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1 **Environmentally-compatible alkyd paints stabilized by wood hemicelluloses**

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13 **Keywords:** Emulsions, alkyds, paints, hemicelluloses, glucuronoxylans, galactoglucomannans

14 **Abstract**

15 Wood biorefining currently involves large-scale industrial processes where a notable portion of raw materials,
16 namely hemicelluloses and lignin, are either lost with the process water, degraded, or burnt for energy. Value-
17 added utilization of polymeric hemicelluloses is challenging due to their intermediate molar mass and the
18 presence of other wood components, such as phenolic residues or wood extractives. Oil-in-water (O/W)
19 emulsions represent a diverse and abundant class of applications in which the natural properties of wood
20 hemicelluloses are beneficial. In the current work, we present highly promising new technical alkyd paint
21 emulsion systems stabilized with hardwood glucuronoxylans (GX) and softwood galactoglucomannans
22 (GGM). Samples from three isolation methods and their further fractionation by ethanol precipitation were

23 systematically compared with regard to hemicellulose composition, interfacial activity, and functionality in
24 emulsions. Emulsification of alkyd resins was successful with both GX and GGM obtained by various
25 biorefining strategies. The highest emulsion stability over storage was achieved using crude non-purified GX
26 and GGM fractions, and was correlated with the presence of phenolic compounds and extractives, interfacial
27 activity, and small droplet size. Hardwood GX and softwood GGM are envisioned as natural emulsifiers of
28 alkyd O/W emulsions, which are examples of diverse and abundantly-used technical dispersions. This study
29 can be utilized as a guideline for targeted extraction of hemicelluloses with desired functionality, and as a
30 protocol for developing environmentally-compatible industrial dispersions.

31 **1 Introduction**

32 As the industrial exploitation of lignocellulosic biomass intensifies, value-added applications of polymeric
33 hemicellulose isolates are still scarce. Hemicelluloses are plant cell wall heteropolysaccharides that are closely
34 associated with cellulose and lignin. They are the most abundant plant polysaccharides other than cellulose,
35 and are biosynthesized in large quantities by trees and other terrestrial plants (Timell, 1967; Mikkonen &
36 Tenkanen, 2012). Thus wood as well as forestry biorefinery streams are abundant sources for hemicelluloses.
37 Methods for recovery of hemicelluloses from wood biomass have been actively developed previously. Those
38 include purification and concentration of softwood thermomechanical pulp (TMP) process water (Willför et al.,
39 2003a), pre-hydrolysis of hardwood dissolving pulp (Saadatmand et al., 2013), pressurized hot water extraction
40 (PHWE) of wood chips or saw meal from either softwood or hardwood (Kilpeläinen et al., 2014), and the BLN
41 process for efficient fractionation and recovery of all main wood components (cellulose, hemicelluloses, and
42 lignin) using vacuum-enhanced aqueous extraction (von Schoultz, 2015), also applicable for both hardwood
43 and softwood.

44 The predominant hemicelluloses in hardwoods are glucuronoxylans (GX), which comprise almost 25% of the
45 wood mass. GX consist of backbones β -D-xylopyranosyl (Xylp) units, linked by (1 \rightarrow 4)-bonds, and (1 \rightarrow 2)-
46 linked 4-O-methyl- α -D-glucopyranosyl uronic acid (MeGlc_pA) and O-acetyl side groups (Sjöström, 1993).

47 Hardwoods also contain 2–5% glucomannans. Softwoods, on the other hand, are rich in galactoglucomannans
48 (GGM), comprising roughly 20% of the wood mass. GGM have a backbone with alternating β -D(1 \rightarrow 4)-
49 glucopyranosyl (Glc p) and β -D(1 \rightarrow 4)-mannopyranosyl (Man p) units, with α -D(1 \rightarrow 6)-galactopyranosyl (Gal p)
50 units linked to the backbone Man p units. The Man p units also carry *O*-acetyl groups at the C-2 and C-3
51 positions. Softwoods also contain 5–10% arabinoglucuronoxylans. The polysaccharide-rich GX and GGM
52 extracts also often contain co-components, such as phenolic residues or other wood-derived extractives
53 (Giummarella & Lawoko, 2017). The extraction conditions, such as temperature and time, affect the extract
54 composition and yield: increase of extraction time and temperature increases the release of hemicelluloses, but
55 concomitantly, the content of co-components in the extracts increase (Song et al., 2011; Pranovich et al., 2016).
56 Covalent bonding between the polysaccharide chains and other structures may occur, and researchers argue
57 whether the origin of such bonds are native structures in wood, or if they result from reactions occurring during
58 the extraction process. For exploitation of hemicelluloses in industrial products, understanding of their
59 structure-dependent functionality arising from different isolation methods is crucial. Molar mass and purity of
60 hemicelluloses is expected to determine their interfacial properties and behavior in dispersed systems
61 (Lehtonen et al., 2018).

