Supporting Information

Solution blown superporous nonwoven hydrogel based on hydroxypropyl cellulose Ting Yang Nilsson^{*a, b}, Markus Andersson Trojer^{a, c}

^aFibre development, Department of Chemistry, Biomaterials and Textiles, RISE IVF, Sweden. ^bLaboratory of Organic Electronics, Linköping University, Sweden. ^cApplied Chemistry, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden.

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2 Dope preparation and rheology

Low molecular weight HPC 30 g Mw 95kDa (15% in dope solution) was used to prepare dope solutions of low viscosity in order to facilitate the production of a large range of solution blown fibre diameter. EtOH 150 g (76% in dope solution) was used as volatile solvent for efficiently drying of the fibre while avoiding sudden drying of dope droplets at the nozzle by the high pressure air stream during solution extrusion. The HPC EtOH solution was slowly stirred overnight at 45 °C in a closed reaction vessel to reach total dissolving. The pure HPC 95kDa EtOH dope could only form thin and weak fibre via the solution blown process. Therefore PEO 1 g Mw 900 kDa (0.5% in dope solution, 3% in HPC fibre) was added to improve the strength and flexibility of the fibre. In addition, the high molecular weight HPC 1g Mw 1 MDa (0.5% in dope solution, 3% in HPC fibre) was added to form thicker HPC fibre during the solution blown process and to increase the mesh size for higher swelling of the HPC network. To be able to form hydrogel network with large mesh size for high swelling, the trifunctional crosslinker citric acid 3.3 g (10% to total dry mass) and 5 g (15% to total dry mass) were dissolved in 10 g distilled water (5% in dope solution) respectively and subsequently added to the HPC/PEO solution drop-wise under stirring for 1 hour to achieve homogeneous mixing respectively. The mixed solution was centrifuged at 2000 rpm for 2 minutes to remove the bubbles prior to the solution blowing. However, the solution blown HPC nonwoven produced from the dope with 10% citric acid to total dry mass was dissolved in water and failed to form hydrogel nonwoven after the thermally crosslinking. Therefore, only the 15% citric acid to total dry mass dope was used for further process and characterization.

2.1 Rheology

The rheological behaviour of the spinning dope is an important parameter which affects the fibre properties during fibre spinning process. The complex viscosity and the phase angle between the loss and storage modulus were studied and plotted as function of stress and frequency respectively to access the spinnability and the spinning window of the dope solution of HPC nonwoven hydrogel.



Fig. S1. a) Stress sweep and b) frequency sweep (σ =10 Pa) at 22°C.

The complex viscosity of the dope solution was 16.6 Pa·s, which is much lower as compared to the dope solution for solution blowing cellulosic fibers¹. The low viscosity of the dope solution is advantageous for the pumping capacity. The plateau viscosity extended over a significant shear stress interval. The dope solution was consequently relatively insensitive to the sudden pressure changes at the ejection of the solution at the nozzle. This allowed for the formation of fine fibers using small nozzle diameters. In Fig. S1, frequency sweep of the dope solution displayed only a weak viscosity dependence in the frequency interval 10⁻² to 10² at controlled stress 10 Pa. The phase angle decreased with increasing frequency indicating a fluid-like solution. This allows for the possibility of large feed rates to form thick fiber. The rheology behaviour of the dope solution displayed a large spinning window to tailor the fibre properties.

3 Fiber and pore size distributions



NW^c-2.35

Fig. S2. Size distribution and fitted normal distribution of the dry (top) and swollen (bottom) fibre diameter (left) and pore size (right) of the crosslinked nonwoven NW^C-2.35.





Fig. S3. Size distribution and fitted normal distribution of the dry (top) and swollen (bottom) fibre diameter (left) and pore size (right) of the crosslinked nonwoven NW^c-3.14.





Fig. S4. Size distribution and fitted normal distribution of the dry (top) and swollen (bottom) fibre diameter (left) and pore size (right) of the crosslinked nonwoven NW^c-3.92.

4 Standardized linear regression

	Dry		Wet	
	$S_{ m eq}$	k	$S_{ m eq}$	k
а	0.6477	0.433	0.4277	0.4682
b	-0.6952	-0.3629	-0.4342	-0.4053
с	0.02669	0.5507	0.5572	0.5519
d	-0.493	4.304	-10.4	-0.1023
\mathbb{R}^2	0.7209	0.9231	0.9868	0.9468
^a Adj R ²	0.3022	0.8078	0.967	0.867
^b SSE	0.1822	0.06212	0.008615	0.04299
^c RMSE	0.3018	0.1762	0.06563	0.1466

Table S1. Correlation parameters.

