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# Hydroplastic polymers as eco-friendly hydrosetting plastics

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Despite the considerable benefits plastics have offered, the current approaches to their production, use and disposal are not sustainable and pose a serious threat to the environment and human health. Eco-friendly processing of plastics could form part of the solutions; however, the technological challenge remains thorny. Here, we report a sustainable hydrosetting method for the processing of a hydroplastic polymer—cellulose cinnamate. Synthesized via facile solvent casting, the transparent cellulose cinnamate membranes are mechanically robust, with tensile strength of 92.4 MPa and Young's modulus of 2.6 GPa, which exceed those of most common plastics. These bio-based planar membranes can be processed into either two-dimensional (2D) or three-dimensional (3D) shapes by using their hydroplastic properties (using water to manipulate the plasticity). These desired shapes maintain stability for >16 months and can be repeatedly reprogrammed into other 2D/3D shapes, substantially extending their lifetime for practical applications.

lastics have become increasingly indispensable in modern life since the 1950s owing to the combination of characteristics, such as light weight, low cost and adaptability<sup>1</sup>. Around 368 million tons of plastics were produced worldwide in 2019<sup>2</sup>. Around 79% of them accumulated in landfills or the natural environment<sup>1</sup>, which caused severe detrimental impacts on nearly all forms of life on earth. Currently, an active research area is to address these challenges, for instance by using depolymerase to break down poly(ethylene terephthalate) (PET) for recycling plastic bottles<sup>3</sup>. Plastics are typically polymers of fossil origin with petrochemicals, such as crude oil and gas, as raw materials<sup>4</sup>. They can nowadays also be partially produced from renewable sources, such as carbon dioxide, vegetable oils and carbohydrates<sup>4</sup>. Cellulose, with an annual production of >75 billion tons globally, is the most abundant natural polymer on earth, constituting virtually an inexhaustible source of raw material for plastics manufacture<sup>5</sup>. Using cellulose as raw material to produce cellulose nitrate as plastics with camphor as plasticizer can be dated back to 1870s6. Later on, cellulose derivatives including cellulose acetates and cellulose butyrates were produced as plastic products<sup>6</sup>.

Currently, widely used plastics can be mainly classified into two categories: thermoplastics and thermosets, while elastomers are comparatively much less<sup>7,8</sup>. Thermoplastics generally comprise single chains of polymers, which remarkably change their states at transition temperatures. Thermosets are composed of polymer networks, which cannot return to a mouldable state once the network is formed. Thus, thermoplastics are remoldable and recyclable via temperature manipulation, while the recycling of thermosets is usually highly challenging<sup>7,8</sup>. On the basis of the aforementioned properties, plastics can be processed via methods ranging from extrusion, injection moudling and thermoforming, through calendaring and compression moudling to additive manufacturing and so on<sup>8,9</sup>. These methods usually involve expensive and complex machines, harsh conditions, such as high temperature, or curing processes with oxygen exclusion<sup>10,11</sup>. New eco-friendly methods for plastics engineering and processing are strongly desired, demanding corresponding new properties of plastics. Instead of conventional characters of polymers, such as thermoplastic and thermosetting, we turned to hydroplastic polymers. Similar to thermoplastic polymers that remarkably change states at their transition temperatures, the states of hydroplastic polymers can be massively influenced by water. We envisage that hydroplastic polymers have great potential as eco-friendly plastics, which can possibly be moulded by using water alone. We attempted to include the following in our study: (1) using sustainable materials as raw materials for the production of plastics, for example cellulose; (2) a corresponding facile and green engineering method for processing obtained plastics; and (3) obtained plastics being reusable and recyclable with highly extended life-cycles.

Herein, we report a new type of plastic, hydroplastic, using a hydroplastic polymer cellulose cinnamate (CCi) derived from cellulose and the facile hydrosetting method for shape-changing or shape-fixing. Plastic strips made of CCi polymers are readily transformed and repeatedly reprogrammed into versatile 2D/3D shapes via hydrosetting and their shapes maintain long-term stability. Dynamic mechanical thermal analysis (DMTA) and dynamic vapour sorption (DVS) analysis under controlled relative humidity (RH) are used to elucidate the effect of water on their hydroplastic properties.