62 Aqueous paints are an example of dispersed systems, and they are environmentally advantageous due to the use
63 of water as the continuous phase, instead of organic solvents. Water is also preferred due to health and safety
64 aspects during paint formulation, storage, and use. Alkyd resins are a group of binders that are increasingly
65 exploited in water-borne dispersions due to their good coating-formation ability, in combination with the
66 advantages of solvent-free coatings (Beetsma, 1998). Alkyd resins are polyesters made by condensation
67 polymerization of polyols, polybasic acids, and fatty acids or triglyceride oils. Alkyd resins have low glass
68 transition temperatures (T_g), which makes them viscous and tacky materials that are difficult to handle (Jones,
69 2016). Emulsification of alkyd resins (Weissenborn & Motiejauskaite, 2000; Watson & Mackley, 2002)
70 facilitates their handling, such as pouring, pumping, and applying on surfaces for coating or paint layer
71 formation. However, the intrinsic nature of emulsions results in thermodynamic instability and tendency for

72 structural breakdown during storage. To stabilize alkyd resin emulsions, the droplet interface is usually covered
73 by compounds that fulfill two basic requirements: they have to be anchored onto the droplet surface and they
74 have to dissolve in the continuous phase, i.e., water (Beetsma, 1998).

75 In general, oil-in-water (O/W) emulsions are prepared and stabilized using either small-molecular amphiphilic
76 surfactants, or macromolecular hydrocolloids, or a combination of both. The former adsorb efficiently at the
77 droplet interface and decrease surface tension, which decreases the energy needed for droplet size reduction.
78 The latter increase the viscosity of emulsions' continuous phase, decreasing the probability for droplet collision
79 and emulsion breakdown (Dickinson, 2009). We have recently presented wood hemicelluloses as new natural
80 emulsifiers and stabilizers, whose characteristics – molar mass, viscosity, and surface activity – lie between
81 those of small-molecular surfactants and macromolecular hydrocolloids (Mikkonen et al., 2016a).

82 We have previously characterized TMP GGM (Mikkonen et al., 2016b; Lehtonen et al., 2016; Lehtonen et al.,
83 2018), PHWE GGM (Mikkonen et al., 2016a, Lehtonen et al., 2018), and PHWE GX (Mikkonen et al., 2016a)
84 as stabilizers of rapeseed o/w model emulsions for food. The presence of phenolic residues in GGM played a
85 major role for emulsification and stabilization: phenolic residues anchored the GGM polysaccharide tails at the
86 oil droplet interface (Lehtonen et al., 2018), where they were considered to induce steric stabilization
87 (Mikkonen et al., 2016a). Systematic comparison between GGM and GX isolation methods, purity, and
88 characteristics (and their effects on emulsification and stabilization capacity in industrially relevant
89 formulations) is needed to take the next steps towards commercial applications of wood hemicelluloses. Our
90 aim in the present study is to evaluate the functionality of hemicelluloses, obtained via alternative wood
91 biorefining strategies, in stabilization of alkyd paints, which are examples of high-volume technical emulsions
92 where the properties of wood hemicelluloses could be beneficial. The results indicate that natural
93 hemicellulose-rich isolates, derived from forestry biomass without chemical modification or derivatization,
94 show promising functionality in industrial dispersions.

