

Hydroplasticity of Nanocrystal Films Induced by Mesopore Change

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Hydroplastification offers an eco-friendly route to plasticize hydrophilic polymers by enhancing chain mobility, yet it remains ineffective for rigid crystalline nanomaterials. Here, we report a novel plasticity mechanism governed by mesopores acting as structural free volume between rigid hydrophilic nanocrystals, cellulose nanocrystals (CNCs). During the mechanosorptive vapor training process to change the mesopores, the plasticity arises from a dynamic competition between external tensile stress and internal capillary forces. We establish a semiquantitative constitutive relationship revealing that the network's wet-state yield strength is critically regulated by the aspect ratio and surface chemistry of the nanocrystals. Specifically, the weak acidity of carboxyl groups ($pK_a \sim 3.2$) combined with high aspect ratios creates a defect-dominated soft skeleton; here, the internal Laplace pressure (~ 26 MPa) exceeds the yield strength, driving the splitting of bottlelike mesopores into smaller domains until a geometric locking limit defined by the nanocrystal diameter is reached. In contrast, strong electrostatic repulsion from sulfonates ($pK_a \sim 1.0$) or spatial jamming in short nanorods results in rigid networks that resist this capillary-driven densification. This novel hydroplastification mechanism by capitalizing on mesopores with competing capillary force, opposing network stress, and external stress enables shaping CNC films into stable geometries, rather than lattice disruption. Moreover, such findings extend hydroplasticity concepts to rigid matter, establishing mesopore engineering as a physical pathway to regulate the plasticity of crystalline nanomaterials.

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I. INTRODUCTION

Plasticity is critical for material processing and subsequent applications, as it allows shaping materials with reduced energy consumption and enables diverse end-use products [1,2]. Traditional plastic processing methods rely heavily on thermal, or solvent based to achieve the necessary chain mobility for polymers [3]. To achieve better plastic properties, plasticizer containing chemical interaction and physical isolation mechanisms, can be used to promote the polymer chain mobility [4]. However, unlike polymers, promoting plasticity in rigid crystals is significantly more challenging. Although crystal plasticity can be induced at the nanoscale by mechanisms such as deformation twins [5],

vacancies [6], lattice distortion [7], and phase transitions [8], traditional plasticizers generally have limited effects on crystals due to the dense lattice structure and lack of accessible free volume [9].

In recent years, hydroplastification has emerged as a greener alternative, harnessing water as a plasticizing agent to soften and reshape materials with hydrophilic domains [10]. By reducing or disrupting intermolecular interactions, water can effectively promote segmental motion at ambient or near-ambient conditions [11]. Yet, this otherwise promising approach falls short for highly crystalline systems, particularly nanocellulose, where rigid crystallites and extensive hydrogen bonding networks confer mechanical robustness but severely curtail flexibility [12]. Among all the nanocellulose materials, cellulose nanocrystals (CNCs), with crystallinity above 85% [13], display remarkable strength [14], potential optical [15,16], reinforcement [17], and other applications [18], but rarely exhibit the plasticity or malleability needed for shaping or forming under mild conditions. Meanwhile, direct solvent- or water-based treatment typically fails to penetrate the robust network of hydrogen bonds among CNCs, yielding negligible gains in plasticity.

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Dynamic environmental factors introduce another dimension to plastic deformation studies, especially for biopolymers. Mechanosorptive creep, a method to increase the creep behavior of materials via an alternative relative humidity (RH) change, has been shown to enhance mobility in cellulose-based systems with moderate crystallinity [19]. Existing studies have largely attributed this enhanced plasticity to molecular-level mechanisms, specifically the water-induced disruption of inter-chain hydrogen bonds and the moisture-regulated relaxation of amorphous domains [20,21]. However, a rigorous multiscale understanding that connects these molecular hydration events to the macroscopic shape ability of highly crystalline, rigid nanomaterials remains elusive. While hydration layers can locally lubricate interfaces, applying such dynamic processing to nanocellulose requires overcoming strong structural confinement, particularly at the mesoscopic level [22]. The dynamic water-induced processing of wood and bamboo provides inspiration of achieving plasticity through an overall structural movement (i.e., vascular bundles in bamboo) [23], and this mechanism is very similar to the free volume change in microscopic scale. When applying the dynamic water to processing nanocellulose, a strong structural confinement at the mesoscopic level needs to be overcome [24]. The discrepancy between molecular softening and macroscopic rigidity suggests that hydroplasticity in CNC films depends less on direct chain-scale plasticization and more on multiscale structural evolution, where the rearrangement of mesopores bridges the gap between molecular interactions and bulk deformation [25].

In this work, we report a new mechanism of plastification governed by the evolution of mesopores acting as structural free volume. We performed mechanosorptive creep tests under varying stress loadings to map the mechanical responsiveness during the vapor training process, complemented by static and dynamic mechanical tests to probe the modulus evolution. To elucidate the underlying physical origin, dynamic vapor sorption (DVS) tests combined with Barret-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) analyses were employed to track the mesopore dynamics. Crucially, we establish a semi-quantitative constitutive relationship revealing that the hydroplasticity is driven by a dynamic competition between the isotropic capillary pressure generated within mesopores and the anisotropic network yield strength. We demonstrate that this competition is intrinsically regulated by the CNC aspect ratio and surface chemistry. Our analysis reveals that this internal capillary pressure can exceed the wet-state yield strength of the network, driving plastic deformation until a geometric locking limit defined by the nanocrystal dimensions is reached. Furthermore, polarized Raman spectroscopy and cross-sectional scanning electron microscopy (SEM) were used to correlate these mesopore changes with CNC alignment. Based on this physical understanding, we developed a

vapor training protocol involving moderate static stress and alternating RH to successfully shape CNC films into stable geometries. Finally, finite element method (FEM) analysis was applied to clarify the stress distribution effects of CNC length and film shapes. This work provides a rigorous multiscale understanding of plasticity from molecular surface chemistry to mesoscopic pore evolution, expanding the potential applications of rigid, nanoparticle-based materials with excellent mechanical properties.

II. EXPERIMENTAL SECTION

A. Materials

Tunicates were purchased from Weihai Sea Food Market in Shandong, China. Microcrystalline (MCC) and acetone was purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 98 wt%), Periodic acid (HI_5O_6) were purchased from Roth. Potassium hydroxide (KOH) and sodium hypochlorite (NaClO , 14 wt% a.q.) were purchased from VWR. Ethanol was purchased from Chemsolute. All chemicals were of analytical grade or higher. Deionized water (DI water) was used throughout the experiments.

B. Preparation and purification of CNCs

The longer CNCs extracted from tunicate shell (tCNCs) were mainly obtained by alkali and acetone treatments, and further oxidation or hydrolysis treatment of tunicate shell. In brief, about 10 g tunicate shell was alternatively treated by 150 mL KOH solution (5 wt%) and 150 mL acetone under ambient environment and then repeated three times (each 3 days) to remove the other components. Then, the shell was washed to neutral and freeze dried, and tunicate powder was prepared by a grinder for further use.

