

Electronic Supplementary information

On the interaction of softwood hemicellulose with cellulose surfaces in relation to molecular structure and physicochemical properties of hemicellulose

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TMP anomeric assignment:

Table S1 ¹H and ¹³C NMR data of the anomeric region for the TMP GGM

Constituent	¹ H (ppm)	¹³ C (ppm)	Annotation	Figure Key
mannose	5.19	94.86	α-ManpR	Mar
	4.94	100.23	-4)-β-Manp-(1-, 2-O-Ac	M2
	4.90	99.64	-4)-β-Manp-(1-, 2-O-Ac	M2
	4.91	94.77	β-ManpR	Mbr
	4.84	100.62	-4)-β-Manp-(1-, 3-O-Ac	M3
	4.76	101.20	β-Manp-(1-	M
	4.74	101.30	-4)-β-Manp-(1-	4Manb
glucose	4.53	103.55	-4)-β-Glcp-(1-	Glcb
	4.52	103.65	4)-β-Glcp-(1-	Glcb
galactose	5.03	99.84	αGalp-(1-	Gala
Other polysaccharides				
arabino glucuronoxylan	4.49	102.76	-3,4)-β-Xylp-(1-	X34b
	5.28	110.37	α-Araf-(1-3	Ara3
arabinogalactan	5.10	108.62		Ara3
β-Galactan	4.64	105.50	-4)-β-Galp-(1-	Galb

Table S2. NMR spectra peak assignment for SP Sample

Constituent	Annotation	Figure Key	1	2	3	4	5	6a	6b						
			¹ H (ppm)	¹³ C (ppm)	¹ H (ppm)	¹³ C (ppm)	¹ H (ppm)	¹³ C (ppm)	¹ H (ppm)	¹³ C (ppm)					
mannose	α-Manp-R	Mar	5.18	94.87											
	-4)-β-Manp-(1, 2-O-Ac	M2	4.94	100.23	5.49	72.82									
	-4)-β-Manp-(1, 2-O-Ac	M2	4.9	99.65	5.42, 5.52	72.72	4.04	71.16	3.82	77.06	3.53	76.14			
	β-Manp-R	Mbr	4.88, 4.91	94.77											
	-4)-β-Manp-(1, 3-O-Ac	M3	4.83	100.72	4.12, 4.2	69.8	5.11	74.48	4.04	74.28					
β-Manp-(1-	M	4.76	101.21	4.07	71.55	3.64	73.89	3.57	67.75	3.43	77.05	3.94	61.99	4	61.31
-4)-β-Manp-(1-	4Manb	4.73	101.3	4.13	71.06	3.79, 3.82	72.53	3.77, 3.81	78.48	3.45	75.94	3.75, 3.9	61.6	3.81	61.8
glucose	-4)-β-Glcp-(1-	Glc b	4.53	103.55	3.36	73.89	3.69	74.97	3.62	79.55	3.79	77.05			
	4)-β-Glcp-(1-	Glc b	4.52	103.65					3.69	79.55					
galactose	αGalp-(1-	Gal a	5.03	99.84	3.82	69.05	3.94	70.48	4.01	70.28	3.91	71.94	3.75	62.29	
Other polysaccharides															
arabino-glucuronoxylan	-3,4)-β-Xylp-(1-	X34b	4.48, 4.49	102.77											
	-4)-β-Xylp-(1-	X4b					3.56	73.8			3.36, 4.13	64.04			
	α-GlcpA-(1-2	aGlc			3.56	72.33									
	α-Araf-(1-3	Ara 3	5.28 ¹												
β-Galactan	-4)-β-Galp-(1-	Gal b	4.64	105.5					4.18	78.77					
Arabinogalactan	-3)-β-Galp-(1-	Gal 3b	4.68	105.11											

¹from 1D 1H spectrum

SP Mannose region assignment:

