

Supporting Information

Accessibility of Fiber Surface Sites for Polymeric Additives Determines Dry and Wet Tensile Strength of Paper Sheets

J.-L. Schäfer,^{1,3} S. Schölch,^{2,3} O. Prucker,² T. Brandstetter,² J. Rühle,^{2,*} A. Ritter v. Stockert,¹
T. Meckel,¹ M. Biesalski^{1,*}

¹ *Department of Chemistry, Macromolecular Chemistry & Paper Chemistry, Technical University of Darmstadt, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany*

² *Department of Microsystems Engineering (IMTEK), Laboratory for Chemistry & Physics of Interfaces, Albert-Ludwigs-Universität Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany, and Freiburg Institute for Interactive Materials and Bioinspired Technologies (FIT), Albert-Ludwigs-Universität Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany*

³ *authors contributed equally*

*correspondence:

e-mail: biesalski@cellulose.tu-darmstadt.de

e-mail: ruehe@imtek.uni-freiburg.de

NMR of the copolymer used in this study

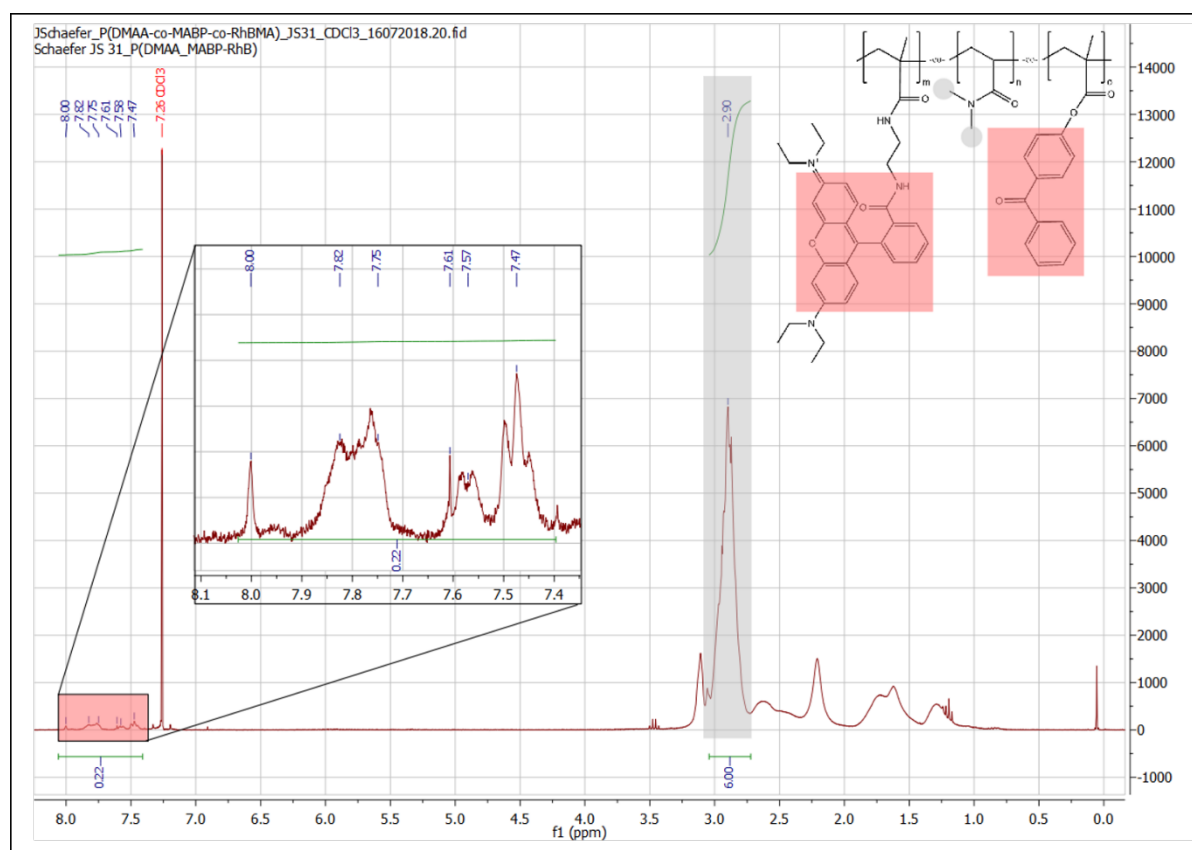


Fig. S1 ^1H -NMR spectrum of the used P(DMAA-co-MABP-co-RhBMA). The aromatic protons of the photo-labile benzophenone group and the fluorescent rhodamine B group are not distinguished and rather labelled together with a red overlay