Resulting tCNCs prepared via alkaline periodic acid oxidation are marked as POTCNCs, which refers to previous work with some modification [26]. In detail, 7.04 g periodic acid were used to oxidize 1.00 g tunicate powder in 150 mL suspension at room temperature for 14 days in dark environment. *pH* value was adjusted to 10.00 ± 0.05 at the beginning of the reaction by 1M KOH. After reaction the suspension was washed and dialysis, then centrifuged at 3000 rpm to remove the sediments. The supernatant was further centrifuged at 6000 rpm to obtain the sediment of longer POTCNC (POTCNC-L), and those in supernatant at 6000 rpm were shorter POTCNC (POTCNC-S).

Another type tCNC prepared via sulfuric acid hydrolysis (StCNC) were prepared via hydrolysis method. Briefly, an amount of 4 g neutral and drying alkali-treated tunicate powder was added into 771 mL H_2SO_4 solution (45 wt%) for reaction at 50°C for 2 h. Then, the supernatant was removed by centrifugation and the sediment was washed and dialysis to neutral.

POCNCs are CNCs extracted from MCC by alkaline periodic acid oxidation method with the same experimental procedure of POTCNC-S.

C. Preparation of CNC films

CNC films were prepared by solvent casting. In brief, about 10 mL 0.05 wt% CNC suspension and 4–8 mL ethanol were evenly mixed and then poured into a polyethylene petri dish. The addition of ethanol can help accelerate the drying process without changing the pore structure in tCNC films. The drying process is carried out under ambient environment for about 5 days until complete drying and obtained uniform films with thickness of 17–19 μm .

D. Characterizations

The transmission electron microscope (TEM) observation was performed on a CM 12 transmission electron microscope (Philips, Netherland), and the CNC samples were prepared from their aqueous suspensions of about 0.01 wt%. Dynamic mechanical thermal analysis (DMTA) measurements were carried out by using a DMA GABO EPLEXOR system (NETZSCH GABO Instruments GmbH) with a force sensor of 50 N. CNC films with a dimension of 30 mm $\times$ 5 mm were loaded into the test machine with a clamp distance of around 10.0 mm and the measurements were conducted with a contact force of 0.1 N, a static strain of $0.100 \pm 0.010\%$ and a dynamic strain of $0.020 \pm 0.010\%$. Humidity sweep tests were carried out with RH increasing rate of $3\% \text{ min}^{-1}$ and frequency of 10 Hz. Mechanosorptive creep behaviors were measured at 25 $^{\circ}\text{C}$ with a constant stress of on CNC films under constant RH of 80% for 2 h and then under cycling RH with repeating change of RH between 30% and 80% with cycling time of 1 h. For each case, at least three measurements were implemented to ensure that the collected data are reliable. The tensile tests of CNC films were carried out on a DMA GABO EPLEXOR system (NETZSCH GABO Instruments GmbH) with a force sensor of 50 N with climate chamber. CNC films with a dimension of 30 mm $\times$ 5 mm were loaded into the test machine with a clamp distance of around 10.0 mm. The tensile speed was 2 mm/min. Polarized Raman spectra were recorded using a LabRAM HR Evolution system (Horiba France SAS) with a 532 nm laser and a neutral-density filter set to 10% transmission. The orientation of CNCs was obtained by divided the intensity of 1096 by 1122 cm^{-1} at different angles [27]. A DVS apparatus (DVS Advantage, surface measurement systems) was used to assess the dynamic water vapor sorption behavior of all CNC films. CNC films with a mass of about 5 mg were prepared in a dimension of 10 $\times$ 10 mm^2 . The measurement was executed at 25 $^{\circ}\text{C}$ with RH first reduced to 0%, until equilibrium with the mass change per minute (dm/dt) $< 0.002\% \text{ min}^{-1}$ over a period of 10 min and the initial dry mass was recorded. Subsequently, the RH was increased from 5% to 95% in 5% steps (adsorption) followed by a decrease to 0% in reverse order (desorption). During each step, the RH was maintained constant until

equilibrium and the mass was detected. The moisture content at each RH was calculated on the basis of the equilibrated mass of the films.

The mesopore size distribution can be calculated from BJH model based on the Kelvin equation [28]:

$$\ln \frac{P}{P_0} = -\frac{2\gamma V_m}{r_k RT} \cos \theta. \quad (1)$$

Here, P is the gas vapor pressure, P_0 is the saturation pressure of adsorbent, γ is the surface tension of water at 298 K (72.0 mN/m), θ is the contact angle (Fig. S1 [29]) between adsorbate (water) and adsorbent (POtCNC-S film), V_m is the molar volume of water (18.02 cm^3/mol), R is the gas constant [8.314 J/(mol $\cdot$ K)], T is the temperature (298 K), and r_k is the Kelvin radius of the pore.

Also, the total radius of mesopores is the combination of Kelvin radius and the adsorbed layer thickness (t), which can be calculated from the Halsey equation [30]:

$$t = \tau \left(\frac{-5}{\ln(\frac{P}{P_0})} \right)^{\frac{1}{3}}, \quad (2)$$

where τ is a constant (0.25) for the adsorbate, and the mesopore size (d_p , and r_p is the radius) can be expressed as

$$d_p = 2r_p = 2(r_k + t). \quad (3)$$

Thus, the mesopore distribution of pristine POtCNC-S and with vapor training processes are calculated from dividing adsorbed water volume change (ΔV) by mesopore size change (Δd_p).

The BET model on the adsorption process from 5% to 35% RH (monolayer adsorption region) is applied to calculate the S_{BET} as follows [31]:

$$\frac{P/P_0}{V(1 - P/P_0)} = \frac{(C_{\text{BET}} - 1)P/P_0}{V_0 C_{\text{BET}}} + \frac{1}{V_0 C_{\text{BET}}}, \quad (4)$$

where V is the adsorbed volume of water, C_{BET} is the sorption constant of the BET model, and V_0 is the monolayer adsorption volume. The C_{BET} and V_0 can be fitted to from the DVS results (Figs. S2–S3 [29]). Thus, the S_{BET} can be calculated by

$$S_{\text{BET}} = \frac{V_0 N_s}{V_m m_{\text{CNC}}}, \quad (5)$$

where N is Avagadros number, s is the adsorption cross section area of water molecules (0.114 nm^2), m_{CNC} is the sample mass at dried state.

E. FEM analysis

The FEM analysis was carried out using COMSOL Multiphysics. In this project, an electromagnetic force-coupled piezoelectric model was adopted, with the

piezoelectric simulations being performed through the solid mechanics module in COMSOL.