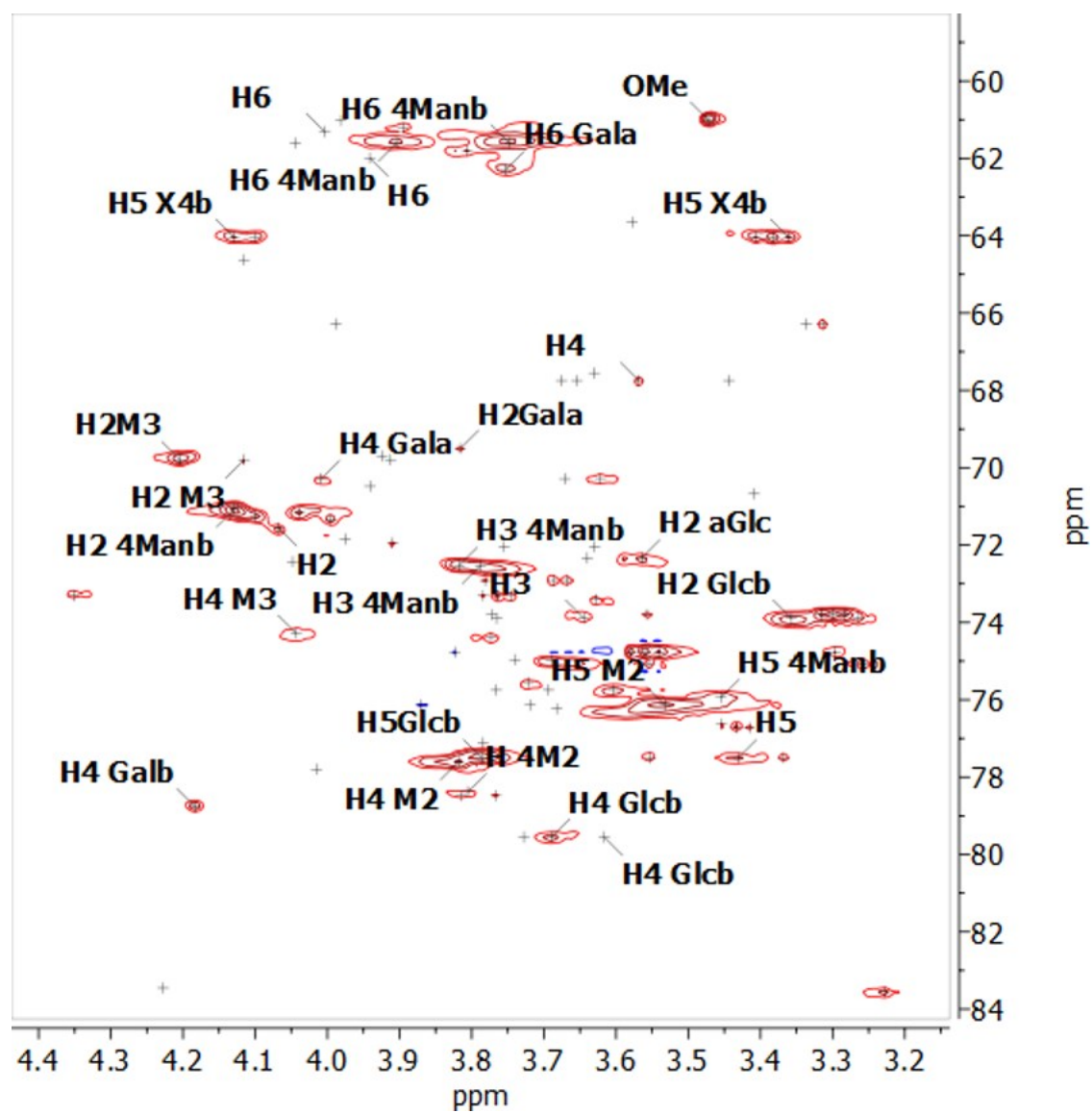


Figure S1 Assignment of cross peaks for mannose in HSQC (Table S2).

DLS autocorrelation functions:

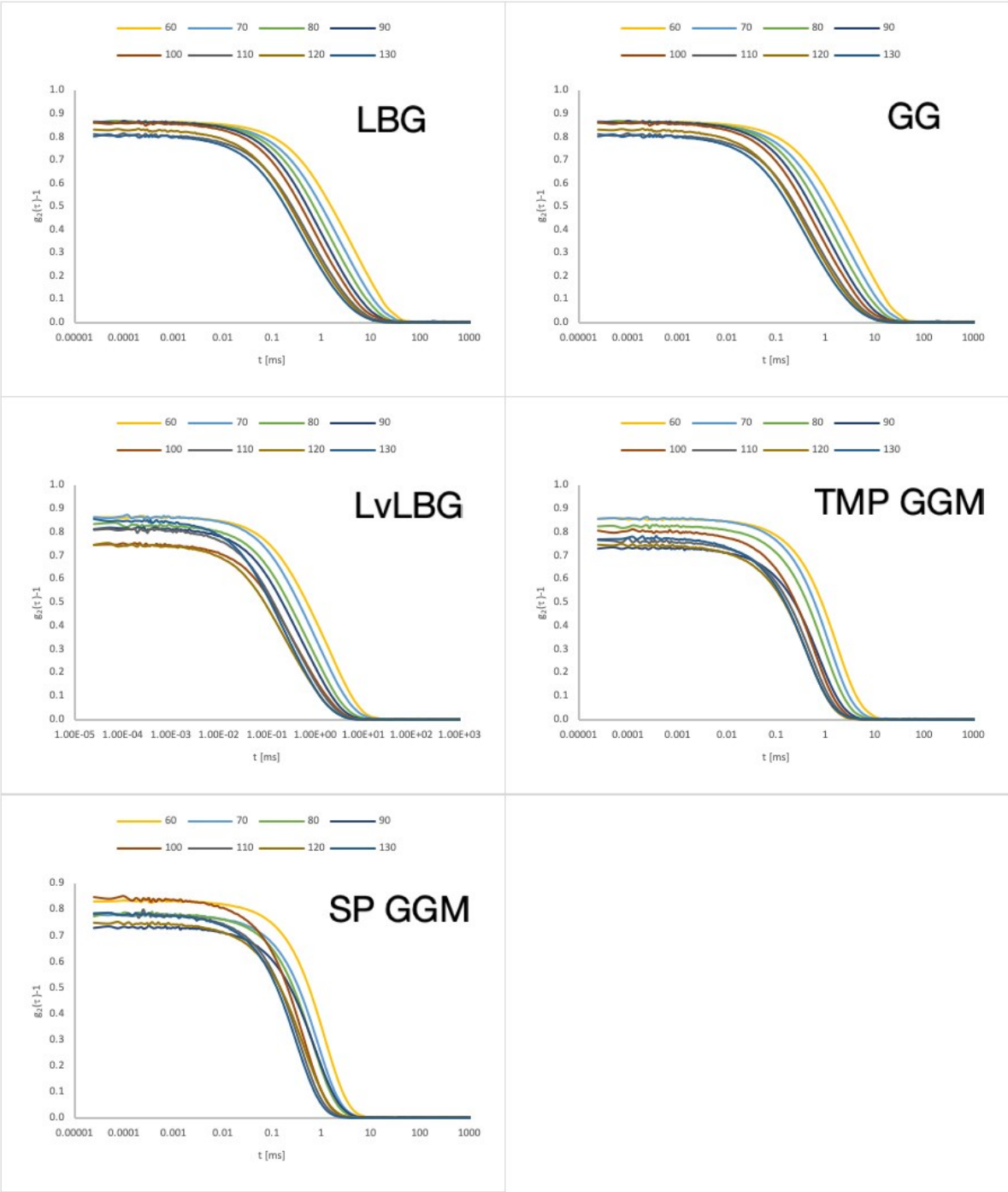


Figure S2 Dynamic light scattering correlation functions of mannans obtained for different angles.

SAXS scattering curves:

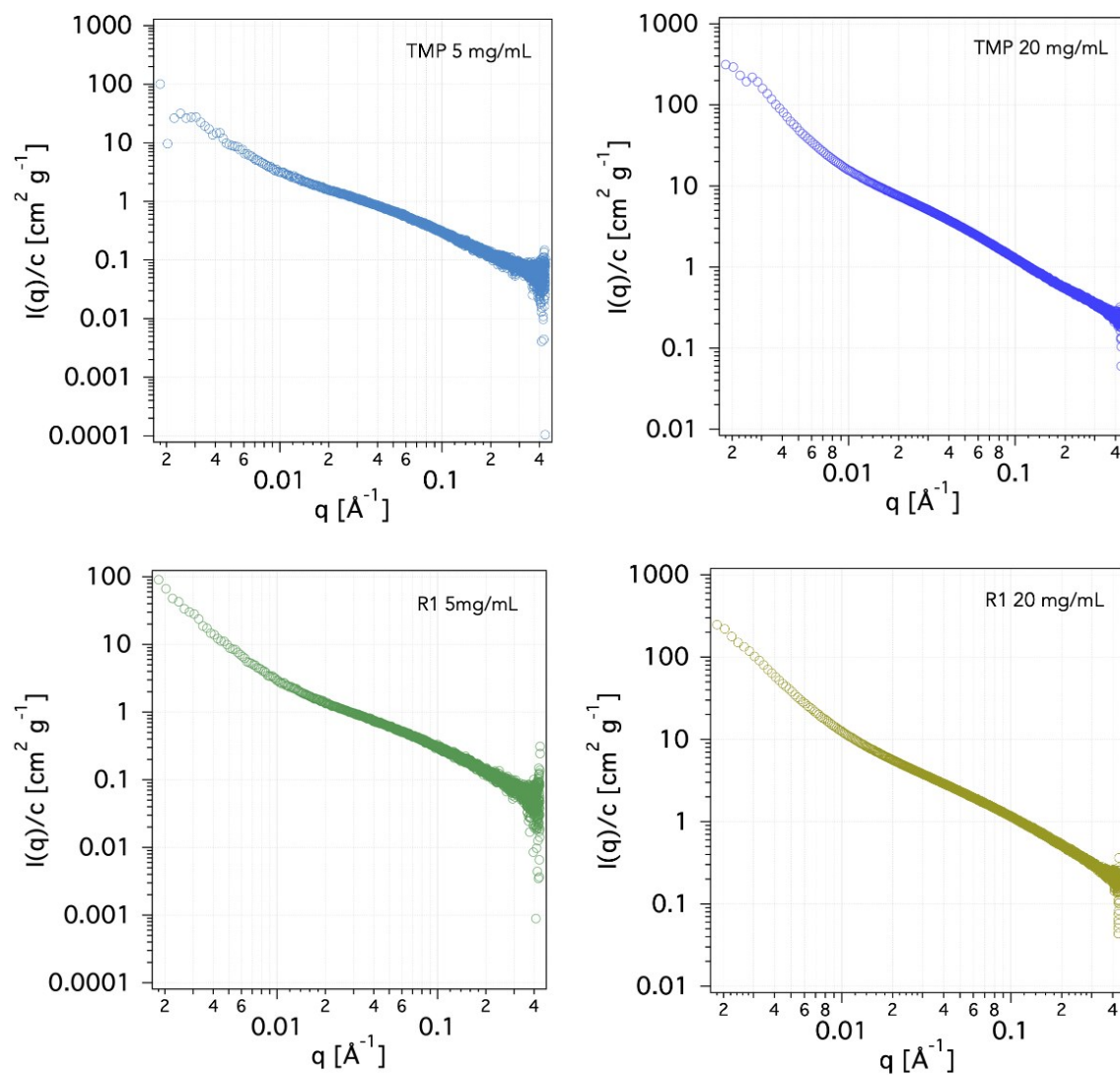


Figure S3 Scattering curves of TMP and SP GGM samples at concentrations of 5 mg/mL and 20 mg/mL.

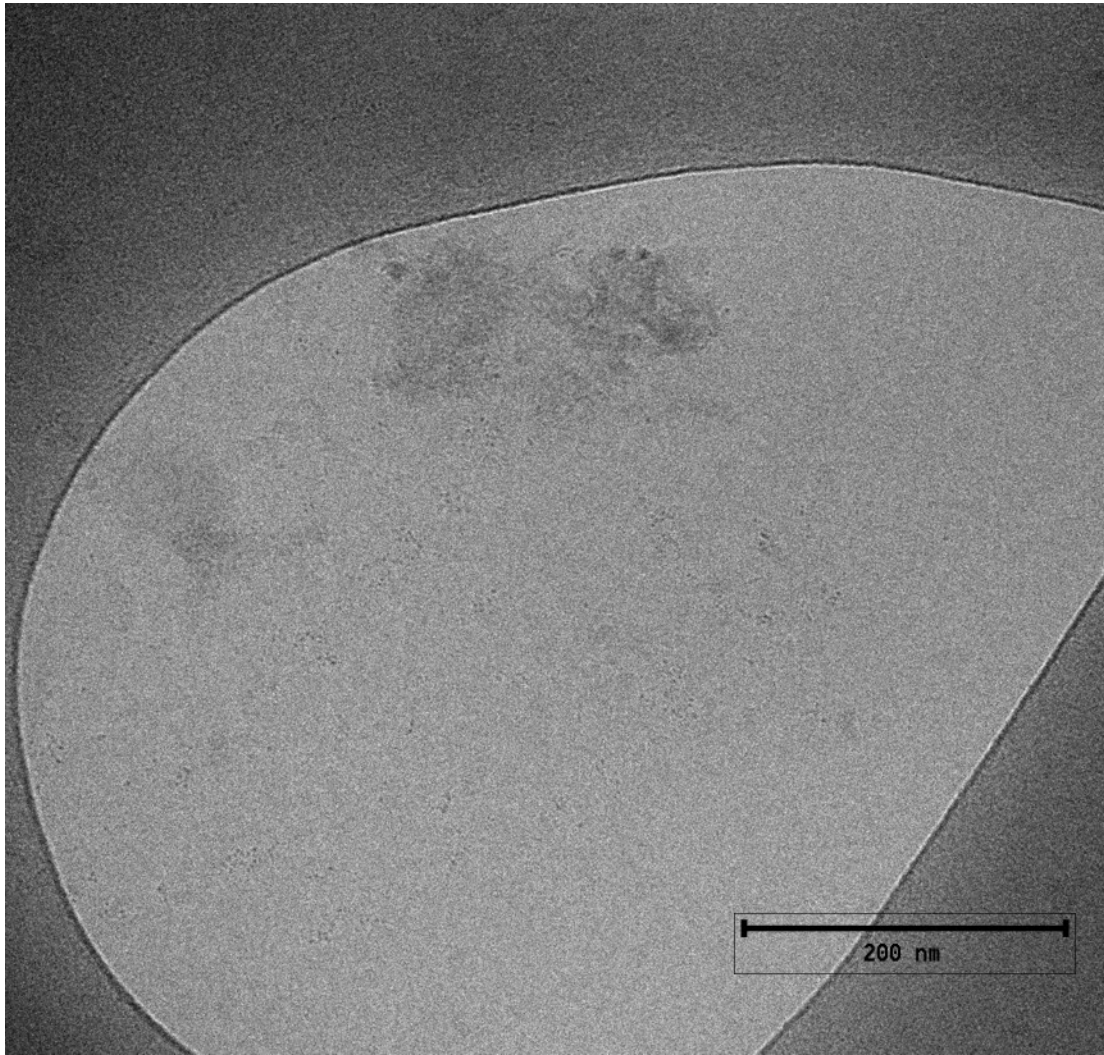


Figure S4 Cryo-TEM image of TMP GGM

Table S3 Ellipsometry results obtained by fitting experimental data on cellulose surface to a 3-layer model.