FT-IR of paper samples

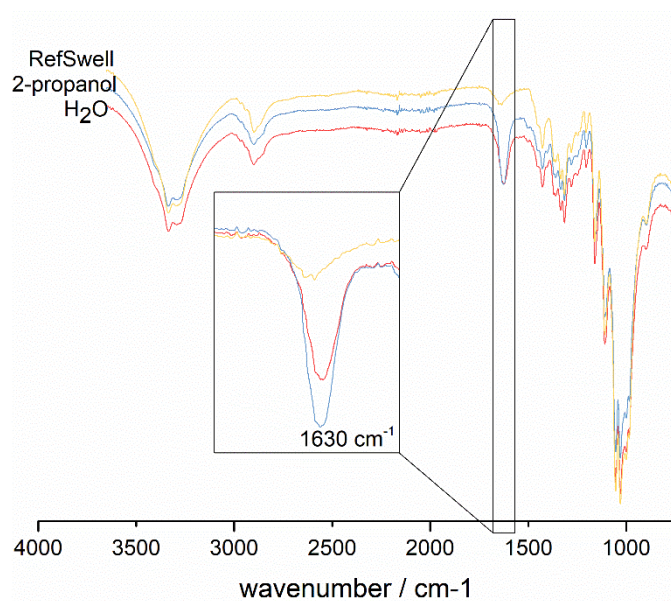


Fig. S2 FT-IR spectra of paper samples without any copolymer and with the copolymer applied via dip-coating from H_2O and IPA. The inset shows the comparison of the intensity of absorption at 1,630 cm^{-1} , which can be attributed to the carbonyl stretching vibration of the dimethylacrylamide of the copolymer

Tensile measurements – drying, swelling & UV-treatment

The following tables show the experimental results of the tensile measurements in the dry and the wet state of completely untreated paper samples (**Ref**) and paper samples treated with an analogous procedure to the copolymer-modification (swelling in solvent → drying → UV-illumination → swelling → drying), but without the copolymer, with the three different solvents (**RefSwell - H₂O/IPA/BuOH**). The dry and wet tensile strength- and tensile index-values are denoted as **S_{dry}** and **S_{wet}** and **I_{dry}** and **I_{wet}** respectively. The coefficients of variation are denoted with as **cv S_{dry}** and **cv S_{wet}** and **cv I_{dry}** and **cv I_{wet}** respectively.

Table S1 Dry and wet tensile strength- and index-values of eucalyptus-sulfate paper samples with a grammage of 80 g m⁻² for: pure cellulose paper samples not subjected to any treatment (Ref) and samples subjected to the procedure for copolymer application, without any copolymer in the solution (RefSwell – H₂O/IPA/BuOH)

dry		S_{dry} / kN m⁻¹	Error S_{dry} / kN m⁻¹	cv S_{dry} / %	I_{dry} / N m g⁻¹	Error I_{dry} / N m g⁻¹	cv I_{dry} / %
	Ref	1.4093	0.0180	1.3	17.6160	0.4181	1.3
	RefSwell (H₂O)	0.7867	0.1127	14.3	9.8336	1.423	14.5
	RefSwell (IPA)	0.9714	0.0686	7.1	12.14282	0.89095	7.3
	RefSwell (BuOH)	0.9797	0.0525	5.4	12.2465	0.70064	5.7
wet		S_{wet} / kN m⁻¹	Error S_{wet} / kN m⁻¹	cv S_{wet} / %	I_{wet} / N m g⁻¹	Error I_{wet} / N m g⁻¹	cv I_{wet} / %
	Ref	0.0200	0.002	9.9	0.2506	0.0252	10.1
	RefSwell (H₂O)	0.0159	0.0021	13.3	0.1984	0.0267	13.4
	RefSwell (IPA)	0.0173	0.007	40.3	0.21565	0.087	40.3
	RefSwell (BuOH)	0.0134	0.0026	19.1	0.16795	0.03229	19.2

Tensile measurements – copolymer H₂O- vs. IPA- vs. BuOH-dip:

In analogy to the tables above, these tables also show the results of the tensile measurements in the dry and the wet state of the samples. The denotations are used accordingly.