#### Results

**Preparation of hydroplastic CCi membranes.** CCi was synthesized by esterifying cellulose with cinnamoyl chloride in *N*, *N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) (Fig. 1a)<sup>12,13</sup>. Its chemical structure was confirmed using <sup>13</sup>C and <sup>1</sup>H nuclear magnetic resonance (NMR) spectra (Supplementary Fig. 1). The degree of substitution was calculated as 0.27 on the basis of the results of elemental analysis (Supplementary Information). CCi is well soluble in dimethyl sulfoxide (DMSO) but not in other common solvents.

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**Fig. 1** Preparation of hydroplastic CCi membranes. a, Synthesis of CCi. b, Schematic illustration for the fabrication of CCi membranes via solvent-casting method as well as the conceptual illustration for the hydrosetting shape-engineering of CCi membranes. c, A representative photo image of a transparent CCi membrane over the printed name of Georg-August-University of Göttingen. d-g, Scanning electron microscopy images showing the top surface (d), bottom surface (e), cross-section (f) and enlarged cross-section (g) of CCi membranes. Scale bars in c-g are 10 mm, 0.5 μm, 0.5 μm, 5 μm and 200 nm, respectively.

CCi membranes with thicknesses of  $10-20 \,\mu$ m were fabricated via facile solvent casting. Obtained CCi membranes were generally flat, highly transparent and could be transformed into other shapes, such as a helix via a facile hydrosetting method by immersing in water and air-drying (Fig. 1b,c). Both the top and bottom surfaces of CCi membranes were highly smooth (Fig. 1d,e), while the interior of the CCi membranes showed a nanocomposite structure with nanoparticles evenly dispersed in a continuous matrix (Fig. 1f,g and Supplementary Fig. 2). The nanoparticles had diameters in the range of 35-50 nm with an average diameter of  $42.0 \pm 3.2 \,\text{nm}$ . The presence of two distinct topographies as nanoparticles and continuous matrix within the same membrane should be due to the phase separation during the drying process of film formation.

Sustainable and highly facile hydrosetting method. CCi membranes were easily transformed into various two-dimensional (2D) or three-dimensional (3D) shapes via the sustainable and facile hydrosetting method (Figs. 1b and 2a). The hydrosetting process comprised (1) the immersion of CCi membrane strips in water for 5 min that allowed the programming into desired shapes in wet state and (2) following air-drying in the ambient environment (room temperature and RH 30-40%) for 10-30 min until constant weights. To fix the shapes, assistant moulds were used only as templates, such as a cylinder or a cube. After drying, self-standing membranes were fixed in distinct shapes, for instance helix, ring, holder and block (Fig. 2a), which were exactly the desired shapes as programmed in the wet state. These fixed shapes maintained stability for a long term of >16 months (Fig. 2a and Supplementary Fig. 3). Moreover, the CCi membranes were sequentially programmed and fixed into versatile 2D/3D shapes in diverse sequences with facile hydrosetting. For example, they were programmed in four exemplarily demonstrated shapes as helix, ring, holder and block with distinct sequences (Fig. 2b-d and Supplementary Fig. 4). Also, these shapes

could be transformed into each other reversibly and arbitrarily (Fig. 2e). Furthermore, one single CCi membrane strip could be continuously reprogrammed and fixed in distinct 2D/3D shapes for >15 cycles via the facile hydrosetting process, which demonstrated the sustainable reusability of these hydroplastic CCi membranes. However, cellulose derivatives with alkane chains of different chain lengths, such as cellulose stearoyl esters and cellulose 10-undecenoyl esters with various degrees of substitution, were found not suitable to be used as hydroplastics (Supplementary Fig. 5).

