0.033 mm2 (width x thickness). A 10 mm gauge length at a constant linear displacement rate of 0.1 mm·min−1 was used for tensile measurements. The materials were found to be strain rate independent within the range of 0.01–1 mm·min−1 linear displacement rate. Specimens were tested under dry conditions at 25 °C under a nitrogen atmosphere. Specimens for dry tensile testing were treated at 200 °C for 20 min under nitrogen in the RSA-G2 forced convection oven to eliminate water. The samples were equilibrated at 25 °C under nitrogen before tensile measurements.

Dynamic mechanical thermal analysis (DMTA) was performed with a Perkin-Elmer Diamond DMTA. DMTA experiments on the films were performed at a frequency of 1 Hz at a heating rate of 2.0 °C/min using films having approximate dimensions of 20 x 3 x 0.020 mm.

Data availability

All relevant data generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request. No data in this paper are restricted in terms of availability. The source data underlying Figs. 2a, 4a and Supplementary Figs. 1, 2c, 3a, c, 5b, 7b, 9, and 10c are provided as a Source Data file.

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Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to T.J.D.

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