Supporting Information

Exploring the rearrangement of amorphous cellulose model thin films upon heat treatment

Tamil Mohan[a,‡], *Stefan Spirk*[a,*,‡], *Rupert Kargl*[b,‡], *Aleš Doliška*[a,‡], *Alenka Vesel*[c], *Ingo Salzmann*[d], *Roland Resel*[e], *Volker Ribitsch*[b,‡], *and Karin Stana-Kleinschek*[a,‡]

[a]Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia.

[b]Karl-Franzens-Universität Graz, Institut für Chemie, Heinrichstraße 28/III, 8010 Graz, Austria.

[c]Jožef Stefan Institute, Ljubljana, Jamova 39, SI-1001 Ljubljana, Slovenia

[d]Humboldt Universität zu Berlin, Institut für Physik, Unter den Linden 6, 10099 Berlin, Germany.

[e]University of Technology Graz, Institute of Solid State Physics, Petersgasse 16, 8010 Graz, Austria.

[‡]Members of the European Polysaccharide Network of Excellence

To whom correspondence should be addressed: stefan.spirk@uni-mb.si

Table S1: Surface tension parameters for the test liquids used for static contact angle measurement. Values are presented in [mJ m^{-2}].

Test liquid	γ_l^{TOT}	γ_l^{LW}	γ_s^+	γ_s^-	Author
Water	72.8	21.8	25.5	25.5	Erbil
Diiodomethane	50.8	50.8	0.0	0.0	Erbil
Glycerol	64.0	34.0	3.9	57.4	vanOss
Formamide	58.0	39	2.3	39.6	vanOss

Table S2. Static contact angle values of the heat treated TMSC and regenerated cellulose films measured using different test liquids at 20°C.

Regeneration time [min]	Water [deg]	Diiodomethane [deg]	Formamide [deg]	Glycerol [deg]
0	95.9 ± 0.1	68.7 ± 1.3	84.3 ± 0.8	91.0 ± 0.4
1	96.1 ± 1.0	68.2 ± 1.1	85.1 ± 0.9	90.0 ± 0.1
2	94.5 ± 1.2	70.9 ± 0.1	85.6 ± 0.3	90.6 ± 0.6
4	79.5 ± 1.0	57.6 ± 0.5	74.4 ± 0.8	73.4 ± 1.1
6	42.9 ± 0.1	25.9 ± 0.2	13.1 ± 0.6	21.7 ± 0.3
10	46.1 ± 0.9	28.0 ± 0.6	15.9 ± 1.2	25.2 ± 0.8
12	46.1 ± 1.2	28.0 ± 0.8	16.0 ± 1.9	25.1 ± 0.4

Table S3. Surface free energy components of the heat treated TMSC and regenerated cellulose films calculated from the contact angle values by the van Oss method.

Regeneration time [min]	γ_s^{TOT} [mJ m^{-2}]	γ_s^{LW} [mJ m^{-2}]	γ_s^{+} [mJ m^{-2}]	γ_s^{-} [mJ m^{-2}]
0	22.6 ± 0.5	22.6 ± 1.1	0.0	4.0 ± 1.4
2	21.4 ± 0.1	21.4 ± 1.0	0.0	5.3 ± 1.2
4	29.7 ± 0.8	29.2 ± 0.4	0.01 ± 0.1	12.1 ± 0.6
6	59.9 ± 1.1	45.2 ± 0.9	2.4 ± 0.9	22.4 ± 0.2
10	58.6 ± 1.1	44.5 ± 1.1	2.5 ± 0.2	20.0 ± 0.7
12	58.6 ± 1.0	44.5 ± 1.1	2.5 ± 0.4	20.0 ± 0.8