95

2 Materials and methods

2.1 Materials

Linseed oil and tall oil -based alkyd resins (LA Sucha and TA 64, respectively) were kindly donated by Tikkurila Ltd. Vacuum-aided hot water extraction (BLN) (Von Schoultz, 2015) was conducted on birch (*Betula* sp.) and spruce (*Picea abies*) wood chips to recover GX and GGM, respectively. The BLN GX were further fractionated into high, medium, and low molar mass GX fractions (HMM, MMM, and LMM GX, respectively) with sequential ethanol (EtOH) precipitation to study the effect of molar mass of GX on their emulsification properties. HMM GX was obtained with precipitation of starting GX concentrate with EtOH at a ratio of 25/75 v/v. The precipitate was separated with centrifugation at 2000 rpm, washed with EtOH, and dried in a vacuum desiccator at 40 °C. EtOH was added into the supernatant to obtain GX concentrate/EtOH at a ratio of 10/90 v/v; the newly-formed second precipitate, i.e. MMM GX, was also separated by centrifugation as described above. The second supernatant was evaporated in a rotor-evaporator under water pump vacuum at 40 °C and dried in a vacuum desiccator as above to yield LMM GX. To obtain HMM GGM with higher molar mass and purity than those of the initial concentrate, the BLN GGM solution was precipitated at a concentrate/EtOH ratio of 25/75 v/v, washed, and dried as described above for the corresponding GX fraction. Pressurized hot water extraction (PHWE) (Kilpeläinen et al., 2014) of birch and spruce saw meal was performed to obtain GX and GGM, respectively. The extracts were either spray dried (SpDr) to yield crude technical samples or precipitated at a concentrate:EtOH ratio of 10/80 v/v to yield samples with higher purity. TMP GGM were obtained from the process water of a Finnish pulp mill in an industrial-scale isolation trial after spray drying, or from ethanol precipitation with a water-to-ethanol volume ratio of 10/90 (Xu et al., 2007; Willför et al., 2003a). Because the TMP EtOH GGM sample contained a small amount of undissolved particles, it was further dispersed in water at 10 g/L, passed through a glass fiber filter to remove the particles, concentrated using a rotary evaporator, and lyophilized before chemical analyses or emulsification studies. The hemicellulose samples and their codes are listed in Table 1.

120 Table 1. Hemicellulose samples.

Abbreviation	Production method	Supplier
BLN GX	Concentrated BLN, solids 40%	CH-Bioforce
BLN HMM GX	Ethanol precipitated ^a BLN, high molar mass	CH-Bioforce
BLN MMM GX	Ethanol precipitated ^b BLN, medium molar mass	CH-Bioforce
BLN LMM GX	Ethanol soluble BLN, low molar mass	CH-Bioforce
PHWE SpDr GX	Spray dried pressurized hot water extract	Luke
PHWE EtOH GX	Ethanol precipitated ^c pressurized hot water extract	Luke
BLN GGM	Concentrated BLN, solids 53%	CH-Bioforce
BLN HMM GGM	Ethanol precipitated ^a BLN	CH-Bioforce
PHWE SpDr GGM	Spray dried pressurized hot water extract	Luke
PHWE EtOH GGM	Ethanol precipitated pressurized hot water extract	Luke
TMP SpDr GGM	Spray dried purified thermomechanical pulp process water	Åbo Akademi
TMP EtOH GGM	Ethanol precipitated ^d and freeze dried, purified thermomechanical pulp process water	Åbo Akademi

121 a) precipitated with water/ethanol at ratio 25/75 v/v.

122 b) precipitated with water/ethanol at ratio 10/90 v/v

123 c) precipitated with water/ethanol at ratio 10/80 v/v

124 d) precipitated with water/ethanol at ratio 10/90 v/v

125

126 **2.2 Methods**127 **2.2.1 Characterization of hemicelluloses**128 *Monosaccharide composition*

129 Sugar analysis was performed to quantify free monomeric sugars and the total carbohydrate composition of the
130 hemicellulose samples. Monosaccharides were determined with a GC-FID on a 25 m × 0.2 mm i.d. column
131 coated with cross-linked methyl polysiloxane (HP-1) after direct silylation of freeze-dried sample. Total
132 carbohydrates in the hemicellulose samples and the isolated fractions were analyzed with a GC after the
133 samples were freeze-dried, subjected to acid methanolysis, and silylated (Sundberg et al., 1996). Minor

134 contents of free monomeric sugars, mainly pentoses, were detected in BLN GGM and GX concentrates as well
135 as in low molar mass BLN GX fraction, PHWE SpDr GX, PHWE EtOH GX, and PHWE SpDr GGM. The
136 carbohydrate composition of hemicelluloses is reported as mg/g of the sample, after subtracting the content of
137 free monosaccharides. The analysis was performed in duplicate.