Table S2 Dry and wet tensile strength- and index-values of eucalyptus-sulfate paper samples with a grammage of 80 g m⁻² for: cellulose paper samples where the copolymer was applied out of H₂O, IPA and BuOH

dry		$S_{\text{dry}} / \text{kN m}^{-1}$	Error $S_{\text{dry}} / \text{kN m}^{-1}$	cv $S_{\text{dry}} / \%$	$I_{\text{dry}} / \text{N m g}^{-1}$	Error $I_{\text{dry}} / \text{N m g}^{-1}$	cv $I_{\text{dry}} / \%$
	H ₂ O	2.9469	0.1202	4.1	36.8364	1.6738	4.1
	IPA	3.7033	0.0901	2.4	46.2906	1.4581	2.4
	BuOH	3.5601	0.2128	6	44.5009	2.8046	6
wet		$S_{\text{wet}} / \text{kN m}^{-1}$	Error $S_{\text{wet}} / \text{kN m}^{-1}$	cv $S_{\text{wet}} / \%$	$I_{\text{wet}} / \text{N m g}^{-1}$	Error $I_{\text{wet}} / \text{N m g}^{-1}$	cv $I_{\text{wet}} / \%$
	H ₂ O	0.7122	0.0270	3.8	8.9026	0.3818	3.8
	IPA	0.1798	0.029	16.1	2.2475	0.3651	16.1
	BuOH	0.1084	0.0052	4.8	1.3546	0.0699	4.8

Dynamic light scattering – copolymer dissolved in H₂O vs. IPA

Table S3 Hydrodynamic radii (R_h) of the copolymer dissolved in H₂O and IPA respectively, as analyzed by dynamic light scattering. The copolymer solutions were prepared with a concentration of 5 mg mL⁻¹

copolymer molecular weight	R_h / nm (in H ₂ O)	R_h / nm (in IPA)
27 000 g mol ⁻¹	9-10	7-7.5

Gravimetric analysis of copolymer amount inside paper samples

In the following tables the results of the gravimetric analysis of the weight change of reference samples and the amount of copolymer inside the copolymer-modified paper samples are shown. All of the samples were weighed after drying and 24-hour equilibration in a climate controlled room (50 % RH and 23 °C). Here the mean-values calculated from 10 different paper samples and their weights are given with their standard deviations.

m (before)	mass paper sample before treatment/modification
m (after)	mass paper sample after treatment/modification
m (delta)	mass change of paper samples after swelling, drying and UV-illumination
m (extraction)	mass paper sample after extraction
m (copolymer-extr)	mass of extracted copolymer
wt% (copolymer-extr)	fraction of extracted copolymer
m (copolymer)	mass copolymer inside paper sample after copolymer impregnation and extraction
m (copolymer) / m (before)	amount of copolymer in paper samples

Table S4 Weight change of cellulose paper samples treated with the same impregnation-procedure from the different solvents but without the copolymer, as analyzed by gravimetric measurements

	m (before)/ mg	m (after)/ mg	m (delta) / mg	m (delta) / m (before) / wt%
RefSwell (H₂O)	144.4	145.3	0.9	0.6
RefSwell (IPA)	145.8	147.2	1.4	0.9
RefSwell (BuOH)	145.3	146.3	1.0	0.7

Table S5 Weight change of cellulose paper samples, where the copolymer is applied via the impregnation-procedure from the different solvents, as analyzed by gravimetric measurements

Solvent	m (before)/ mg	m (after) /mg	m (extraction) / mg	m (copolymer-extr) / mg	wt% (copolymer-extr)	m (copolymer) / mg	m (copolymer) / m (before) / wt%
H₂O (JS53)	147.8 ± 0.7	171.2 ± 1.0	164.7 ± 0.8	6.5 ± 0.5	27.8 ± 1.6	16.9 ± 0.4	11.4 ± 0.3
IPA (JS55)	140.7 ± 0.9	154.0 ± 1.1	151.9 ± 1.3	2.2 ± 0.4	16.1 ± 3.3	11.2 ± 0.7	8.0 ± 0.5
BuOH (e89)	149.0 ± 0.5	158.5 ± 0.4	157.6 ± 0.4	0.8 ± 0.3	8.8 ± 2.9	8.7 ± 0.5	5.8 ± 0.4