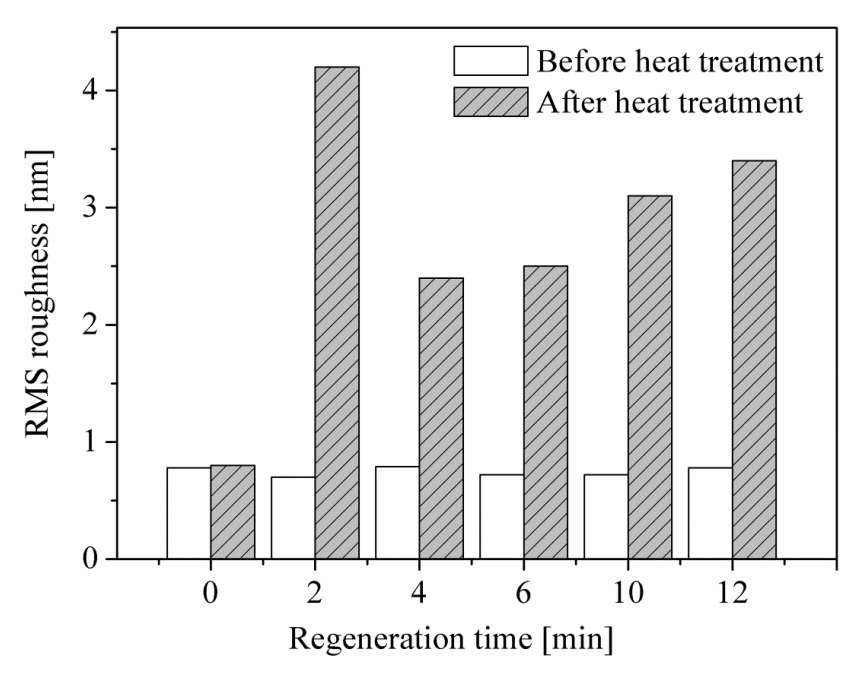

Figure S1. Root mean square roughness (RMS) of heat and non heat treated surfaces in dependence of regeneration time as determined by AFM.

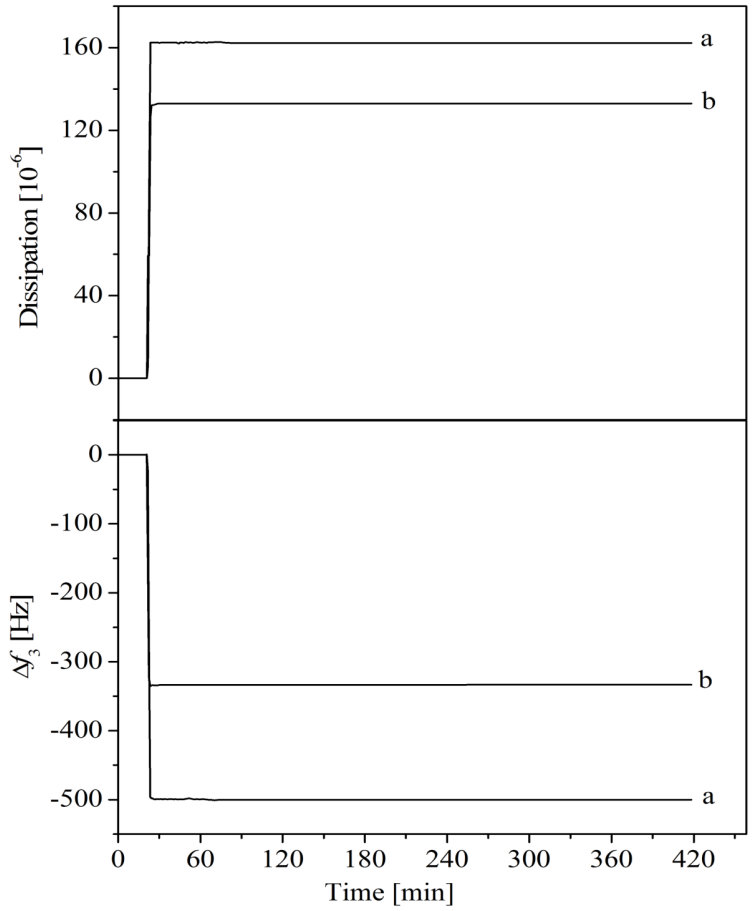

Figure S2. Changes in the frequency and dissipation response of swollen cellulose films before (a, RT 12 min) and after (b, RT 12 min) heat treatment.

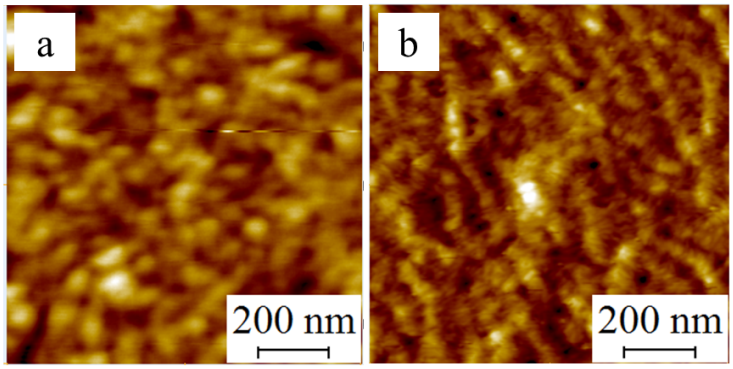

Figure S3. AFM topography images of heat treated cellulose surfaces before (a) and after swelling (b) for 24 hours.