138 *Phenolic compounds and extractives*

139 For complementary analysis of the extract composition and content of co-components, the total phenol content
140 was analyzed spectrophotometrically by the Folin-Ciocalteu method, using a gallic acid calibration curve
141 (Slinkard & Singleton, 1977). The results are given as gallic acid equivalent (GAE). Results were corrected for
142 the contribution from monomeric reducing sugars. Lignans and lipophilic extractives were analyzed by
143 capillary GC-FID and GC-MS (Willför et al. 2003b) after liquid-liquid extraction with MTBE (Örså &
144 Holmbom, 1994) from water solutions prepared by weighing out about 50 mg dry sample into 3 ml of distilled
145 water.

146 *Molar mass analysis*

147 Molar mass analysis was performed to correlate the molar mass characteristics of the studied samples with
148 their functionality. All samples were dissolved at 2 mg/mL in 0.1 M aqueous sodium nitrate. HPSEC was used
149 on a two-column system, Ultrahydrogel TM 500 7.8 × 300 mm + Ultrahydrogel TM 120 7.8 × 300 mm
150 columns (Waters, Milford, MA), connected in series, equipped with a MALLS (miniDAWN, Wyatt
151 Technology) and RI detectors, as described earlier (Song et al., 2008). The dn/dc value of 0.15 mL g⁻¹ was
152 used for all samples (Michielsen, 1999).

153 *Degree of acetylation*

154 Acetyl groups in hemicelluloses were released by alkaline treatment in 2.35 mg/mL sodium hydroxide
155 solutions at 70°C for 20 h. Hydrolyzed acetic acid was analyzed by HPLC (Agilent Technologies 1269,
156 Waldbronn, Germany) with a Synergi Hydro-RP 80R HPLC Column (250 mm x 4.6 mm, 4 μm, Phenomenex,

157 Torrance, CA, USA). The pH of samples was adjusted to 2.6 with 30% ortho-phosphoric acid. The eluent
158 contained 20 mM KH₂PO₄ in deionized water and pH was adjusted to 2.5 with ortho-phosphoric acid. The
159 eluent was filtered with a 0.1- μ m filter (Anodisc 47, Whatman International, Maidstone, UK). The flow rate of
160 eluent was 1.0 mL/min and the injection volume was 20 μ l. Degree of acetylation (DA) was calculated as mol-
161 % of backbone carbohydrates (Xylp in GX samples and Manp and Glcp in GGM samples).

162 *Surface tension and pH*

163 Surface tension of aqueous hemicellulose solutions (0.5, 1, and 5 wt.-%) was measured to evaluate the surface
164 activity, i.e. the interfacial behavior of the samples. The measurements were done against air using a du Noüy
165 tensiometer with a platinum ring (KSV Sigma 70, KSV, Finland). The surface tension was calculated from the
166 maximum force needed to separate the ring from the liquid-air interface. Three replicate measurements were
167 performed and the average was calculated. The pH of aqueous hemicellulose solutions at the concentration of
168 the continuous phase of emulsions (13.3 wt.-%) was measured.

169 **2.2.2 Emulsion preparation**

170 O/W emulsions were prepared using 40 wt.-% alkyd resins and 8 wt.-% hemicelluloses, to test the capacity of
171 hemicelluloses to emulsify and stabilize technical dispersions. Alkyd resins were heated up to 62 °C to
172 improve their flowability before the desired amount was weighed. Hemicelluloses were dissolved in reverse
173 osmosis purified water at room temperature (RT) for 2 h using a magnetic stirrer with the lowest possible speed
174 in order to avoid foaming. They were then heated up to 62 °C prior to emulsification. Emulsification was done
175 in water bath at 62 °C, using an Ultra Turrax (T-18 basic, IKA, Staufen, Germany) equipped with an
176 emulsification mixing blade (diameter 25 mm), at mixing speed of 11000–13000 rpm for 15 min.
177 Emulsification experiments of all studied hemicellulose samples with LA were made as duplicates.
178 Furthermore, the most interesting hemicellulose samples: PHWE SpDr GGM, PHWE EtOH GGM, PHWE
179 SpDr GX, and BLN EtOH HMM GX, were selected for emulsion testing with TA.

181 2.2.3 Emulsion characterization

182 *Droplet size distribution*

183 Droplet size distribution of emulsions was measured directly after preparation and after one week and one
184 month of storage to evaluate emulsion stability. The droplet size distribution was characterized by static light
185 scattering using a Mastersizer Hydro 3000 SM (Malvern Instruments Ltd, Worcestershire, UK) using refractive
186 index of 1.59, absorption index of 0.1 and density value of 1 g/cm³. Due to high viscosity and turbidity of the
187 emulsion samples, they were diluted in deionized water for the analysis. Furthermore, selected emulsions were
188 diluted ten-fold, stored, and characterized for droplet size distribution. Droplet size distribution was reported as
189 an average of three replicate measurements.