3D-printed drying equipment

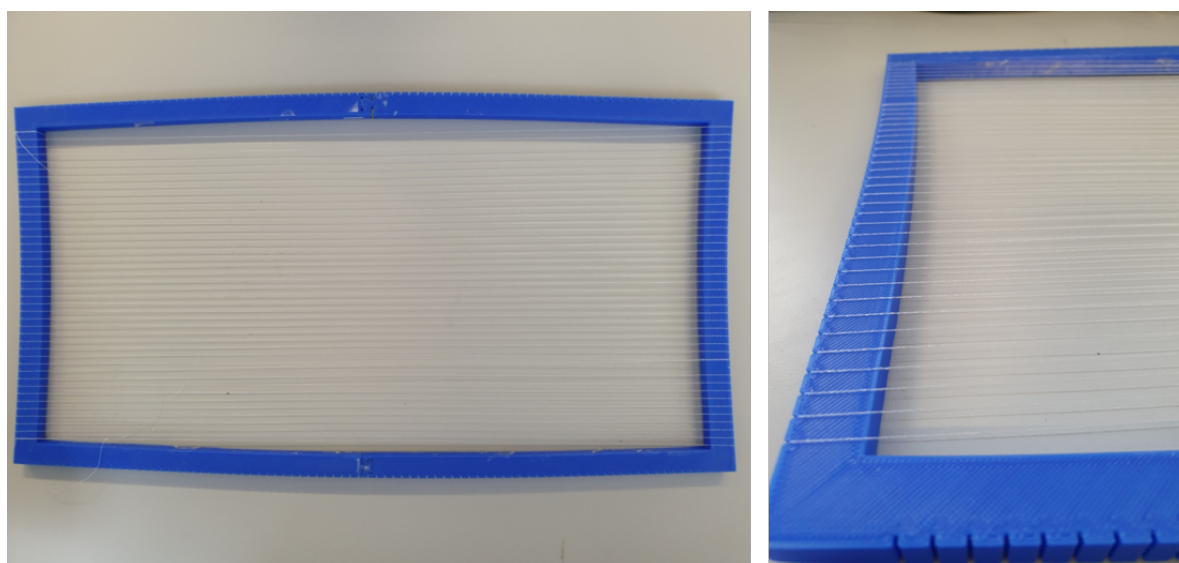


Fig. S3 Contraption for drying of the paper samples under climate controlled conditions. 3D-printed with PLA with inert Teflon yarn as a supporting surface

Significance of staining of cellulose fibers for confocal laser scanning microscopy

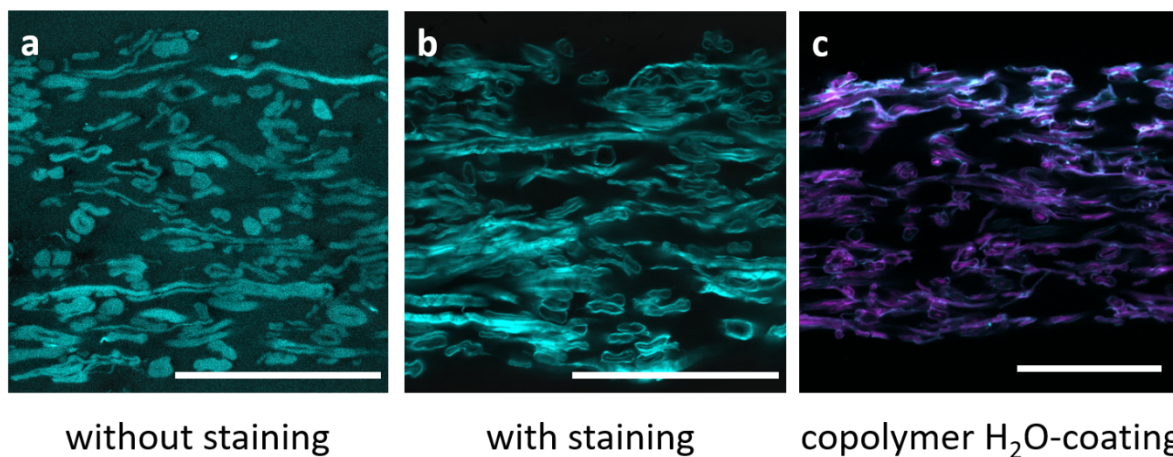


Fig. S4 Comparison of cross-sections of eucalyptus-sulfate paper samples treated without calcofluor white as staining agent (a), with staining (b) and dip-coated with copolymer-solution from H₂O prior to staining (c). In order to increase the visibility for the non-stained sample, the gain of the detector had to be increased to such high levels, that the noise becomes clearly visible. Scale bars are 100 μ m