Static mechanical properties. Static mechanical properties of as-prepared CCi membranes (cycle 0) as well as those after 5, 10 and 15 times of hydrosetting shape-programming (cycles 5, 10 and 15) were analysed (Fig. 3). As-prepared membranes were strong, stiff and tough with a tensile strength of  $92.4 \pm 2.2$  MPa, Young's modulus of  $2.6 \pm 0.1$  GPa, elongation at break of  $15.2 \pm 1.8\%$  and fracture energy of  $11.9 \pm 1.6$  MJ m<sup>-3</sup>. The presence of nanoparticles in the matrix should dissipate much energy when loaded with stress. The numerous entanglements between polymer chains as well as other interactions, including hydrogen bonds and  $\pi$ - $\pi$  stacking should also contribute to the high strength, stiffness and toughness of as-prepared CCi membranes. The hydrosetting process would induce minor relaxation and rearrangement of CCi polymer chains in each cycle of shape-programming. However, the relaxation and rearrangement were so small that, after five hydrosetting cycles, the tensile strength, Young's modulus, elongation at break and fracture energy of CCi membrane strips maintained at  $92.0 \pm 6.1$  MPa,  $2.0 \pm 0.1$  GPa,  $15.7 \pm 2.8\%$  and  $11.9 \pm 3.0$  MJ m<sup>-3</sup>, respectively. The relaxation and rearrangement of CCi polymer chains continued to accumulate with more hydrosetting cycles. After ten hydrosetting cycles, the CCi membranes became slightly stiffer and stronger with trivial loss of ductility and toughness. The tensile strength and Young's modulus increased slightly to  $120.9 \pm 8.2$  MPa and



**Fig. 2 | Sustainable and highly facile hydrosetting shape-programming of CCi membranes. a**, Schematic diagram and experimental demonstration for programming CCi plastic strips into diverse 2D/3D shapes via the hydrosetting method and their shape stability (Supplementary Fig. 3). Scale bars, 5 mm. Transparent CCi membrane strips (30 × 5 mm<sup>2</sup>) were stroked by mark pens on the edges for clarity. **b**-**d**, Schematic flow charts showing the continuous programming of the same CCi membrane strip into versatile shapes in diverse sequences via the hydrosetting process as helix-ring-holder-block-ring (**b**), ring-helix-block-holder-helix (**c**) and block-helix-holder-ring-block (**d**). See also Supplementary Fig. 4 for experimental demonstrations. **e**, A summary chart exemplifying the reversible and random transformation of CCi membranes from one 2D/3D shape to another via the facile hydrosetting method.

 $3.0 \pm 0.2$  GPa, while the elongation at break and fracture energy decreased to  $11.2 \pm 0.1\%$  and  $10.5 \pm 0.7$  MJ m<sup>-3</sup>, respectively. All relaxation and rearrangement of CCi polymer chains that hydrosetting processes could cause should have occurred during the first ten cycles of shape-programming. More hydrosetting cycles could not induce further substantial changes of the mechanical properties of hydroplastic CCi membranes. Thus, with the shape-programming increased to 15 cycles, the CCi membranes showed similar tensile strength and Young's modulus of  $113.4 \pm 8.4$  MPa and  $3.0 \pm 0.2$  GPa, while the elongation at break and fracture energy also remained around  $11.5 \pm 0.3\%$  and  $10.4 \pm 1.6$  MJ m<sup>-3</sup> compared to those after ten cycles. Notably, as-prepared CCi membranes as well as those after 5, 10 and 15 cycles of hydrosetting shape-programming showed comparable or superior tensile strengths and Young's moduli,

compared with currently widely used thermoplastic materials, such as PE, PP, PET, PVC and thermosetting plastic materials including epoxies and phenolics (Fig. 3d)<sup>14</sup>.