190 *Optical microscopy and visual observation*

191 The emulsion morphology was characterized using optical microscopy (AxioScope A1, Carl Zeiss Inc.,
192 Oberkochen, Germany) directly after preparation and after one week and one month of storage (RT). At the
193 same time, emulsions were visually observed for syneresis and sedimentation. Emulsions (~10 ml) were stored
194 in 15 ml plastic vials, and the height of separated layers was measured using a ruler and reported as volume
195 percentage.

196 *Rheological properties*

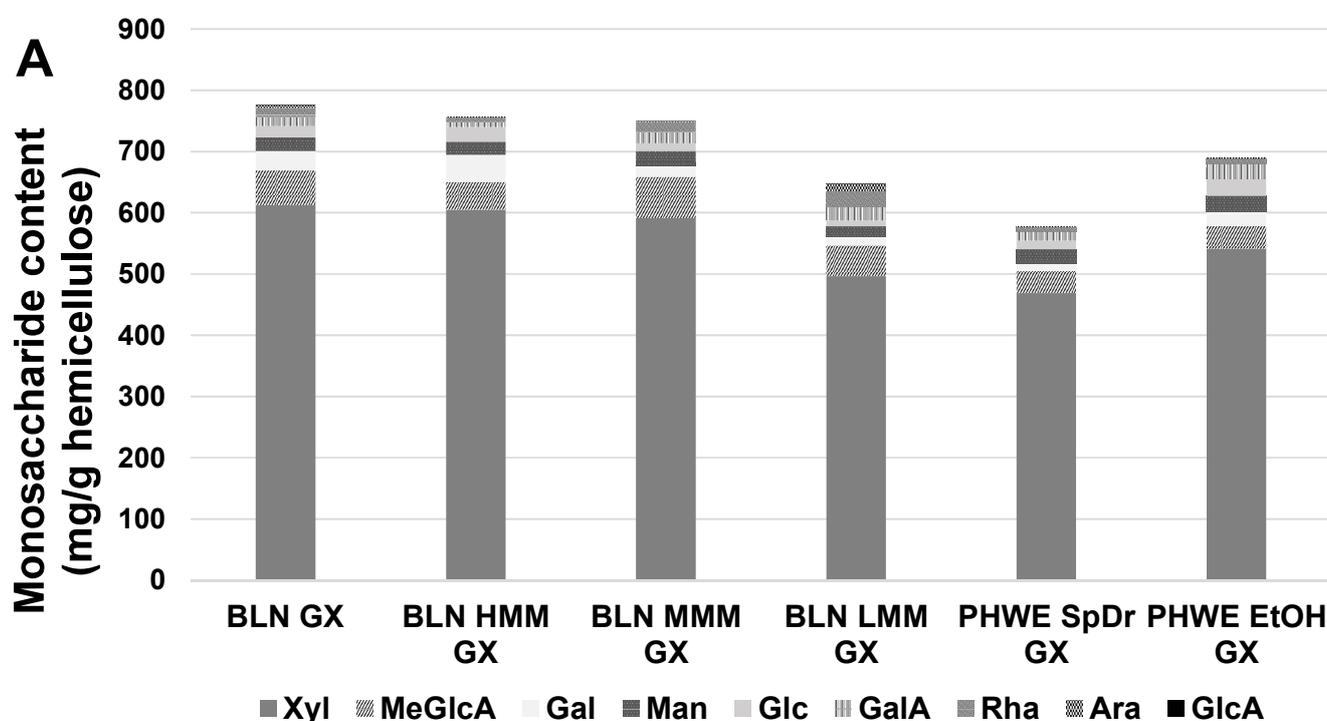
197 Rheological measurements were taken for selected emulsions as fresh and after one month of storage, using a
198 Haake RheoStress 600 rheometer (Thermo Electron GmbH, Germany) with a cone and plate geometry (60 mm,
199 1°). The measurements were done at 20 °C with a stepwise rotation program: shear rate was increased
200 logarithmically from 3 s⁻¹ to 100 s⁻¹ after which the shear rate was reduced logarithmically back to 3 s⁻¹.
201 Power function was fitted to the reducing shear rate data and the viscosity at shear rate 50 s⁻¹ were calculated
202 from the model. The analyses were done in triplicate.