Table S4. Comparison of static contact angles of the different cellulose films using different test liquids at 20°C. All values are given in deg.

Sample	Water	Diiodomethane	Formamide	Glycerol
Cellulose as prepared	24.6 ± 0.6	35.2 ± 0.9	6.9 ± 0.8	14.5 ± 1.4
Cellulose swollen in water for 15 min	19.7 ± 0.1	24.8 ± 0.4	5.4 ± 0.1	10.3 ± 0.1
Cellulose swollen in water for 24 hour	17.4 ± 1.4	22.5 ± 1.3	2.2 ± 0.1	7.2 ± 0.1
Cellulose swollen in water and dried at 105°C	31.0 ± 0.1	25.5 ± 0.5	8.7 ± 1.6	10.5 ± 1.0

Table S5. Comparison of the surface free energy components of the different cellulose film calculated from the contact angles by the van Oss method. All values are given in mJ m^{-2}.

Sample	γ_s^{TOT}	γ_s^{LW}	γ_s^{+}	γ_s^{-}
Cellulose as prepared	58.6 ± 1.0	31.6 ± 0.6	4.2 ± 0.4	42.7 ± 0.9
Cellulose swollen in water for 15 min	61.3 ± 0.2	25.8 ± 0.1	6.3 ± 0.1	49.1 ± 0.2
Cellulose swollen in water for 24 hour	66.2 ± 0.9	19.4 ± 0.1	8.5 ± 0.1	64.5 ± 1.1
Cellulose swollen in water and dried at 105°C	62.6 ± 0.5	45.4 ± 0.2	2.3 ± 0.1	31.8 ± 0.2

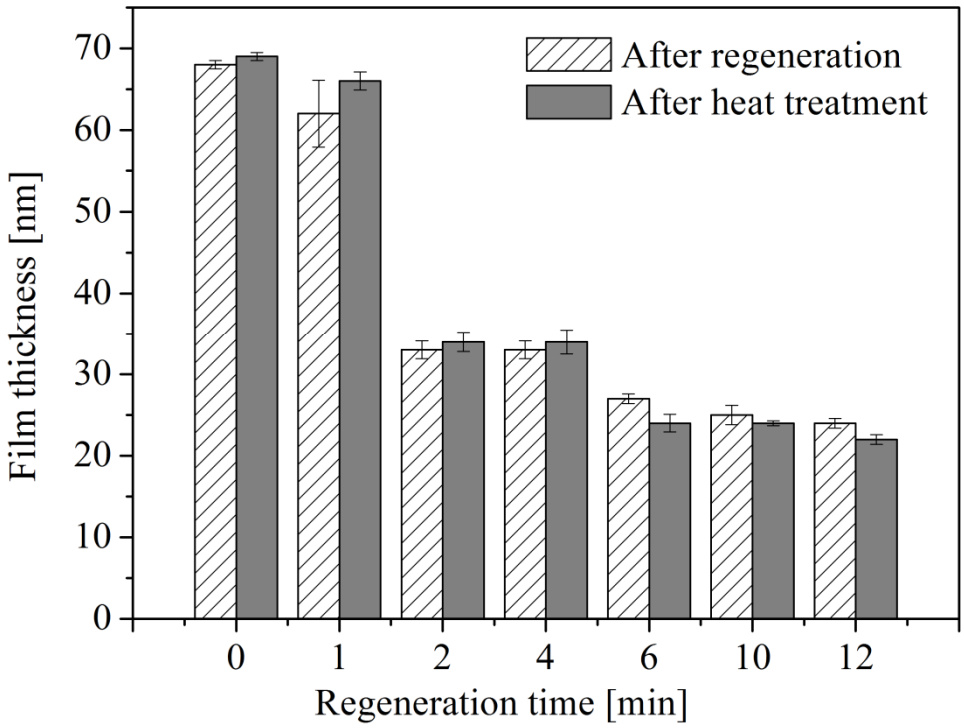

Figure S4. Comparison of the film thicknesses before and after heat treatment in dependence of the regeneration time determined by the Sarfus method.