The importance of water during dynamic hydrosetting process. DVS analysis was executed to reveal the hydroplastic properties of CCi membranes (Fig. 4a). The sorption isotherms resembled type IV according to IUPAC classifications<sup>15</sup>. The sorption curve was analysed with the Guggenheim–Anderson–de Boer (GAB) model<sup>16</sup>, which is usually expressed as:

$$M = \frac{CKM_0 a_{\rm w}}{(1 - Ka_{\rm w})(1 - Ka_{\rm w} + CKa_{\rm w})}$$
(1)



Fig. 3 | Static mechanical properties of hydroplastic CCi membranes. a, Stress-strain curves. b, Tensile strength and Young's modulus. c, Elongation at break and fracture energy of as-prepared CCi membranes (cycle 0) as well as those after 5, 10 and 15 times of shape-programming (cycle 5, 10 and 15) via hydrosetting. d, Tensile strengths and Young's moduli of CCi hydroplastics compared with currently widely used thermoplastics and thermosetting plastics<sup>14</sup>.

where M is the equilibrated water content (g per 100 g solid),  $a_w$  is water activity (RH),  $M_0$  is the water content in monolayer (g per 100 g solid), C is the Guggenheim constant that is related to the different enthalpy of monolayer and multilayer sorption and K is a constant related to the different sorption heat of multilayer water and bulk liquid water. The sorption curve was well fitted to the GAB model with  $R^2$  of 0.999 and  $M_0$ , C and K of 4.84, 5.15 and 0.85, respectively. As shown in Fig. 4a, the water vapour sorption rose slowly at low RH ranges with the gradual occupation of the primary sorption sites. This could be explained by the hydrophobic character of the CCi membranes with a static water contact angle of  $91.0 \pm 6.2^{\circ}$ . Then, the sorption rose gradually without a distinctive 'knee' point, which implied a significant overlap of the total coverage of the monolayer and the beginning of the multilayer sorption<sup>15</sup>. The steep increase of sorption in high RH range was mainly due to the multilayer sorption and the equilibrated water content reached 22 wt% at 93% RH. The desorption curve ended up in the negative range at 0% RH, which should be due to the water sorption within CCi membranes during storage in ambient environment. On the basis of GAB fitting, the cluster number of water in dependence of water activity was estimated according to the following equation<sup>17</sup>

$$N_{\rm C} = -(1-\varphi_1) \times \left(\frac{\varphi_1}{M_0 C} \left(-2CKa_{\rm w} + 2Ka_{\rm w} + C - 2\right) - 1\right)$$
(2)

where  $N_c$  is the cluster number of water and  $\varphi_1$  is the volume fraction of water. Surprisingly, the cluster number decreased from 1 to 0.84 when water activity increased from 0.004 to 0.93, which indicates no water clustering even at high RH region (Fig. 4a). Several reasons could account for this result. On the one hand, a large  $M_0$  value from GAB fitting indicates a large amount of primary sorption sites for monolayer sorption. On the other hand, the significant overlap of the monolayer coverage and the beginning of multilayer sorption also implies the difficulty of forming water clusters. In fact, the absence of water clusters should hinder water

transport within CCi membranes. Fast water transmission facilitates quick plasticity change in sorption/desorption processes for precise shape-programming and rapid shape-fixing of CCi membranes. It also favours the shape stability of programmed shapes due to rapid and thorough removal of water during the drying process.

In addition to DVS analysis, DMTA provided further information about the hydroplastic properties of CCi membranes (Fig. 4). The storage moduli of as-prepared CCi membranes decreased gradually from  $4.94 \pm 0.12$  GPa to  $3.54 \pm 0.02$  GPa with increasing RH from 23 to 78% (Fig. 4b). Then, it dropped drastically to  $1.92 \pm 0.03$  GPa, when the RH further rose to 93%. Correspondingly, the damping factors increased gently from  $0.056 \pm 0.001$  to  $0.073 \pm 0.002$  in the RH range of 23-78% and intensely to  $0.121 \pm 0.005$  at 93% RH. No substantial change of loss moduli with the variation of RH was observed (Supplementary Fig. 6). According to DVS analysis, the water content at 78% RH was 13.2 wt% with multilayer water. Thus, the mobility of CCi polymer chains should have increased gradually with monolayer water sorption at low RH range and drastically when the total amount of water sorption was larger than 13.2 wt% with multilayer water sorption. Moreover, the RH-dependent development of the storage and loss moduli of CCi membranes after multiple shape-programming steps was similar to those of as-prepared ones but their storage moduli varied and reached  $5.21 \pm 0.16$  GPa,  $5.12 \pm 0.57$  GPa and  $4.69 \pm 0.38$  GPa at 23% RH for samples after 5, 10 and 15 cycles, respectively (Fig. 4b and Supplementary Fig. 6). Therefore, the effect of water on CCi membranes after diverse shape changes should be similar and multiple shape-programming did not substantially affect the hydroplastic properties of CCi membranes.