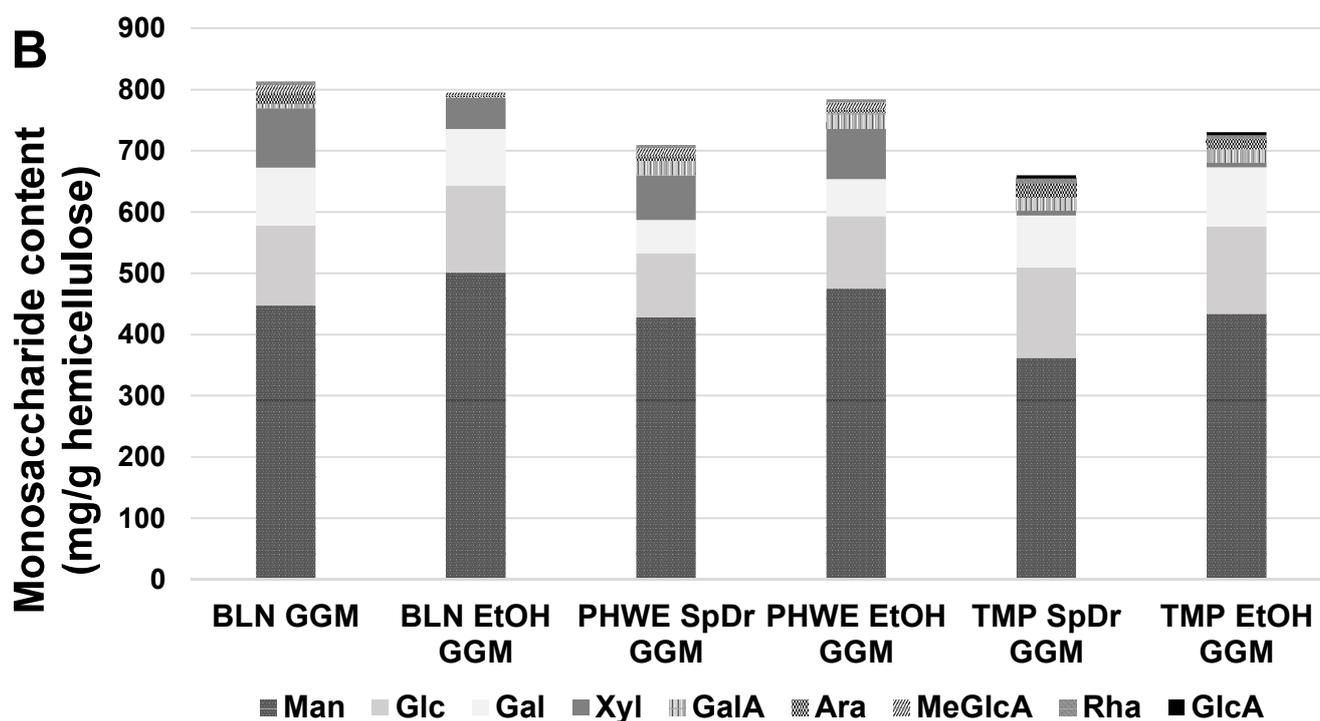
203

204 **3 Results**205 **3.1 Composition of hemicellulose isolates**

206 Chemical analysis of the hemicellulose samples was performed to characterize the composition, purity, and
 207 molar mass of hemicelluloses recovered from birch and spruce, using various biorefining strategies and
 208 fractionation steps.

209 The main carbohydrates comprising the isolated GX samples were *Xylp* units, which accounted for about 80%
 210 of the carbohydrates. Secondly, the *MeGlcA* content of different GX samples varied between 5 and 9 %, and
 211 other carbohydrates were present at minor quantities (Figure 1A). The GGM samples were mainly composed
 212 of *Manp*, *GlcA*, and *GalA* units, with some *Xylp* units, especially in the PHWE GGM and BLN GGM samples
 213 (Figure 1B). The characterized carbohydrates summed up to about 600–800 mg/g of the samples, the BLN
 214 GGM concentrate showing the highest content of carbohydrates. In general, the carbohydrate content of EtOH
 215 precipitated hemicelluloses was higher than that of SpDr hemicelluloses, as expected (Figure 1).