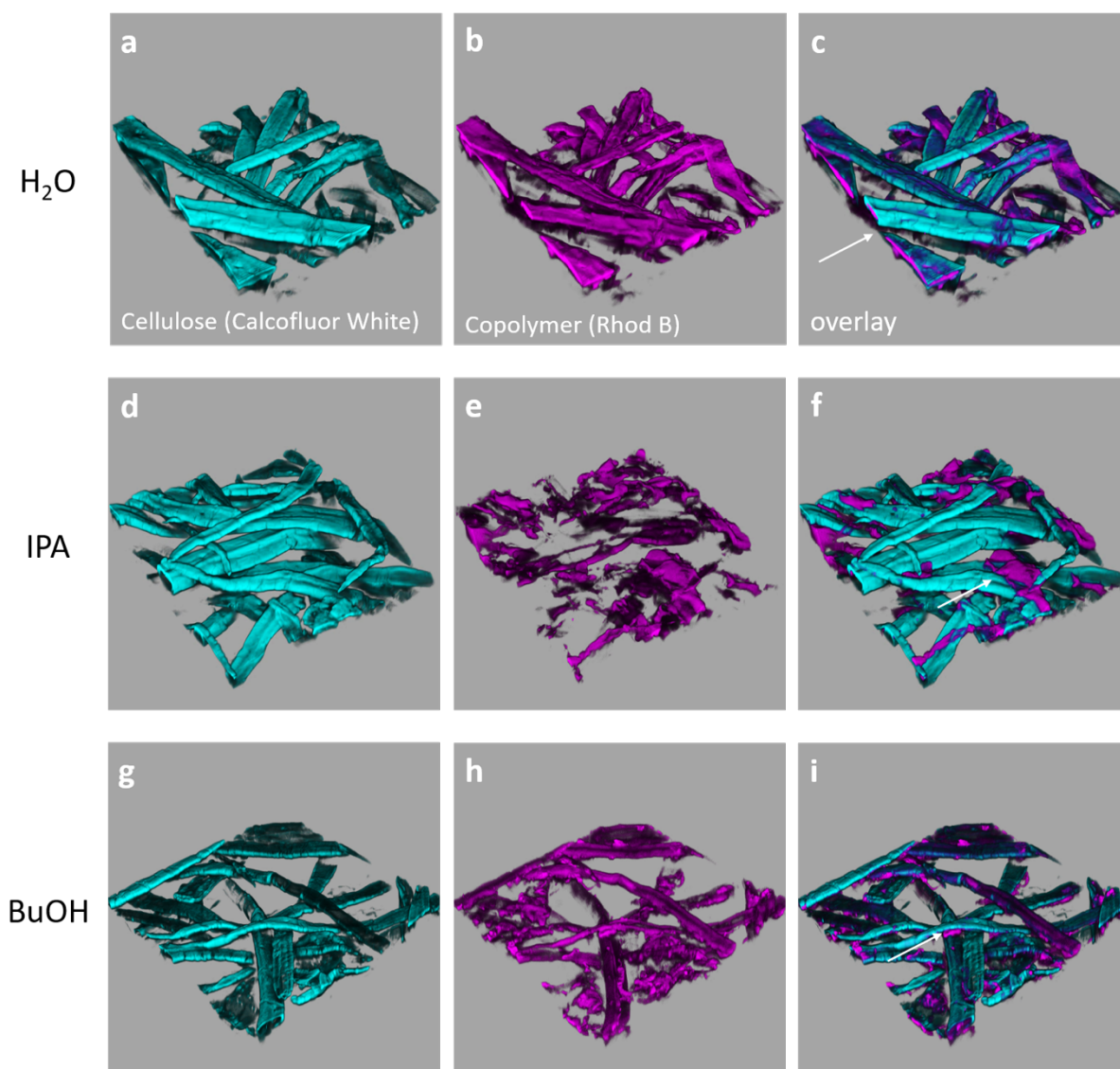


Fig. S5 3D-stacks of paper samples with the fluorescently labelled copolymer applied out of H_2O (a,b,c), IPA (d,e,f) and $BuOH$ (g,h,i), respectively, beforehand. The images show a side view of cellulose fibers stained by CW (a,d,g), PDMAA labelled by RhB (b,e,h) and overlays of the latter (c,f,i). Overlays of both fluorescent signals appear as blue in 3D-renderings. Edge length 196,79 μm