In the solid mechanics setup, the following equations apply:

$$\nabla \cdot (F \cdot S)^T + F_V = 0, \quad (6)$$

$$F = I + \nabla u_{\text{solid}}, \quad (7)$$

$$\varepsilon = \frac{1}{2} [(\nabla u_{\text{solid}})^T + \nabla u_{\text{solid}} + ((\nabla u_{\text{solid}})^T \cdot \nabla u_{\text{solid}})], \quad (8)$$

$$\begin{pmatrix} S_{xx} \\ S_{yy} \\ S_{zz} \\ S_{yz} \\ S_{xz} \\ S_{xy} \end{pmatrix} = \frac{E}{(1+\nu)(1-2\nu)} \begin{pmatrix} 1-\nu & \nu & \nu & 0 & 0 & 0 \\ \nu & 1-\nu & \nu & 0 & 0 & 0 \\ \nu & \nu & 1-\nu & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.5-\nu & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.5-\nu & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.5-\nu \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{xz} \\ \varepsilon_{xy} \end{pmatrix}, \quad (9)$$

where $\mathbf{F}$ denotes the deformation gradient, I is the identity tensor, S is the 2nd Piola-Kirchhoff stress, $\mathbf{F}_V$ is the volumetric force, $\mathbf{u}_{\text{solid}}$ is the displacement field. Equation (8) defines the Green-Lagrange strain tensor (ε). Equation (9) represents the constitutive relation (St. Venant-Kirchhoff model) linking the energetic conjugate stress S to the strain ε . E is the Young's modulus, and ν is the Poisson's ratio.

For the POCNC and POCNC-S model, both short POCNC and long POCNC-S are subjected to the same strain (0%–10%), and then computing the stress distribution. In the POCNC film shaping model, different stress conditions (bending, twisting, and folding) are applied to evaluate the resulting stress distributions.

III. RESULTS AND DISCUSSIONS

A. RH-dependent plastification behavior of one-dimensional CNCs

In this work, one-dimensional nanorods, CNCs, were prepared for the plastification behavior studies. tCNCs with very high aspect ratio with 70–200 are much longer than CNC prepared from MCC [32]. An alkaline periodic acid oxidation method [22] was used to prepare POCNCs with high aspect ratio, and centrifugation is further applied to separate the POCNC-L and POCNC-S, respectively. As the comparison, StCNCs and POCNCs are applied to investigate the influences of surface chemical environment and morphology on CNC hydroplasticity.

Mechanosorptive creep is a good method to show the relaxation process of CNC films, and the tests are performed under 1.5, 3, or 5 MPa stress, cycling RH between 80% and 30% [Fig. 1(a), and these films after mechanosorptive creep tests are referred to as creep trained in this work]. While CNC films generally display a highly confined structure with smaller strain variations compared to amorphous cellulose [24], POCNC-S films (length 695.2 ± 210.6 nm) exhibit a

surprising, nonmonotonic strain evolution [Fig. 1(a)]. At a low stress of 1.5 MPa, the film displays a net strain reduction of -0.35% , highlighting an intrinsic tendency for the CNC network to consolidate or shrink under cyclic humidity. Increasing the stress to 3 MPa effectively balances this internal contractile force against the external pull, yielding minimal net strain changes (0.00%). Only when the stress reaches 5 MPa is the shrinkage entirely overcome, resulting in a normal positive strain of 0.12%. These results reveal a counterintuitive, stress-regulated competition between external extension and internal consolidation. As seen in right part of Fig. 1(a), this “anomalous” shrinkage is even more pronounced in films of longer nanocrystals, with POCNC-L (length 1237.5 ± 586.3 nm) displaying a -0.82% reduction at 1.5 MPa. Also, the plasticity tendency of POCNC-L at 3 and 5 MPa external force are similar with those of POCNC-S (Fig. S4 [29]). In contrast, StCNC (length 927.1 ± 402.3 nm) and POCNC (length 245.6 ± 71.8 nm) films, characterized by shorter lengths or stronger inter-particle interactions, exhibit only ordinary and minor strain increases (0.02% and 0.04%, respectively) attributed to slight structural reorganization.

The fundamental driver for these rearrangements is elucidated by the mechanical responsiveness to humidity [Figs. 1(b) and 1(c)]. Tensile experiments reveal a substantial drop in Young's modulus for POCNC-S [Fig. 1(b), with POCNC-L and StCNC results as shown in Fig. S5 [29] when RH increases from 30% to 80%, while fracture strain remains stable. This indicates a distinct hard-soft transition [33] where the softened matrix at high RH facilitates plastification, allowing the stress-regulated consolidation or elongation to occur. Furthermore, continuous humidity sweeps reveal that water desorption is slower than adsorption in POCNC films [Fig. 1(c), with POCNC-L and StCNC results as shown in Fig. S6 [29], resulting in a pronounced hysteresis. This suggests strong interactions