	Layer	Refractive index	Thickness [Å]	Adsorbed amount [mg/m ²]	
1	LBG	1.416	57	3.1	
	Cellulose	1.424	450	28.1	
	SiOn	1.470	274		
	Si	5.512			
2	LBG	1.408	50	2.4	
	Cellulose	1.420	460	27.4	
	SiOn	1.466	279		
	Si	5.475			
1	GG	1.418	44	2.5	
	Cellulose	1.423	460	28.4	
	SiOn	1.467	297		
	Si	5.515			
	2	GG	1.413	56	2.9
		Cellulose	1.421	414	24.9
		SiOn	1.465	270	
		Si	5.470		
1	LvLBG	1.421	37	2.2	
	Cellulose	1.425	394	24.9	
	SiOn	1.472	268		
	Si	5.478			
	2	LvLBG	1.418	35	2.0
		Cellulose	1.423	439	27.1
		SiOn	1.471	267	
		Si	5.479		
1	TMP	1.417	38	1.9	
	Cellulose	1.413	438	23.7	
	SiOn	1.472	278		
	Si	5.478			
	2	TMP	1.417	39	2.0
		Cellulose	1.423	486	30.0
		SiOn	1.471	260	
		Si	5.477		
1	SP	1.416	41	2.0	
	Cellulose	1.42	411	24.4	
	SiOn	1.468	276		
	Si	5.478			
	2	SP	1.412	37	1.7
		Cellulose	1.417	432	24.7
		SiOn	1.468	261	
		Si	5.481		