217

218 Figure 1. Carbohydrate composition of A) glucuronoxylan (GX) and B) galactoglucomannan (GGM) samples
 219 after subtracting the content of free monosaccharides. Please refer to Table 1 for the sample codes.

220 Compared to the total content of carbohydrates, the content of phenolic compounds and extractives in the
 221 hemicellulose samples followed an opposite trend. The results showed relatively large amounts of phenolic
 222 compounds from the Folin-Ciocalteu assay (Table 2) and GC analysis identified extractives (Table 3) in all
 223 three SpDr hemicelluloses. Notably, these hemicelluloses also contained some relatively high molar mass co-
 224 mponents that are hypothesized as oligolignols or oligolignans. The “monomeric” components that
 225 dominated among the extractives were lignin fragments (phenolics), lignans, and (oxidized) resin acids.

226 The TMP GGM samples had the highest molar mass of the studied hemicelluloses (Table 2). The molar mass
 227 of the other hemicelluloses decreased in the following order: BLN HMM GGM, PHWE GGM samples and
 228 BLM GX HMM, followed by the PHWE GX samples and the other BLN GGM and BLN GX samples. As
 229 expected, the BLN GX LMM exhibited the lowest molar mass.

230 The DA of GX samples was between 49 and 63% and that of the GGM samples was between 28 and 39%
 231 (Table 2). Generally, the EtOH precipitated hemicelluloses and the EtOH soluble BLN LMM GX showed
 232 slightly higher DA than the concentrates and SpDr hemicelluloses.

233 Table 2. Total content of phenolic compounds and molar mass of hemicelluloses and pH of aqueous hemicellulose
 234 solutions. Please refer to Table 1 for the sample codes.

Sample	Total phenolic compounds, mg Gallic acid equivalent / g hemicelluloses	Molar mass, g/mol	Degree of acetylation, mol-%	pH
BLN GX	4.2	4700	51	3.6
BLN HMM GX	4.1	8300	49	3.9
BLN MMM GX	6.1	3000	53	3.7
BLN LMM GX	22.2	1900	63	3.5
PHWE SpDr GX	71.1	4000	55	6.2
PHWE EtOH GX	10.8	4300	58	3.4
BLN GGM	nd	5300	28	2.7
BLN HMM GGM	2.3	10000	30	2.8
PHWE SpDr GGM	48.7	8200	36	5.3
PHWE EtOH GGM	15.8	8200	38	4.9
TMP SpDr GGM	19.4	48 000	35	4.4
TMP EtOH GGM	5.1	27 600	39	4.9

235 nd = not detected

236

237

238

239

240

241

242 Table 3. Extractives in hemicelluloses (mg/g). Please refer to Table 1 for the sample codes.

Sample	Dioic acids (C5–C10)	Fatty acids (C14–C22)	Resin acids	Oxidized resin acids	Simple phenolics	Lignans (identified)	Unknown lignans*	Total extractives
BLN GX	nd	0.04	0.03	0.005	0.008	0.03	0.04	0.17
BLN HMM GX	0.005	0.03	0.03	0.008	0.002	0.01	0.06	0.16
BLN MMM GX	0.006	0.04	0.006	nd	0.04	0.02	0.03	0.15
BLN LMM GX	0.08	0.04	0.01	0.009	0.4	0.2	0.3	1.1
PHWE SpDr GX	0.06	0.2	0.01	0.03	2.4	4.2	3.4	10.5
PHWE EtOH GX	0.02	0.03	nd	nd	0.2	0.3	0.2	0.83
BLN GGM	0.004	0.03	0.003	nd	0.005	0.01	0.03	0.11
BLN HMM GGM	nd	0.03	0.03	0.01	nd	0.02	0.04	0.14
PHWE SpDr GGM	0.08	0.05	0.3	0.3	1	1	2	5.1
PHWE EtOH GGM	0.02	0.04	0.04	0.005	0.07	0.07	0.1	0.36
TMP SpDr GGM	0.7	0.09	0.2	1.4	0.7	3.2	2.4	9.1
TMP EtOH GGM	0.1	0.04	0.03	0.1	0.2	0.1	0.1	0.89

243 *Based on unidentified peaks in the same retention time region as identified lignans.