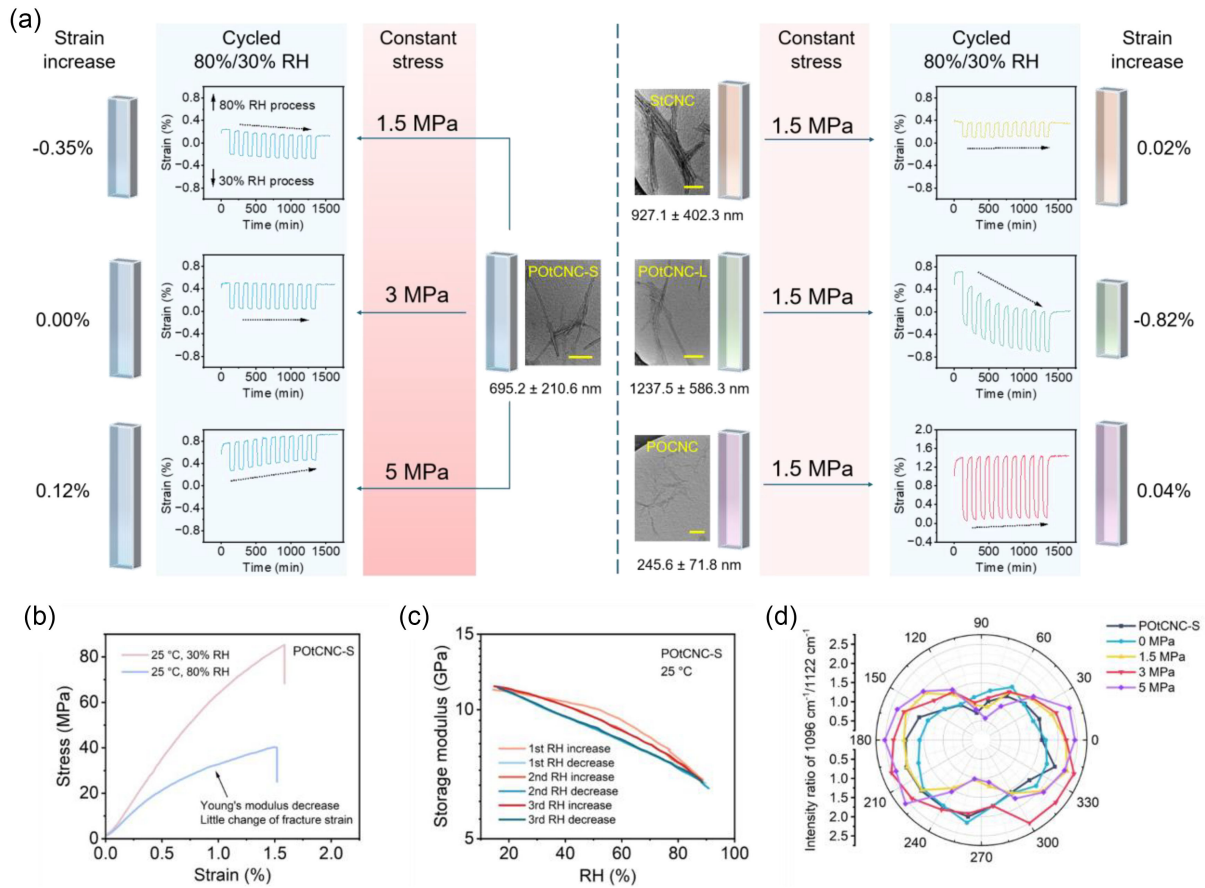


FIG. 1. Mechanical behaviors and analysis of CNC films based on RH and stress regulations. (a) Mechanosorptive creep under 1.5, 3, and 5 MPa loading stress results and TEM image of POTCNC-S films (left side), along with TEM images and mechanosorptive creep under 1.5 MPa loading stress results of StCNC, POTCNC-L, and POCNC films as a comparison. The scale bars are 200 nm in all TEM images. (b) Tensile process of POTCNC-S films under 30% and 80% RH at 25 °C, respectively. (c) Cyclic DMTA humidity sweep results of POTCNC film at 25 °C. (d) Orientation analysis of pristine and POTCNC-S film after mechanosorptive creep under different stresses based on polarized Raman results.

between POTCNC and water that may induce internal structural locking, pointing to a plasticity mechanism governed by mesoscale porosity changes rather than simple polymer chain mobility.

Polarized Raman measurement was used to show the formation of molecular orientation, which indicates the orientation of the CNCs as represented by the axial ratio. As POTCNC films subjected to 0 MPa under alternate RH cycles underwent little orientation change (axial ratio changes from 1.40 to 1.36), external stress of 1.5, 3, and 5 MPa considerably highly enhanced the axial ratios to 1.95, 1.72, and 2.71, respectively [Fig. 1(d)]. Because of the integrity of cellulose chains within the crystalline regions of POTCNCs that will not break under exerted external stress, these higher axial ratios suggest stronger POTCNC orientation, rather than polymer chain mobility. This oriented arrangement of POTCNCs should involve the dimension change of mesopores within the films, because of the CNC rigidity, and thus adjusts the shape and plasticity of POTCNC films.

B. Mechanism of mesopore-induced hydroplasticity

To investigate the mesopore-governed plastification mechanism of nanocrystal films, the relationship between mesopore change and mechanical properties shall be analyzed. In particular, the mechanosorptive creep training of the POTCNCs films at different RH and external stresses exhibit lasting but different effects on the mesopores. DVS measurements provide insights into reconfigured mesopore structures in POTCNC-S films via mechanosorptive creep training [Fig. 2)]. Below ~30% RH, both pristine and creep-trained POTCNC-S samples exhibit similar monolayer adsorption behavior. This result is consistent with GAB model fitting (Figs. S2–S3 [29]), which indicates a water monolayer capacity of around 2.7 wt% at 25% RH. Once the RH surpasses 30%, the multilayer adsorption starts, and creep-trained POTCNC-S films begin to adsorb water more rapidly than pristine films until 80% RH. The faster water adsorption suggests the formation of more accessible or abundant water transport pathways in creep-trained POTCNC films. Once RH exceeds 80% (where