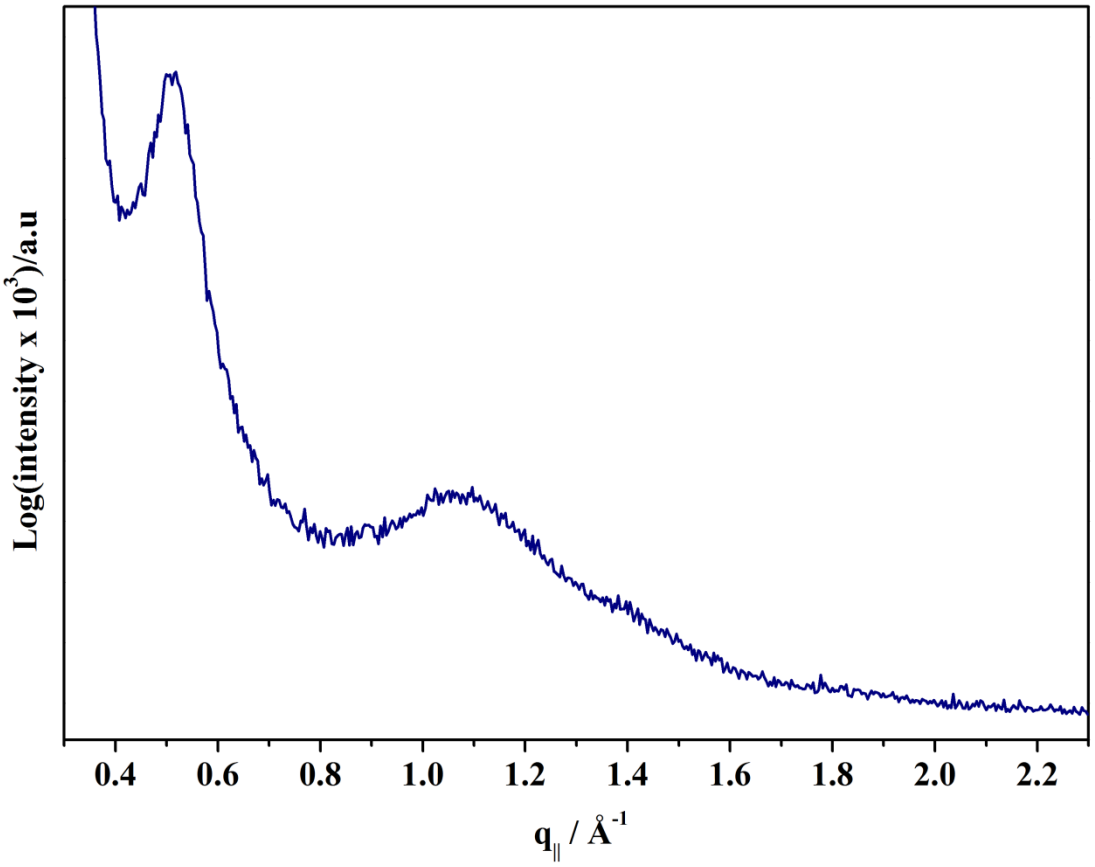

Figure S5. GIXD pattern of a TMSC film showing the amorphousness of the film.