RH-dependent hydroplasticity of CCi membranes led to higher storage and loss moduli at lower RH; for example,as-prepared CCi membranes showed higher storage and loss moduli of  $5.85 \pm 0.58$  GPa and  $0.30 \pm 0.05$  GPa at 30% RH than at  $3.79 \pm 0.36$  GPa and  $0.26 \pm 0.07$  GPa at 80% RH, respectively (Supplementary Fig. 6). In comparison, the storage moduli and damping factors of as-prepared CCi membranes remained stable after 4 h at 10 Hz or between 0.1 and 100 Hz at fixed RH of 30 or 80%. The constant moduli and damping factors within the frequency sweep tests indicate the



**Fig. 4 | Effect of water on the hydroplastic properties of CCi membranes. a**, Dynamic water vapour sorption isotherm of as-prepared CCi membranes, GAB fitting of the sorption curve and calculated cluster number of water. Inset shows the static water contact angle on a CCi membrane. b, Humidity sweep of as-prepared CCi membranes (cycle 0) as well as those after 5, 10 and 15 times of shape-programming (cycles 5, 10 and 15) via hydrosetting processes. **c**, Mechanosorptive creep behaviours of as-prepared CCi membranes. See Supplementary Fig. 8 for the experimental scheme. **d**, Temperature sweep of as-prepared CCi membranes at RH of 30 and 80%. See Supplementary Fig. 6 for the data of loss moduli and other DMTA measurements.

strong interactions between CCi chains in CCi membranes. These results explained the prominent long-term shape stability of CCi membranes under a constant condition (Supplementary Fig. 3). However, CCi membranes gradually changed their shapes under surroundings with varying RH (Supplementary Fig. 3). The shape stability under constant RH and instability with varying RH should be related to the mechanosorptive creep of CCi membranes (Fig. 4c). The creep under constant RH of as high as 80% was very small, with the strain increasing very slightly from 2.78 to 2.84%. Nevertheless, the strain increased at a relatively higher rate under cycling RH that alternatively changed between 30 and 80%. Such mechanosorptive creep behaviours could generally be attributed to the sorption-induced gradient stress changes within the CCi membranes<sup>18,19</sup>.

The hydroplastic CCi membranes also showed thermoplastic characters, while the performance highly depended on the RH (Fig. 4d). When the temperature increased from 20 to 88 °C, the storage moduli decreased steadily (24%) from  $5.70 \pm 0.19$  GPa to  $4.32 \pm 0.31$  GPa, while damping factor increased (25%) from  $0.056 \pm 0.005$  to  $0.070 \pm 0.001$  at 30% RH. This indicated the higher mobility of CCi polymer chains at higher temperature. This thermoplastic character was greatly enhanced at 80% RH with drastic decrease of storage moduli (69%) from  $4.05 \pm 0.43$  GPa to  $1.26 \pm 0.17$  GPa and prominent increase of damping factor (96%) from  $0.068 \pm 0.005$  to  $0.23 \pm 0.04$ . These results further approved the prominent impact of high RH on the mechanical properties and thus the hydroplastic character of CCi membranes. Therefore, CCi membranes showed hydroplastic and RH-dependent thermoplastic properties but RH played the predominant role in the hydrosetting processes.

#### Discussion

In summary, we used a hydroplastic polymer CCi for the formation of hydroplastics. The hydroplastic features of CCi membranes allowed their highly facile and sustainable hydrosetting shape-programming. They were programmed into various 2D/3D shapes in wet state, which were fixed after air-drying. The programmed shapes maintained long-term stability and could be further reprogrammed and fixed in other arbitrary 2D/3D shapes with different sequences multiple times via hydrosetting. Moreover, the CCi hydroplastics showed prominent mechanical properties compared with currently widely used plastics. The findings in this study provide insights into hydroplastic polymers, which opens a window for eco-friendly and sustainable processing as well as reusing of plastics.