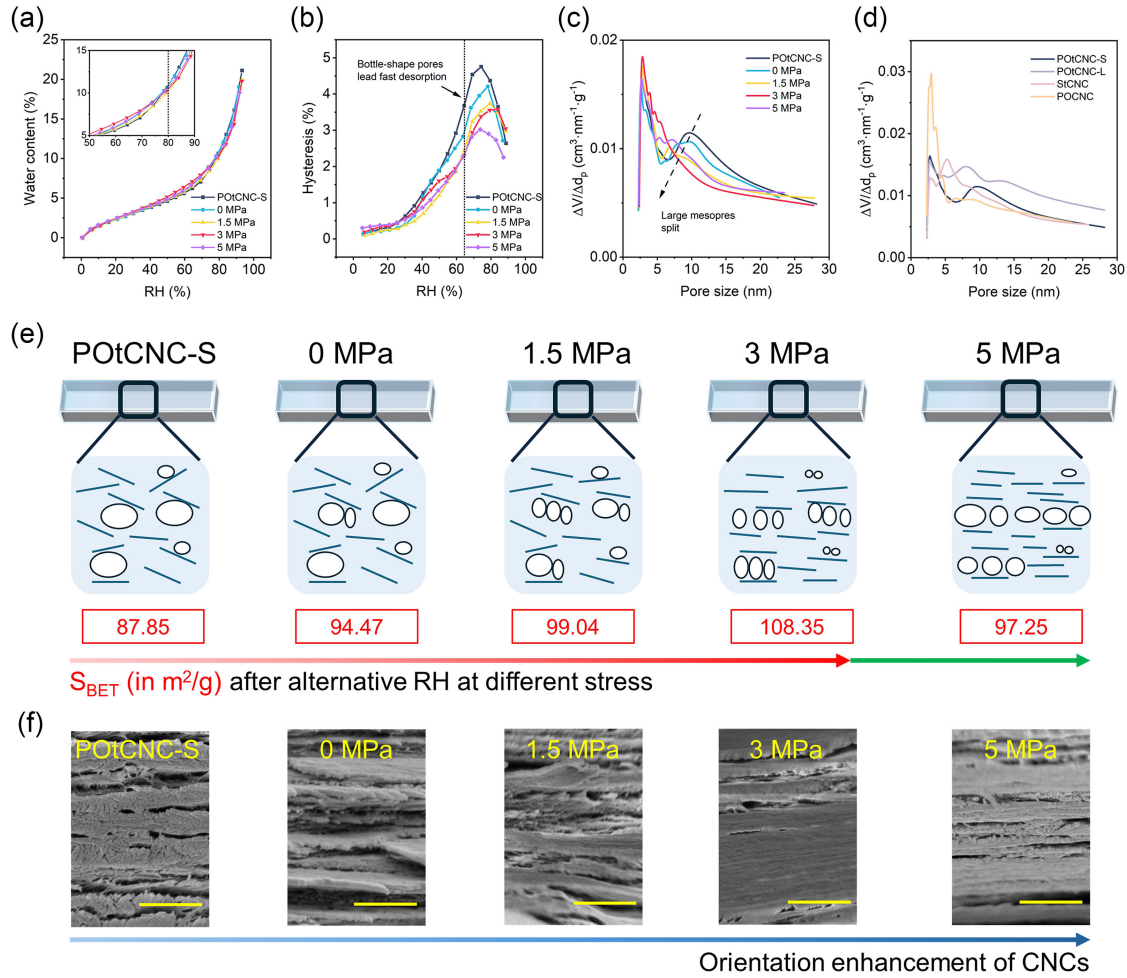


FIG. 2. Mesopore change and hydroplastication process analysis of creep-trained POTcNC films. (a) Water adsorption process of pristine and creep-trained POTcNC-S films under different stresses. (b) Water adsorption-desorption hysteresis of pristine and creep-trained POTcNC-S films under different stresses. (c) Mesopore distribution analysis on pristine and creep-trained POTcNC-S films under different stresses. (d) Mesopore distribution analysis on pristine POTcNC-S and other CNC films. (e) Schematic diagram of final POTcNC-S and mesopore status change after mechanosorptive creep trainings, with increasing loading stress during the creep processes. The numbers below the schematic images indicate the average values of specific surface area of the films. (f) SEM cross-section images of pristine and creep-trained POTcNC-S films under different stresses, and the scale bars all indicate 2 μm .

severe water condensation occurs, Fig. S7 [29]), creep-trained films subjected to higher stress display a reduced overall water uptake. This reduction implies the reconfigured or partially constricted mesopores under such stresses during the mechanosorptive creep training, inhibiting further infiltration of liquid water.

Hysteresis analyses of the adsorption-desorption curves [Figs. 2(b), S2, and S3 [29]] show more details on mesopore changes. In the desorption process, POTcNC-S samples showed a sudden decrease in water content at around 75% RH (Fig. S7 [29]), accompanied by a pronounced hysteresis maximum that is characteristic for bottle-like mesopores [34]. As the applied stress during mechanosorptive creep training increases from 0 to 5 MPa, such maximum value of the hysteresis gradually diminishes, pointing to a “bottleneck” that has widened or been partially split apart

under stress. Correspondingly, BJH model calculations reveal clear change of the mesopore sizes, as shown by the mesopore size distributions in Fig. 2(c) (detailed results in Table I). Although pristine POTcNC-S and the 0 MPa creep-trained sample both show the largest mesopore peak near 9.2 nm, 1.5 MPa external stress reduced the average pore size to 8.0 nm. With increasing external stress to 3 and 5 MPa for the creep training, the average pore size first decreased to 5.3 and then increased to 7.6 nm. We attribute this counterintuitive change of mesopore sizes to a quantitative competition between internal capillary forces and the material’s yield strength.

To elucidate the fundamental physical origin of this mesopore evolution on one-dimensional nanocrystals, we first propose a constitutive model based on the strain rate ($\dot{\epsilon}$) of the nanocrystal network acting on the pore walls

TABLE I. Mesopore sizes with corresponding potential Laplace pressure during 30%/80% RH trainings and specific area of various POCNC-S films.

Samples	POtCNC-S	0 MPa	1.5 MPa	3 MPa	5 MPa
d_p (nm)	9.2 ± 0.3	9.0 ± 0.4	8.0 ± 0.4	5.3 ± 1.2	7.6 ± 0.7
P_{cap} (MPa)	26.2	26.8	29.9	45.7	31.8
S_{BET} (m ² /g)	87.85 ± 0.47	94.47 ± 1.16	99.04 ± 1.10	108.35 ± 2.40	97.25 ± 3.81

constructed by CNCs. The driving force for the structural rearrangement is governed by the competition among three distinct stress fields: the anisotropic external load (σ_{ext}), the isotropic capillary suction (Laplace pressure, P_{cap}), and the opposing network stress (σ_{net}) inherent to the rigid CNC network [35,36]. The system evolves towards a mechanical equilibrium defined by

$$\eta \dot{\epsilon} = \sigma_{\text{ext}} - P_{\text{cap}} + \sigma_{\text{net}}. \quad (10)$$

Here, η is the viscosity of the system, σ_{ext} promotes expansion and alignment, while P_{cap} generates immense compressive suction (> 26 MPa) driving pore collapse. Crucially, this capillary-driven collapse is not unbounded but is resisted by σ_{net} , which arises from the bending stiffness (σ_{yield}) of the nanocrystals and the steric hindrance (σ_{geom}) as the pores shrink due to the geometric locking. More importantly, considering the surface properties and aspect ratio (λ) of rodlike nanocrystals, the bending stiffness part can be further described by [37]

$$\sigma_{\text{yield}} = \sigma_0 \chi \lambda^{-n}, \quad (11)$$

where σ_0 is the referring bending stiffness, typically regarded as the yield strength of POCNC-S film at 80% RH (23.1 MPa), while χ is the interaction factor brought by special surface groups on CNC surfaces, and λ^{-n} indicates the stiffness difference brought by CNC sizes, which is widely suitable for one-dimensional cellulosic materials [38]. The χ can be further expressed as a function of the degree of ionization (α) for the groups [39]

$$\chi = f(\alpha) = f\left(\frac{1}{1 + 10^{pKa - pH}}\right), \quad (12)$$

where pKa is the acid dissociation constant, which is 1.0 for $-\text{OSO}_3^-$ [40] and 3.2 for $-\text{COO}^-$ [41], while pH values for the initial CNC suspensions are the same (5.0). The surface interactions and sizes both affect the assembly structure during the drying processes, and finally indicate the difficulty for changing the formed pores with capillary force. As for the σ_{geom} , this force can be described by introducing a steric repulsion term similar to a Lennard-Jones term [42,43] as

$$\sigma_{\text{geom}} = k \left(\frac{d_{\text{CNC}}}{d_p} \right)^m, \quad (13)$$

where d_{CNC} is the diameter of CNCs, k and m are the constants, and d_p is the diameter of the mesopores. In addition, with a measured contact angle (θ) of around 33° (Fig. S1 [29]), the initial mesopores generate an immense Laplace pressure (P_{cap}), which can be expressed as [44]

$$P_{\text{cap}} = \frac{2\gamma \cos \theta}{r_p}, \quad (14)$$

where γ is the surface tension of the water, r_p is the average radius of the pores. Thus Eq. (10) can be finally expressed as

$$\eta \dot{\epsilon} = \sigma_{\text{ext}} - \frac{2\gamma \cos \theta}{r_p} + \sigma_0 f\left(\frac{1}{1 + 10^{pKa - pH}}\right) \lambda^{-n} + k \left(\frac{d_{\text{CNC}}}{d_p} \right)^m. \quad (15)$$

Thus, the mesopore changes can be analyzed according to different σ_{ext} and CNC properties (size and surface chemical properties). At low σ_{ext} of 1.5 MPa, P_{cap} dominates the initial yield strength, driving the network to consolidate until the rising σ_{net} (specifically the steric repulsion of POCNCs near the geometric locking limit) counterbalances the capillary pressure. Consequently, the observed hydroplasticity represents a stress-regulated shift in this thermodynamic equilibrium. Moderate σ_{ext} of 3 MPa lower the energy barrier for rearrangement, allowing the system to find a highly densified, locked configuration (due to the high σ_{geom}), whereas excessive σ_{ext} of 5 MPa override these internal balances to induce pore coalescence in parallel to macroscopic alignment [Fig. 1(d)].