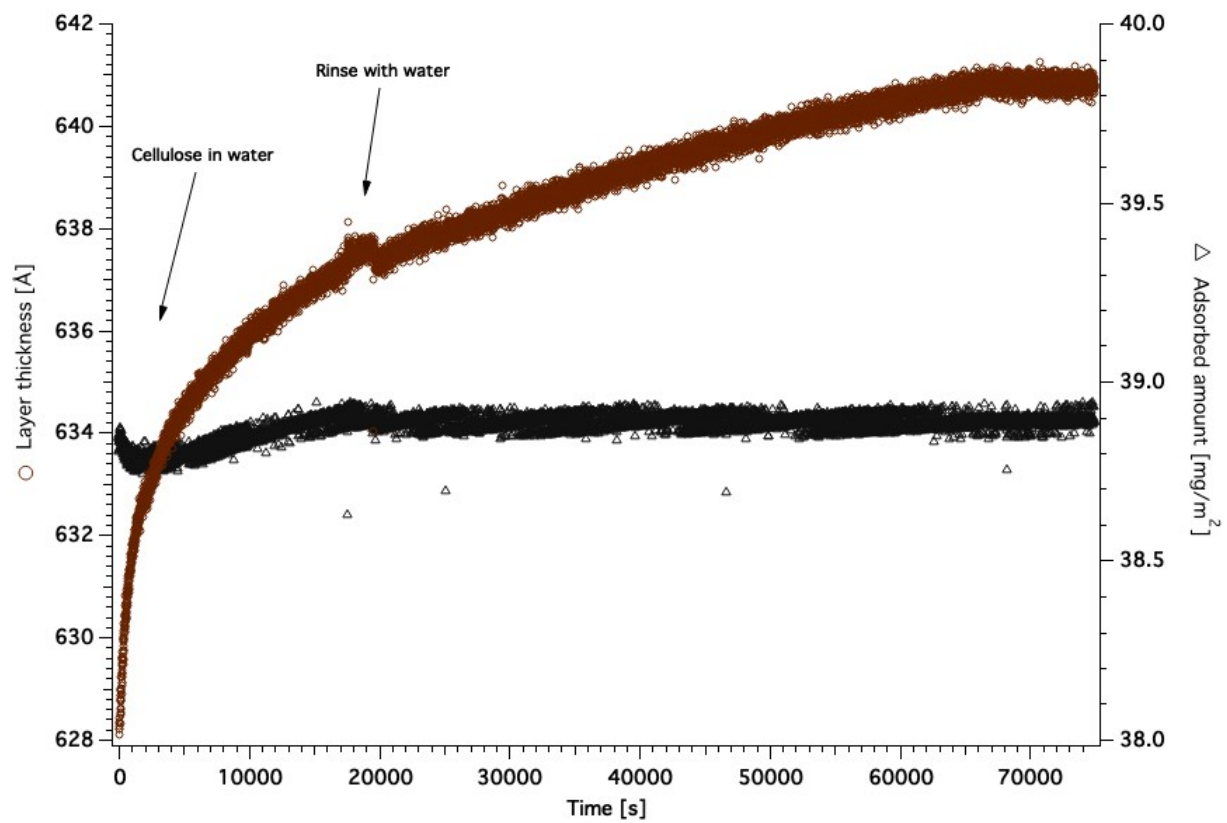


Figure S5 Cellulose film swelling in water as observed with null ellipsometry

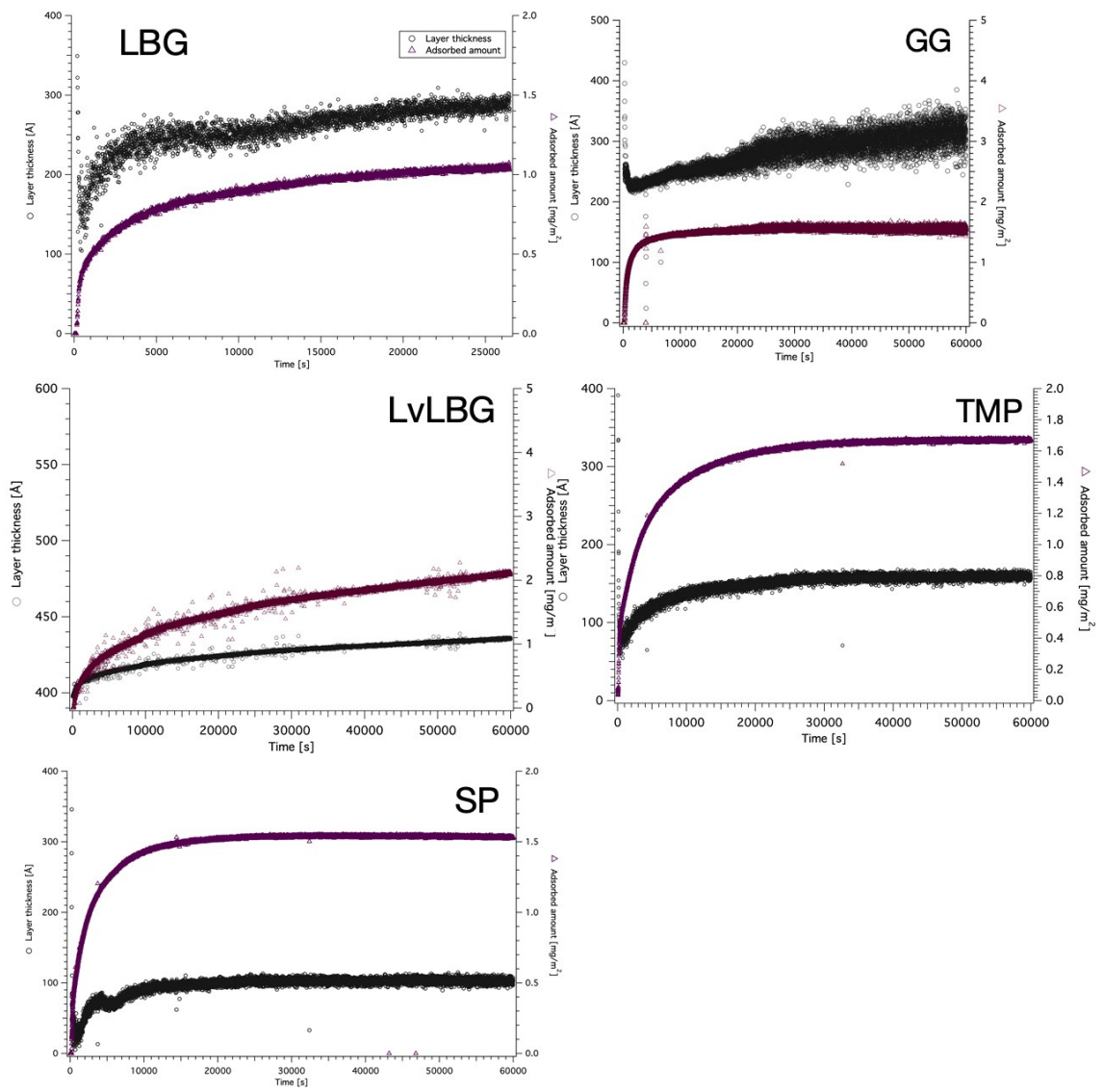


Figure S6 Mannan adsorption