This work provides a feasible strategy to design eco-friendly hydroplastics with superior mechanical properties from renewable resources, for example cellulose, which should stimulate further exploration of other bioplastics with sustainable characters and superior properties. The hydroplastic feature of CCi could spark the development of more types of hydroplastics as well as diverse hydroplastics-based materials with prominent properties and functions. The unique hydrosetting method for plastics processing with only water under ambient conditions as the processing medium avoids expensive and complex machines and harsh processing conditions. This eco-friendly method highly simplifies the procedure of plastics processing, makes their processing and recycling more economic and sustainable and provides tremendous potential for plastics to be applied in various advancing scenarios, such as biology, electronics and medicine. In particular, the detrimental effects of plastics on the environment, life on earth and human society would be minimized by reusing of hydroplastics with their unique features.

#### Methods

**Materials.** Commercial microcrystalline cellulose with a particle size of  $50 \,\mu\text{m}$  and degree of polymerization of ~270 was purchased from Sigma–Aldrich Chemie GmbH (Steinheim). DMAc (99.5%) and cinnamoyl chloride (98%) were purchased from J&K Scientific GmbH. LiCl was purchased from MP

Biomedicals. Pyridine (99%) was purchased from abcr GmbH. DMSO (99.5%) was purchased from Carl Roth GmbH & Co. KG. Methanol (99.8%) was purchased from TH. Geyer GmbH & Co. KG. Dummy CZ-Si wafer was purchased from MicroChemicals GmbH.

Synthesis of CCi. CCi was synthesized by the acylation of cellulose under homogeneous condition according to a previously reported method with modifications<sup>12,13</sup>. Briefly, 1 g of previously dried microcrystalline cellulose and 40 ml of DMAc were fed into a 100-ml three-necked flask, which was equipped with a magnetic stir bar and connected to a condenser. The mixture was stirred at 130 °C for 30 min, followed by adding 3 g of LiCl under stirring. After cooling down to room temperature, a clear cellulose solution was obtained. The solution was then heated to 60 °C before 2.00 ml of cinnamoyl chloride and 2.24 ml of pyridine were added under stirring. The reaction was carried out by maintaining the temperature at 60 °C with stirring for 3 h. The mixture was subsequently precipitated in 200 ml of methanol. The product was collected by centrifugation and purified by repeated dissolution in DMSO and precipitation in methanol. The pure product was dried in vacuum before being dissolved in DMSO for storage.

NMR spectroscopy. CCi was dissolved in deuterated DMSO for liquid-state <sup>1</sup>H NMR and <sup>13</sup>C NMR measurement on a Bruker DRX 500 spectrometer (Bruker, BioSpin GmbH) with a frequency of 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR. Totals of 65 and 16,000 scans were collected for <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, respectively. The repetition delay was 5 s for <sup>1</sup>H NMR and 1 s for <sup>13</sup>C NMR spectra.

**Elemental analysis.** Elemental analysis was performed on an elemental analyser Vario EL III CHN instrument from Elementar (Hanau).

**Preparation of CCi membranes.** CCi membranes were prepared via facile solvent casting. Firstly, a mould was assembled by sandwiching a wafer substrate between two blocks of Teflon. The wafer substrate  $(60 \times 60 \times 0.7 \text{ mm}^3)$  was sonicated twice at 37 Hz,  $60 \,^{\circ}$ C in DMSO and deionized water for 3 min, respectively, followed by blow-drying with nitrogen before use. The Teflon blocks were  $90 \times 90 \times 15 \text{ mm}^3$  in size with a hollow cylinder ( $\emptyset = 50 \text{ mm}$ , h = 15 mm) in the centre of the upper block as well as thread in the surrounding margin for assembly fixation and level adjustment. Then, 5 ml of CCi solution with a concentration of 10 mg ml<sup>-1</sup> was transferred into the assembled moulds. CCi membranes were formed after drying at 80 °C and 15 mbar in a vacuum oven for overnight. The membranes were peeled off wafer after disassembly of the moulds.