The P_{cap} of different POCNC-S samples is placed in Table I. Crucially, this internal pressure exceeds the wet-state yield strength of the CNC network [regarding the yield stress of 23.1 MPa from Fig. 1(b)]. At a low σ_{ext} of 1.5 MPa, the system has a negative $\eta \dot{\epsilon}$ of -1.6 MPa, which means the mesopore is dominated by the capillary force, driving a capillary yielding process where CNCs are pulled into voids, causing the observed macroscopic shrinkage.

Moreover, raising the stress further to 3 MPa shrinks large mesopores even more strongly to about 5.3 nm. While

TABLE II. Unified semiquantitative analysis of hydroplastic mechanisms across different CNC networks with σ_{ext} of 1.5 MPa.

Samples	POTCNC-L	POTCNC-S	StCNC	POCNC
Length	Long (1237 nm)	Medium (695 nm)	Medium (927 nm)	Short (245 nm)
Surface group/pKa	$-\text{COO}^-/3.2$	$-\text{COO}^-/3.2$	$-\text{OSO}_3^-/1.0$	$-\text{COO}^-/3.2$
Initial network	Loose or defective	Moderate	Dense and bundled	Packed
d_p (nm)	13.2	9.2	5.5	4.8
P_{cap} (MPa)	18.3	26.2	43.4	> 50
Theoretic σ_{net}	Low (soft skeleton)	Low (soft skeleton)	High (chemically and geometrically lock)	Infinite (geometrically lock)
$\eta\dot{\epsilon}$ (MPa) at initial	-2.0	-1.6	≈ 0	≈ 0
Governing factor	Network collapse	Network collapse	Surface chemistry and geometry	Geometry-dominated
Elongation at 1.5 MPa	Shrink (-0.82%)	Shrink (-0.35%)	Stable (0.02%)	Stable (0.04%)

this reduction theoretically elevates P_{cap} to 45.7 MPa, further collapse is arrested by a hard-geometric constraint, and the pore diameter falls below the characteristic diameter of individual nanocrystals (~ 8 nm). According to Eq. (13), this creates a state of “steric locking” where CNCs cannot physically insert further, maximizing the fragmentation of free volume into the finest domains without total collapse. Besides, the limitation of this “steric locking” of CNC films is around 5 nm, considering the pore size of POTCNC-S sample (3 MPa), POCNC, and the StCNC samples.

Interestingly, pushing the stress to 5 MPa partially reverses this trend, expanding the dominant pore sizes back up to around 7.6 nm and the P_{cap} to 31.8 MPa. Here, the external stress becomes sufficient to override the capillary suction, inducing rigid-body rotation and forcing the coalescence of these fine and locked domains. Despite the existing small mesopores with pore size less than 5 nm in pristine POTCNC-S films, some medium mesopores occur in creep-trained samples. Overall, while moderate stress favors the formation of multiple smaller mesopores via capillary-driven splitting, excessive stress (more than 3 MPa) appears to compress or reshape these pores, possibly merging them again through tensile alignment. These results indicate the larger mesopores in POTCNC-S films play a similar role of free volume in polymer materials [45], providing additional space for shaping and deformation. Besides, pore size distributions for other CNC variants highlight the role of CNC dimensions and surface chemistry [Fig. 2(d) and Table II]. In addition, POTCNC-L tends to form a looser structure with larger mesopores (~ 13.2 nm), which can be ascribed to more spacious voids or defects formed by longer nanocrystals. In contrast, shorter POCNC and StCNC with stronger interactions produce denser networks [24] and smaller pores of < 5 and ~ 5.5 nm, respectively.

In parallel, the mesopore rearrangements of POTCNC-S samples coincide with CNC orientation [Fig. 2(d)], particularly under moderate or low stress. To clarify why 5 MPa prompts a partial recovery to larger pore sizes and

understand the transition with high applied stress during mechanosorptive creep, the BET model was applied to the 10%–35% RH adsorption data and calculated specific surface area (S_{BET}) shown in Fig. 2(e) and Table I. Samples subjected to 0–3 MPa display progressively higher S_{BET} relative to pristine POTCNC-S, reflecting mesopore splitting into smaller units and enhanced surface area. In comparison, S_{BET} decreases again at 5 MPa, suggesting that strong tensile forces compress or partially merge the newly formed pores. This finding is consistent with cross-sectional SEM images [Fig. 2(f)], where moderate stress compacts the CNC network most densely at 3 MPa, whereas 5 MPa reintroduces structural looseness. Taken together, these micro- and mesoscale observations demonstrate that mesopore size adjustments and CNC arrangement play a central role in vapor-induced hydroplastication. While moderate stresses fragment bottlelike mesopores into smaller domains, boosting orientation and increasing surface area, excessive stress may drive partial pore closure. Consequently, the stress during mechanosorptive creep training must be optimized to balance CNC alignment with mesopore variation for achieving superior hydroplastic properties.

As for the influences of different sizes and surface groups, we summarize the factors of different CNCs at $\sigma_{\text{ext}} = 1.5$ MPa in Table II. First, POTCNC-L represents a defect-dominated network collapse regime. Despite exhibiting the lowest theoretical P_{cap} of 18.3 MPa due to its large initial pore size (13.2 nm), it paradoxically displays the most significant shrinkage (-0.82% elongation). This behavior is attributed to the high λ and the weak acidity of surface carboxyl groups (a pKa of 3.2). The partial ionization leads to a loosely assembled scaffold with a high density of topological defects, resulting in a soft skeleton with a wet-state yield strength ($\sigma_{\text{yield}} = 14.8$ MPa in Fig. S5 [29]) insufficient to counteract even the moderate capillary suction. Consequently, the net stress becomes negative ($\eta\dot{\epsilon} = -2.0$ MPa), driving the structural collapse. In contrast, StCNC exemplifies a surface chemistry and geometry-dominated stability mechanism. Although its smaller pore size (5.5 nm) generates a much higher P_{cap}