^aAdj R² is the adjusted R² value, ^bSSE is the sum of squares due to errors and ^cRMSE is the root mean squared error.

5 FTIR



Fig. S5. FT-IR transmittance spectra of PEO, HPC, citric acid, the crosslinked HPC nonwoven; NW^C-2.35, NW^C-3.14, NW^C-3.92 and the films; F^C-2.35, F^C-3.14, F^C-3.92.

Table S2. Band assignment²⁻⁶.

Wavenumber [cm ⁻¹]	Assignment
Citric acid	
3494 s	v(O-H) (peripheral)
3278 s	v(O-H) (H-bonded)
2998 w	$v_{\rm a}({\rm CH}_2)$ (in phase)
2983 w	$v_{\rm a}({\rm CH_2})$
2958 w	$v_{\rm s}$ (CH ₂) (in phase)
2935 sh	$v_{\rm s}$ (CH ₂)
1745 vs	v(C=O) dimer
1693 vs	v(C=O) dimer
1730 vs	v(C=O) monomer
1172 s	v(C-O) (middle carboxylic)
1136 s	v(C-O)
781 s	δ(COO)
595 m	τ (O–H), δ (COO),
	δ (C–C–C), ρ (COO), Combination band
545 m	$\rho(\text{COO})$

PEO	
2981 w	v _a (CH ₂)
2946 w	$v_{\rm a}({ m CH_2})$
2887 s	$v_{\rm s}({\rm CH_2})$
2862 s	$v_{\rm s}({\rm CH_2})$
1467 w	$\delta(\mathrm{CH}_2)$
1342 s	$\omega(CH_2)$
1278 m	<i>τ</i> (CH ₂)
1224 w	$\tau(CH_2)$
1143 s	v(C-O)
1095 vs	v(C-O)
1076 s	v(C-O)
960 m	$ ho(\mathrm{CH}_2)$
840 m	$ ho(\mathrm{CH}_2)$

HPC

2972 s	$v_{a}(CH_{3})$
2923 s	$v_{a}(CH_{2})$
2900 s	$v_{\rm s}({\rm CH}_3) + v_{\rm a}({\rm CH})$ methyne
2875 s	$v_{\rm s}({ m CH_2})$
1108 sh	$v_{a}(ring)$ in-phase + $v(C-O)$ ether (PPO)
1070 vs	v(C-O) ether (ring)
1053 vs	v(C-O) ether (ring)
848 sh	$\delta(\text{C-CH}_3)$
842 w	$\delta(\text{C-CH}_3)$

NWC	
3680 w	v(O-H (non-bonded)
2980 (split)	Combination 2980 2990 CA and PEO
1778 m	v(C=O) cyclic anhydride (CA)
1731 vs	v(C=O) ester + v C=O carboxylic acid
1590 s	v(C=O) carboxylate
1640 w	δ (H-O-H) (water)
1146 sh	v(C-O) ester

Assignments: Stretching vibrations: v stretching. Deformation vibrations: δ in-plane bending, τ torsion, ω wagging, ρ rocking,

Indices: a asymmetric, s symmetric

Intensities: vs very strong, s strong, m medium, w weak, vw weak, sh shoulder

5.1 NW^{i} -2.35 and F^{i} -2.35



Fig. S6. FTIR spectra of native and base-treated NW^N-2.35, NW^C-2.35, F^N-2.35 and F^C-2.35.



Fig. S7. Magnification of the FTIR spectra in the v(OH), v(CH) and v(C=O) region for native and base-treated NW^N-2.35, NW^C-2.35, F^N-2.35 and F^C-2.35.



Fig. S8. FTIR spectra of native and base-treated NW^N-3.14, NW^C-3.14, F^N-3.14 and F^C-3.14.



Fig. S9. Magnification of the FTIR spectra in the v(OH), v(CH) and v(C=O) region for native and base-treated NW^N-3.14, NW^C-3.14, F^N-3.14 and F^C-3.14.

5.3 NWⁱ-3.92 and Fⁱ-3.92





Fig. S11. Magnification of the FTIR spectra in the v(OH), v(CH) and v(C=O) region for native and base-treated NW^N-3.92, NW^C-3.92, F^N-3.92 and F^C-3.92.