In Fig. S6 the same 3D-images of the cellulose fiber networks are shown from the side. This tilted view highlights the differences in spatial distribution of the copolymer between H_2O -, IPA - and $BuOH$ -dip-coating in more detail. In analogy to the thin cross-sections in Fig. 7, the copolymer in the case of H_2O -dip-coating can be observed inside the fiber walls and fiber lumen in Fig. S6 (c). However, it should be noted that these images were generated from confocal stacks, and are thus, as already mentioned above limited in their axial resolution. Therefore, these observations must be interpreted with caution. In the case of the IPA -dip-coated samples, Fig. S6 (f) highlights the sleeve-like-aggregates of copolymer inside the fiber network, which are not fully wrapping around the fibers, as already observed in Fig. 8 (f). The fluorescence images in Fig. S6 (h) and (i) show that dip-coating from $BuOH$ leads to a more homogeneous distribution of the copolymer, although copolymer-agglomerates at fiber-fiber crossings are also observable.

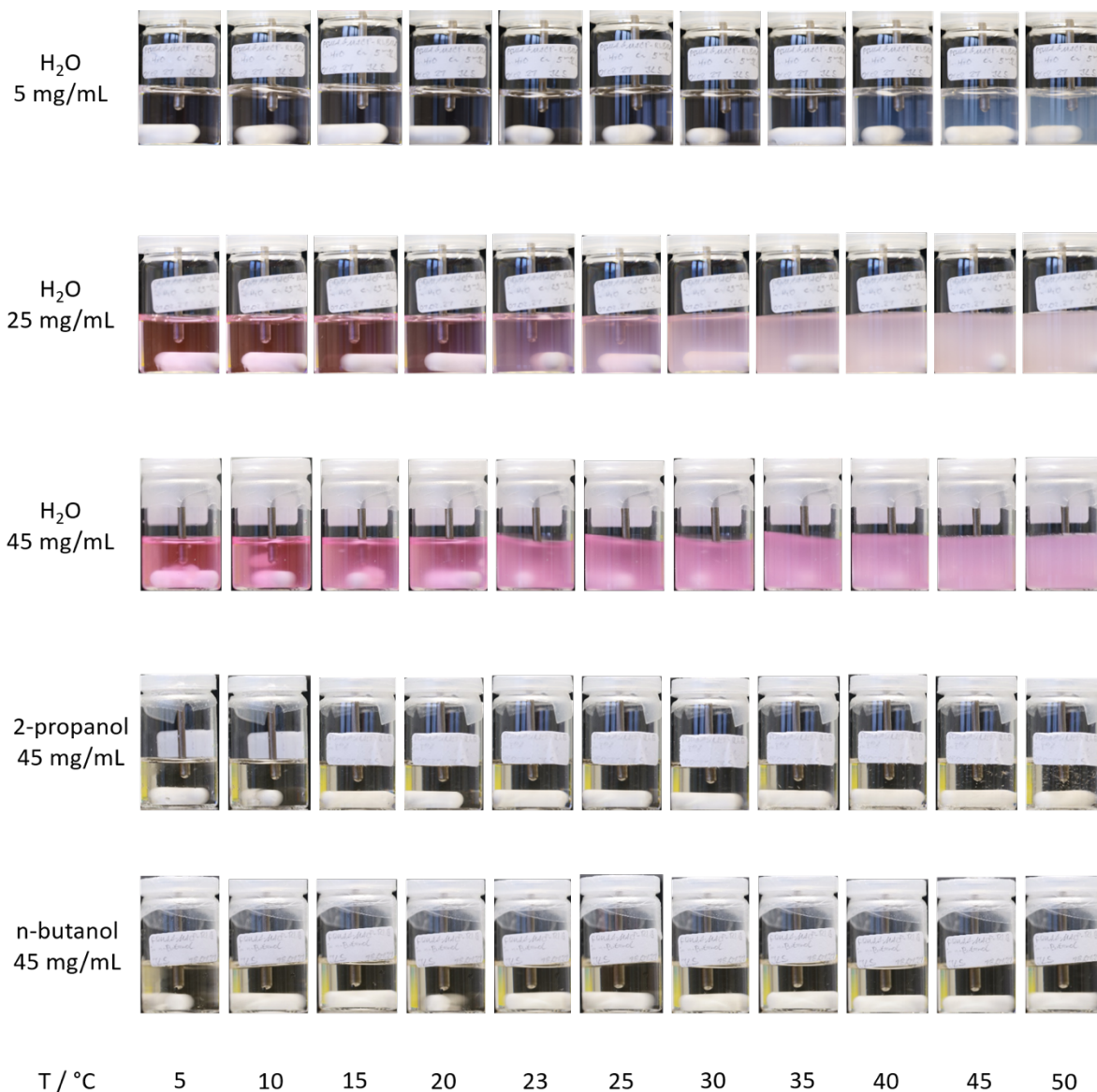


Fig. S6 Turbidity experiments with varying concentrations in H₂O (5, 25 and 45 mg mL⁻¹) and highly-concentrated copolymer-solutions (45 mg mL⁻¹) in the other solvents, 2-propanol (*IPA*) and 1-butanol (*BuOH*), used for impregnation. Demixing only observable for the solution in H₂O, starting at around 13, 21 and 36 °C for 5, 25 and 45 mg mL⁻¹, respectively, and intensifying with increasing temperature. At the relevant conditions for impregnation, 25 mg mL⁻¹ and r.t., only H₂O shows light clouding, indicating the formation of copolymer-agglomerates only for this solvent, but not for *IPA* and *BuOH*. For *IPA*, bubbles observable starting at 45 °C are due to low boiling point of the alcohol

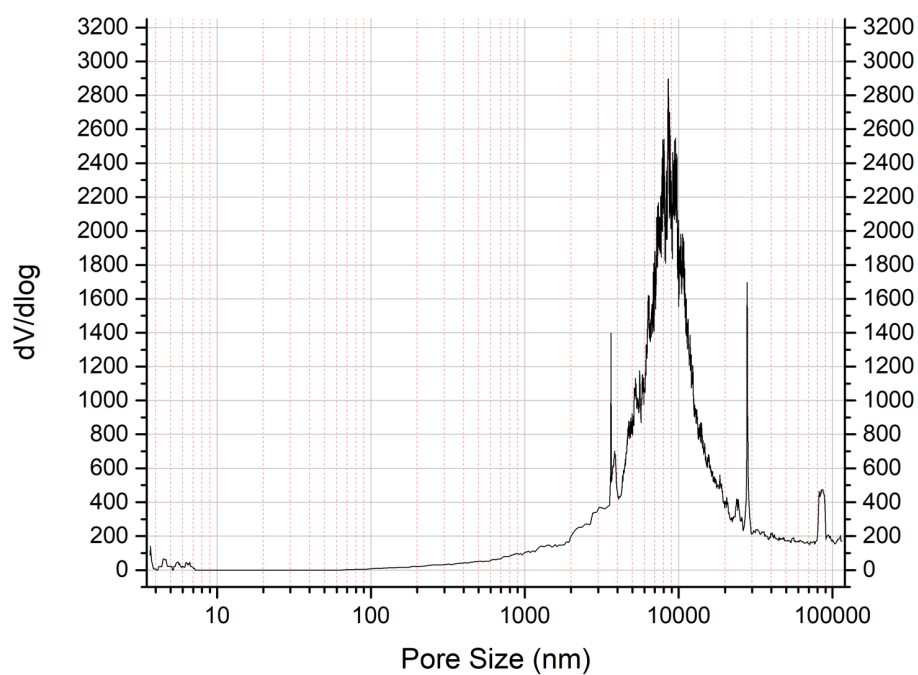


Fig. S7 Pore size distribution of a eucalyptus sulfate paper sample with a grammage of 80 g m⁻² measured by mercury intrusion porosimetry with maximum test pressure of 400 MPa