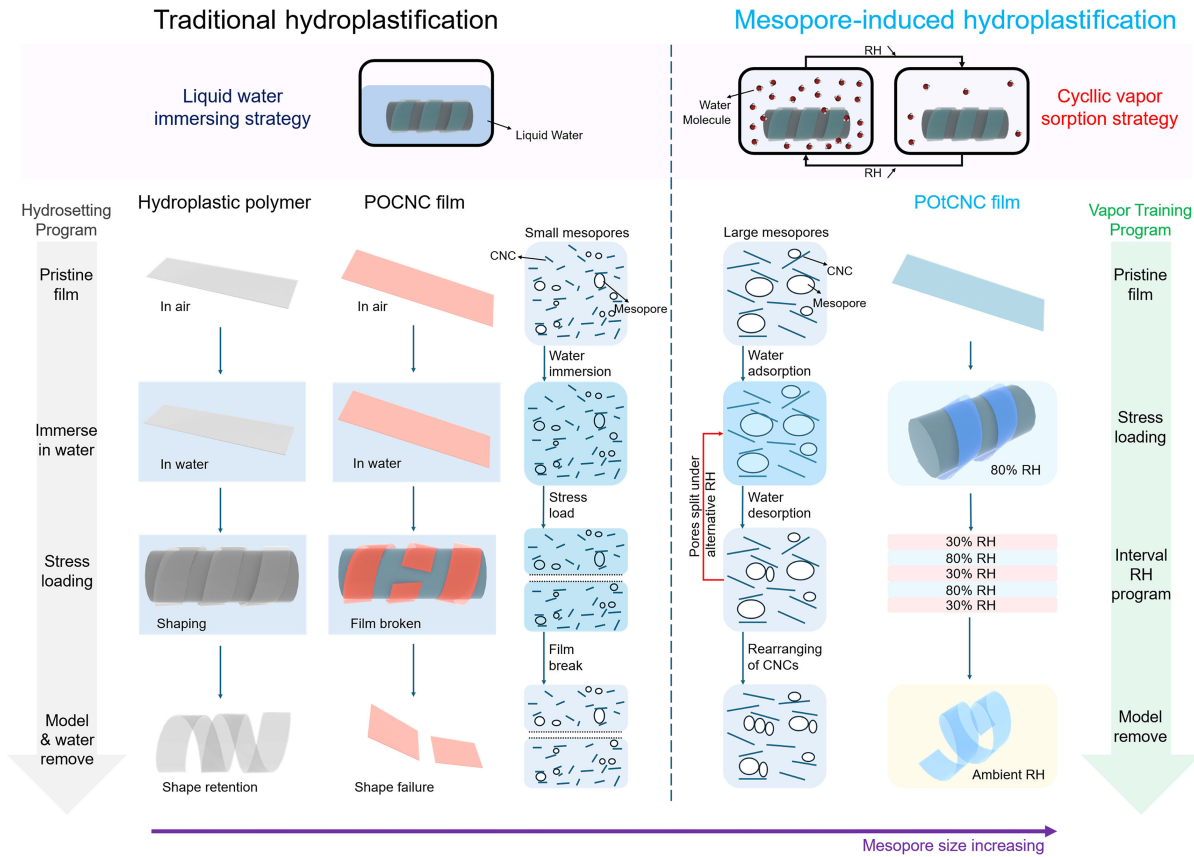


FIG. 3. Schematic diagram of traditional hydroplastication on hydroplastic polymers and CNC films, and mesopore-induced hydroplastication on POTcNC films via vapor training program.

of 43.4 MPa, the film remains dimensionally stable (0.02% elongation). This stability originates from the low pK_a (1.0) of the sulfonate groups, which ensures full ionization and strong electrostatic repulsion during assembly [Eqs. (11) and (12)]. This chemical reinforcement creates a dense, stiff network with a yield strength that effectively exceeds the capillary driving force ($\sigma_{\text{yield}} > P_{\text{cap}}$), preventing densification along with high σ_{yield} . Finally, POCNC illustrates the geometry-dominated locking limit. With pore sizes approaching the CNC diameter, the theoretical capillary pressure exceeds 50 MPa. However, the network is effectively incompressible as it hits a geometric “hard wall” where steric hindrance provides infinite resistance to further shrinkage (an infinite σ_{geom} due to very small mesopores). At this status, σ_{geom} can usually balance the P_{cap} . Regardless of the immense capillary potential and the absence of free volume locks the structure, POCNC film results in negligible elongation of 0.04% governed solely by external creep.

C. Hydroplasticity of CNCs via the vapor-training program

Based on the mesopore change-induced plastification behavior of creep-trained CNC films, we develop a new vapor training method to make rigid nanocrystal films

plastic and shapable into different structures. Unlike a traditional hydroplastication program with the aim on rearranging polymer chains in hydroplastic materials with a high amount of water molecules for sufficient swelling (Figs. 3 and S8 [29]), hydroplastication via vapor training is based on the mesopore change that leads to the overall structural change during the adsorption-desorption program with a much lower amount of water molecules. In this approach, POTcNCs (> 700 nm) are proposed to form neat films, and further exposed to 80% RH for 30 min to soften the material, then molded against a model. Following multiple cycles of RH alternation (30%/80%, each 30 min), the film acquires a stable shape under ambient RH, such as a helical configuration. The larger mesopore sizes from longer POTcNCs bring better shaping ability, where the stress and water sorption are applied to adjust the mesopores and render the POTcNC films hydroplastic. In comparison, the traditional hydroplastication mechanism brings little change of the mesopores. Especially, because CNCs possess high crystallinity and brittleness (Fig. S9 [29]), shaping them directly in liquid water often leads to film fracture.

While vapor training enables the hydroplastic shaping of CNC films based on mesopore change, the morphology and surface chemistry of the CNCs profoundly affect the