**Scanning electron microscopy.** The images of cross-section and surfaces of CCi membranes were measured using an SEM Leo SUPRA 35 instrument (Carl Zeiss SMT GmbH). A 10-nm layer of carbon was vacuum-coated on the samples before observation. The sizes of nanoparticles were measured by using the program Nano Measure and 40 nanoparticles were measured to calculate the average diameter and standard deviation.

Static mechanical test. Mechanical tests were performed on a Z3 microtensile test machine with a 50-N load cell (Grip-Engineering Thümler GmbH). CCi membranes with a dimension of  $30 \times 5 \text{ mm}^2$  were loaded into the test machine with a clamp distance of 8.0 mm and subjected to uniaxial extension with a constant rate of 2 mm min<sup>-1</sup> until rupture. In each case, at least six equal samples were measured to ensure accuracy of the results. The stress was calculated by dividing force by cross-section area, while the strain (%) was defined as  $(L - L_0)/L_0 \times 100\%$ , where *L* is the instantaneous length and  $L_0$  is the initial length of the sample. Toe compensation was performed before any calculation to obtain correct values by using stress–strain curves. The calculation of tensile strength, Young's modulus, elongation at break and fracture energy, as well as the toe compensation were performed according to ASTM D882-02 (ref. <sup>20</sup>).

**Dynamic vapour sorption.** A DVS apparatus (DVS Advantage, Surface measurement systems) was used to assess the dynamic water vapour sorption behaviour of CCi membranes. CCi membranes with a mass of ~11.5–11.8 mg were prepared in a dimension of 10×10 mm<sup>2</sup>. The measurement was executed at 20 °C with RH first reduced to 0%, until equilibrium with the mass change per minute (dm/dt) <0.002% min<sup>-1</sup> over a period of 10 min and the initial dry mass was recorded. Subsequently, the RH was increased from 5 to 95% in 10% steps (sorption) followed by a decrease to 0% in reverse order (desorption). During each step, the RH was initiated 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 membranes.

Static water contact angle. The wetting properties of CCi membranes were assessed on a Contact Angle System OCA 15EC (dataphysics). Static water contact angles were measured by using the sessile droplet method with a dosing volume of  $2.0\,\mu$ l and dosing rate of  $1.0\,\mu$ l s<sup>-1</sup>. The result was acquired by taking the average value from more than ten measurements.

## **NATURE SUSTAINABILITY**

**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 150 N. CCi membranes with a dimension of 30 mm × 5 mm were loaded into the test machine with a clamp distance of 8.0 mm and the measurements were conducted with a contact force of 0.5 N, a static strain of 0.5  $\pm$  0.2% and a dynamic strain of 0.1  $\pm$  0.05%. Humidity sweep tests were carried out with RH increasing rate of 2% min<sup>-1</sup> at 25 °C and frequency of 10 Hz. Mechanosorptive creep behaviours were measured at 25 °C with a constant stress of 1.5 MPa under constant RH of 80% and subsequently under cycling RH with repeating change of RH between 30 and 80% with cycling time of 2 h. The samples were preconditioned at 25 °C and 80% RH for 30 min before loading. Temperature sweep tests were measured with temperature increasing rate of 0.5 °C min<sup>-1</sup> and frequency of 10 Hz. All measurements were implemented within linear viscoelastic region of CCi membranes (Supplementary Fig. 7). For each case, at least three to five measurements were implemented to ensure that the collected data are reliable.

#### Data availability

The data supporting the findings are provided within this Article and its Supplementary Information and are available from the corresponding author on reasonable request. Source data are provided with this paper.

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#### Author contributions

K.Z. and J. Wang conceived the idea and designed the experiments. K.Z. supervised the project. J. Wang conducted the experiments with the assistance of L.E. and P.V. The data were analysed and processed by J. Wang, J. Wu and K.Z. J. Wang and K.Z. prepared the manuscript and all authors contributed to the revision.

#### **Competing interests**

The authors declare no competing interests.

#### **Additional information**

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