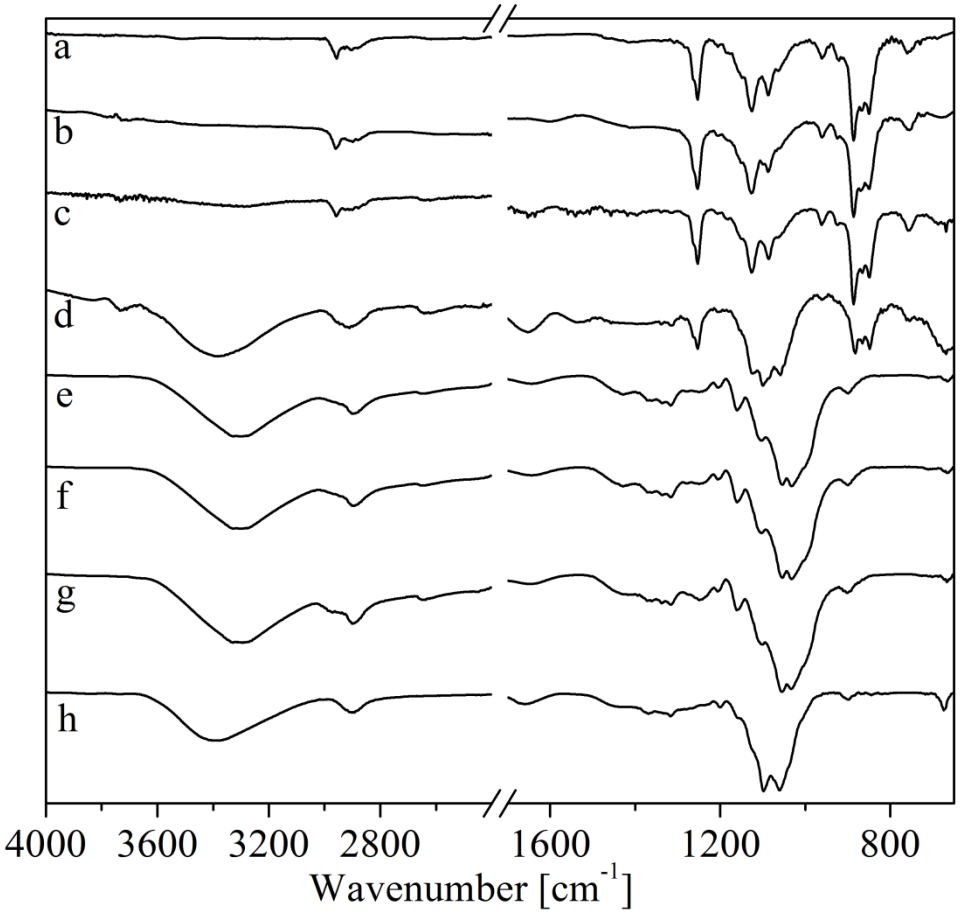

Figure S6. Comparison of ATR-IR spectra of heat treated surfaces in dependence of regeneration time (a-g; a: 0, b: 1, c: 2, d: 4, e: 6, f: 10, g: 12 minutes of regeneration) and a non heated surface (h, 12 minutes of regeneration).

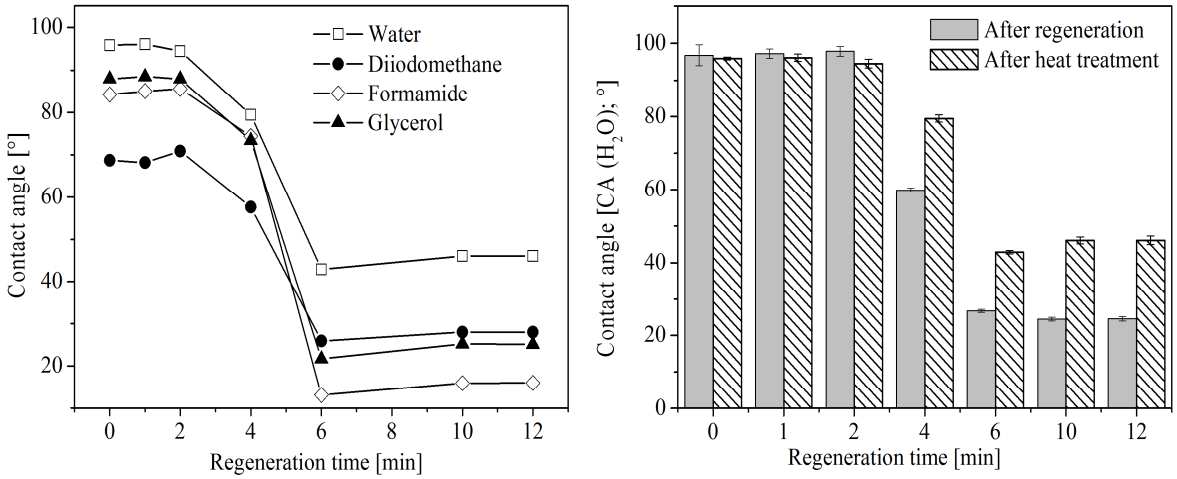

Figure S7. Left: Static contact angle values of different test liquids on time-dependent regenerated heat treated cellulose surfaces. Right: Comparison of static water contact angles on time-dependent regenerated cellulose surfaces before and after heat treatment.

Table S6: Water content of the different cellulose films deterimed by QCM-D using a H_2O/D_2O solvent exchange procedure.

Samples	Frequency change f_3 [Hz]	Δf_{film}-$\Delta f_{crystal}$ [Hz]	Water content of the films [µg cm^{-2}][a]
Pure Au crystal	70.2 ± 1.8		
Cellulose as prepared	81.5 ± 1.3	11.3 ± 0.1	1.869 ± 0.002
Cellulose dried at 105°C	76.3 ± 0.1	6.2 ± 1.7	1.017 ± 0.03
Cellulose swollen in water and dried at 105°C	78.9 ± 0.1	8.7 ± 1.7	1.439 ± 0.03

a - the water content of the film was determined using the equation (8) and (9) in the main manuscript