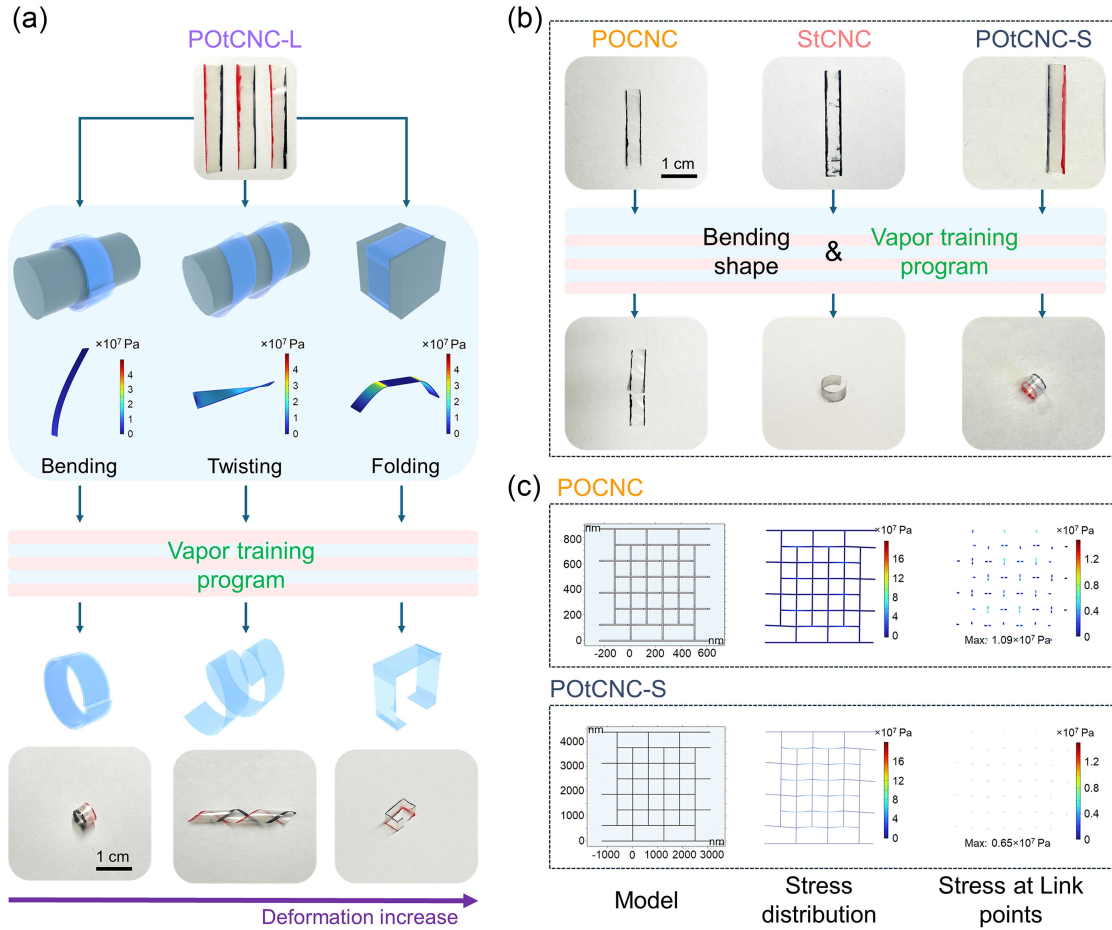


FIG. 4. Characteristics influencing mesopore-induced hydroplasticity of CNC films. (a) Different shapes of POTCNC-L films via vapor-training program and the stress distribution analysis by FEM method. (b) Further hydroplasticity results on short POCNC and long StCNC and POTCNC-S films. (c) FEM on stress distribution of CNC films fabricated by short POCNC and long POTCNC.

outcome by governing mesopore characteristics. This mesopore-induced hydroplasticity can be extended to practically adjust the geometries of CNC films. As shown in Fig. 4(a), POTCNC-L films can be bent, twisted, or folded under vapor training, with FEM estimates indicating maximum stresses of 6.0, 24.3, and 49.1 MPa, respectively. Although bending or twisting deformations can be reversed by exposing the film to high RH ($> 80\%$, for example shown in Fig. S10 [29]), the folded sample maintains its shape under similar conditions. Besides, this characteristic also makes these POTCNC films loaded with larger stress irreversible for the shaping via vapor training (Fig. S11 [29]), but applying a small stress during vapor training can make the film reshapeable for at least 20 times (Fig. S12 [29]). These observations imply that CNC-based hydroplastics can withstand substantial stresses of over 20 MPa without catastrophic failure, whereas stresses above ~ 40 MPa induce microscopic damage consistent with tensile data [Figs. 2(b) and S5 [29]].

CNC morphology and surface functionality also affect the hydroplastic capability via vapor training as further highlighted in Fig. 4(b). Under a vapor training program of

bending, POCNC films fracture immediately, while StCNC forms only a partial bend, failing to close into a ring. POTCNC-S can achieve ring formation but struggles with more severe deformations like twisting (Fig. S13 [29]), producing a larger radius than POTCNC-L samples. Moreover, at high RH, bent StCNC film remains curved, whereas POTCNC-S reverts to a flat shape similar to POTCNC-L (Fig. S10 [29]). The discrepancy between StCNC and POTCNC arises from their differing surface groups. StCNC carries sulfonic acid moieties ($-\text{SO}_3^-$) that reinforce interparticle interactions, leading to more tightly bundled suspensions, and finally smaller mesopores [Fig. 2(d)]. Smaller mesopores limit the deformation of StCNC films. Additionally, fewer hydrogen bonds break in StCNC at elevated RH (DMTA humidity sweep results in Fig. S6 [29]), reinforcing the film's resistance to shape change. The different shape ability of POCNC and POTCNC films can be ascribed to the stress distribution of CNC networks. Usually, longer nanocrystals introduce more defects during film formation, yielding a looser cross-sectional structure (Fig. S14 [29]) that promotes easier deformation. Stress distribution analysis [Fig. 4(c) from

FEM results shows that longer nanocrystals lower the stress at mechanical link points, reducing stress concentration and brittleness. Consequently, shorter POCNCs are more prone to breakage, also in liquid water. Hence, modulation of CNC morphology and surface properties alters mesopore characteristics, thereby enabling vapor training to effectively reshape CNC films through hydroplastification.

IV. CONCLUSIONS

This study demonstrates a new plastification mechanism of tuning mesopore structures and nanocrystal arrangement through a vapor training program. Especially, this plastification mechanism enables efficient shaping of hydrophilic CNC films while overcoming the brittleness associated with their high crystallinity. In contrast to traditional water-immersion methods that often lead to CNC film fracture, the vapor training process efficiently adjusts mesopore sizes, especially those films with longer CNCs. Alternative RH change leads to cyclic adsorption-desorption processes of CNC films, promoting CNC orientation under moderate stress. As a result, POTCNC films achieve enhanced plasticity and stable final shapes, such as helical deformation, after the vapor training program. The mechanosorptive creep results highlight that film strain does not uniformly increase under cyclic RHs, revealing shrinkage at lower stresses of 1.5 MPa and balanced or progressive creep at higher stresses of 3 MPa and 5 MPa, respectively. To explain this phenomenon, we establish a semi-quantitative constitutive relationship revealing that the hydroplastic behavior is governed by the dynamic competition between the anisotropic external stress and the isotropic internal capillary pressure. Crucially, we demonstrate that this competition is intrinsically regulated by the network's wet-state yield strength, which depends on the CNC aspect ratio and surface chemistry. Specifically, for POTCNCs with high aspect ratios, the weak acidity and topological defects create a soft skeleton. The internal Laplace pressure (~ 26 MPa) exceeds the network's yield strength, driving the splitting of bottle-like mesopores into smaller domains until a geometric locking limit defined by the nanocrystal diameter is reached. In contrast, strong electrostatic repulsion from fully ionized sulfonates or steric jamming in short nanorods creates rigid networks that arrest this capillary-driven densification. Conversely, excessive stress leads to pore coalescence and partial closure, coinciding with significant cross-section morphology changes and enhanced alignment. Furthermore, morphology and surface chemical properties of the nanocrystal both critically influence mesopore distribution, enabling precise control over mechanical behavior and shape abilities. In summary, the mesopore regulation based on the vapor training program provides a new method to tune hydroplastic behaviors of hydrophilic nanocrystals, expanding the plastic response mechanism and application of rigid nanomaterials.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [46].

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