on hydrophobic surface measured with ellipsometry

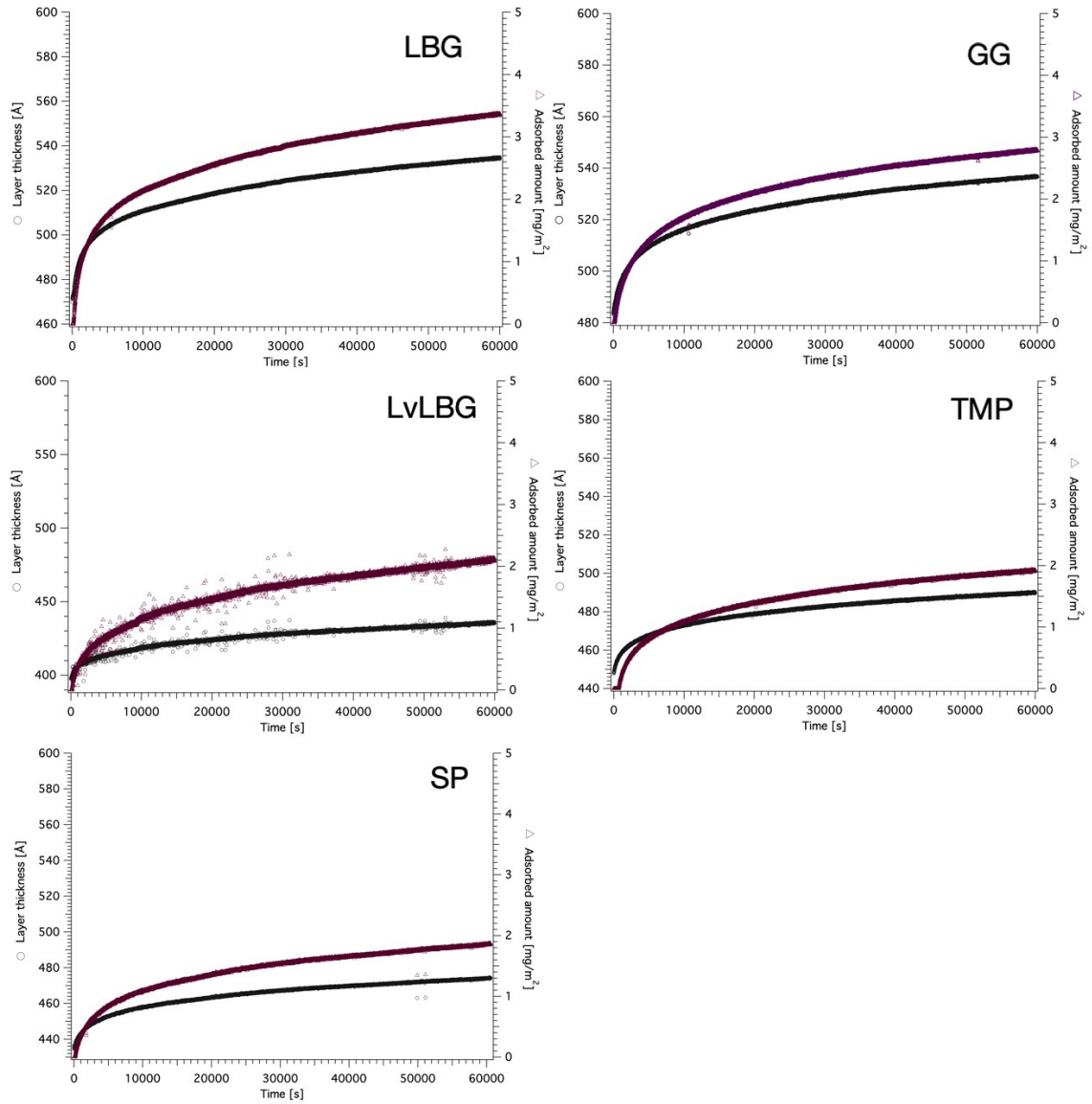


Figure S7 Mannan adsorption on cellulose surface measured with ellipsometry

QCM-D data and fitting:

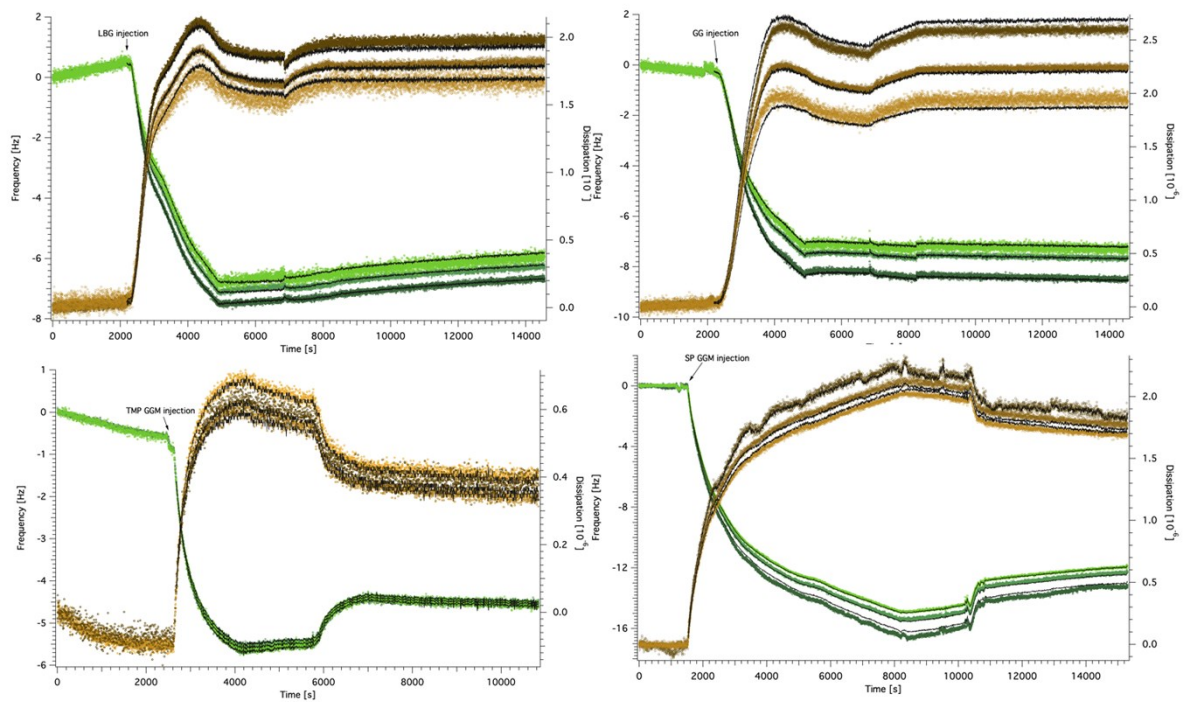


Figure S8 Mannan adsorption on hydrophobic surface measured with QCM-D. Results were fitted to the Voigt viscoelastic model using at least three overtones. Theoretical fit is represented by solid lines.

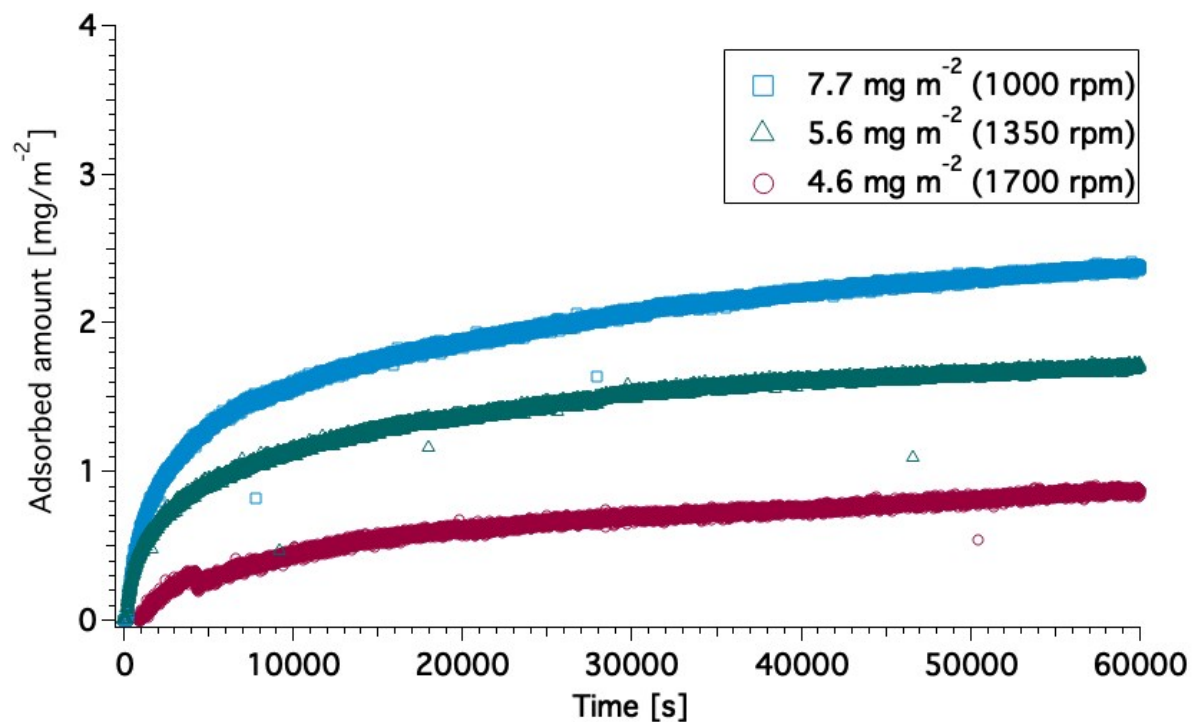


Figure S9 The adsorbed amount of GG on the cellulose films spin coated at different speeds determined with ellipsometry