6 DSC

HPC is a thermotropic liquid crystalline polymer with a complex thermogram displaying several transitions⁷. This fact is a consequence of HPC displaying; several main chain and side chain relaxation processes; solid and liquid crystalline phase transitions; significant effects of thermal history and preparation conditions; in the temperature interval -50-250°C⁷⁻⁹.

6.1 Comments on the sample preparations

Since the thermogram of pure HPC is complicated, it was difficult to precisely determine the phase transitions for the nonwovens and films since these samples are further complicated by the transitions of PEO and high molecular weight HPC. Therefore, the more detailed thermal analyses were performed on pure low molecular weight HPC which had been precrosslinked with citric acid from aqueous solutions at 140 °C according to the equivalent procedure as for the nonwovens and films. In addition, corresponding non-crosslinked samples were analysed in an attempt to *in-situ* investigate the crosslinking reaction and its consequences on subsequent heating cycles.

6.2 Results

Films of HPC cast from water have been shown to form metastable liquid crystals⁸. Upon heating, an irreversible phase transition is observed⁸ which we ascribe to the first broad phase transition in the 1st heating cycle which is absent in the 2nd and 3rd heating cycles (see Fig. S13). At higher temperatures, a second endotherm is observed which remains in the subsequent heating cycles, is consistent with the literature and has been ascribed to a nematic-to-isotropic liquid T_{ni} (i.e. melting) phase transition^{9, 10}.



Fig. S12. Thermograms of pure HPC displaying the 1st (30K/min), 2nd (20K/min) and 3rd heating cycle (10K/min).

As seen in Fig. S13, the thermogram of precrosslinked HPC is similar to that of pure HPC displaying the irreversible transition in the 1st heating cycle. However, it is apparent that the crosslinking reaction prevents the material to melt since the second melting endotherm is absent which is consistent with thermoset materials. The melting endotherm is also absent for the crosslinked nonwoven samples.



Fig. S13. Thermograms of pure HPC precrosslinked at 140 °C - according to the same procedure as for the NW^Cs and F^Cs - displaying the 1st (30K/min), 2nd (20K/min) and 3rd heating cycle (10K/min). In addition, the thermogram of NW^C-3.92 is displayed for the 3rd heating cycle (10K/min).

A more detailed comparison of the transitions of pure and precrosslinked HPC is provided in Fig. S14. The position of the glass transition temperature (T_g) is inconsistent in the literature and varies over a range of 200°. Most attempts which combine DSC measurements with other techniques (DMA, dielectric spectroscopy) usually assign T_g to a weak DSC transition at low temperatures (-5-20) rather than high temperatures^{7, 9}. We have therefore tentatively assigned T_g to a very weak transition at -2°C which is slightly increased for crosslinked HPC to approximately 0°C. However, it must be emphasized that this assignment is highly uncertain.

In addition to the second reversible melting endotherm, a transition is for pure HPC at approximately 105 which for precrosslinked HPC (and crosslinked nonwovens) is reduced to approximately 90°C. This transition is often designated as a solid microcrystalline-to-liquid crystalline phase transition in the literature^{7, 10}. It is reasonable to assume that the citric acid crosslinking interferes with the efficiency for crystal packing while still allowing for some flexibility of the polymer chain for liquid crystalline formation in a semi-molten state.



Fig. S14. Comparison of the thermograms for pure HPC and precrosslinked HPC.

The thermal esterification does not display a well-defined reaction exotherm (Fig. S15). Instead, a vague broad peak is observed (when compared with the thermogram of pure HPC) which is unfortunately visually obstructed by the irreversible transition below 100°C. However, it is clear that *in-situ*-crosslinked HPC lacks the second melting endotherm in conformity with the precrosslinked HPC samples.



Fig. S15. Thermogram of pure and non-crosslinked HPC displaying the 1st heating cycle of both and the 2nd heating cycle

7 TGA

TGA thermograms for pure HPC and the NW^C-2.35 are provided in Fig. S16. Pure HPC starts to degrade at approximately 300°C. NW^C-2.35 degrades in a two-step process with an initial slight degradation that starts at approximately 210°C and a second main degradation at 300°C in conformity with that of pure HPC.



Fig. S16. TGA Thermogram for pure HPC (red curve) and NW^c-2.35 (black curve).

8 Shape memory



Fig. S17. A ca 5.5x1 cm² nonwoven sheet (left) keeps it shape and dimensions after swelling (middle) and subsequent drying (right).

9 References

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