244 nd = not detected

245

246 Surface tension of aqueous hemicellulose solutions was measured to evaluate their interfacial activity. The
247 measurement was performed against air and not against the alkyd resins due to the viscous and tacky
248 consistency of alkyd resins that makes them difficult to handle. All hemicelluloses decreased the surface
249 tension of water. In general, the SpDr hemicelluloses decreased the surface tension more than the EtOH
250 precipitated ones. The lowest surface tension values were observed with TMP SpDr GGM and PHWE SpDr
251 GX. Furthermore, a decreasing trend in surface tension with increasing hemicellulose concentration was
252 observed (Table 4).

253

254

255 Table 4. Surface tensions of GX- and GGM-water solutions. Please refer to Table 1 for the sample codes. Surface tension
 256 of ion exchanged water was 71.1 ± 0.3 mN/m ($T=23$ °C).

Sample	Content (weight %)		
	0.5	1.0	5.0
BLN GX	60.5 ± 0.2	60.2 ± 0.2	56.9 ± 0.4
BLN HMM GX	62.6 ± 0.1	61.9 ± 0.1	60.3 ± 0.2
BLN MMM GX	58.9 ± 0.3	60.6 ± 0.1	57.6 ± 0.1
BLN LMM GX	58.9 ± 0.3	60.6 ± 0.1	57.6 ± 0.1
PHWE SpDr GX	57.3 ± 0.3	53.9 ± 0.4	38.6 ± 0.5
PHWE EtOH GX	59.6 ± 0.3	57.9 ± 0.3	55.0 ± 0.3
BLN GGM	64.6 ± 0.2	63.3 ± 0.2	65.6 ± 0.1
BLN HMM GGM	67.1 ± 0.3	69.3 ± 0.2	64.4 ± 0.3
PHWE SpDr GGM	59.5 ± 0.3	57.6 ± 0.3	49.5 ± 0.3
PHWE EtOH GGM	66.0 ± 0.1	65.1 ± 0.3	59.3 ± 0.4
TMP SpDr GGM	48.4 ± 0.3	46.1 ± 0.2	41.7 ± 0.2
TMP EtOH GGM	63.4 ± 0.2	55.1 ± 0.3	49.1 ± 0.2

257

258 3.2 Emulsion formation and stability

259 Alkyd resins and the aqueous hemicellulose solutions were mixed directly through a straightforward one-step
 260 process to prepare finely dispersed alkyd resin droplets in water. Emulsification was successful with all TMP

261 and PHWE hemicelluloses and with the BLN GX, BLN HMM GX, and BLN HMM GGM. The BLN GGM,
262 BLN LMM GX, and BLN MMM GX did not form emulsions, as the alkyd resins and hemicellulose solutions
263 separated into liquid and semi-solid phases during mixing.

264 The surface average droplet size $D[3,2]$ of all LA emulsions was about 3 μm (Table 5). Because the $D[3,2]$
265 value considers the ratio of surface area to the volume of droplets, it emphasizes the numerous small droplets
266 present in the emulsions. Larger differences between the studied emulsion types were detected in the volume
267 average droplet size $D[4,3]$ values, which varied between 5–14 μm . The $D[4,3]$ is more sensitive to the
268 presence of few large droplets in emulsions, and thus the values were higher than the $D[3,2]$ values.

269 Correspondingly, the $D(10)$ values (meaning that 10% of lipid droplets were smaller than the $D(10)$), were
270 similar ($\sim 1 \mu\text{m}$) for all emulsions. The $D(50)$ (median size) varied between 2.7 and 5.1 μm . Largest differences
271 were observed in the $D(90)$ values of emulsions (meaning that 90 % of lipid droplets were smaller than the
272 $D(90)$). The most promising emulsions, namely, those stabilized by PHWE SpDr GGM, PHWE EtOH GGM,
273 and PHWE SpDr GX, showed $D(90)$ values of about 10 μm . The BLN HMM GX –stabilized emulsions also
274 showed $D(90)$ values lower than 20 μm . The average droplet size of all emulsions was generally maintained at
275 the initial level throughout the one-month storage time. Furthermore, ten-fold dilution of emulsions did not
276 change the droplet size during storage (data not shown). Syneresis of 2 to 16 % of the emulsion volume (i.e.,
277 separation of an aqueous layer on top of emulsions) was monitored in some samples during storage (Table 5).
278 In emulsions stabilized with the PHWE SpDr GX, sedimentation was also observed, which could be due to LA
279 droplets and/ or non-dissolved GX (Table 5).

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285 Table 5. Average droplet size and standard deviation, syneresis, and sedimentation of LA emulsions as fresh and after
 286 one week (1 w) and one month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

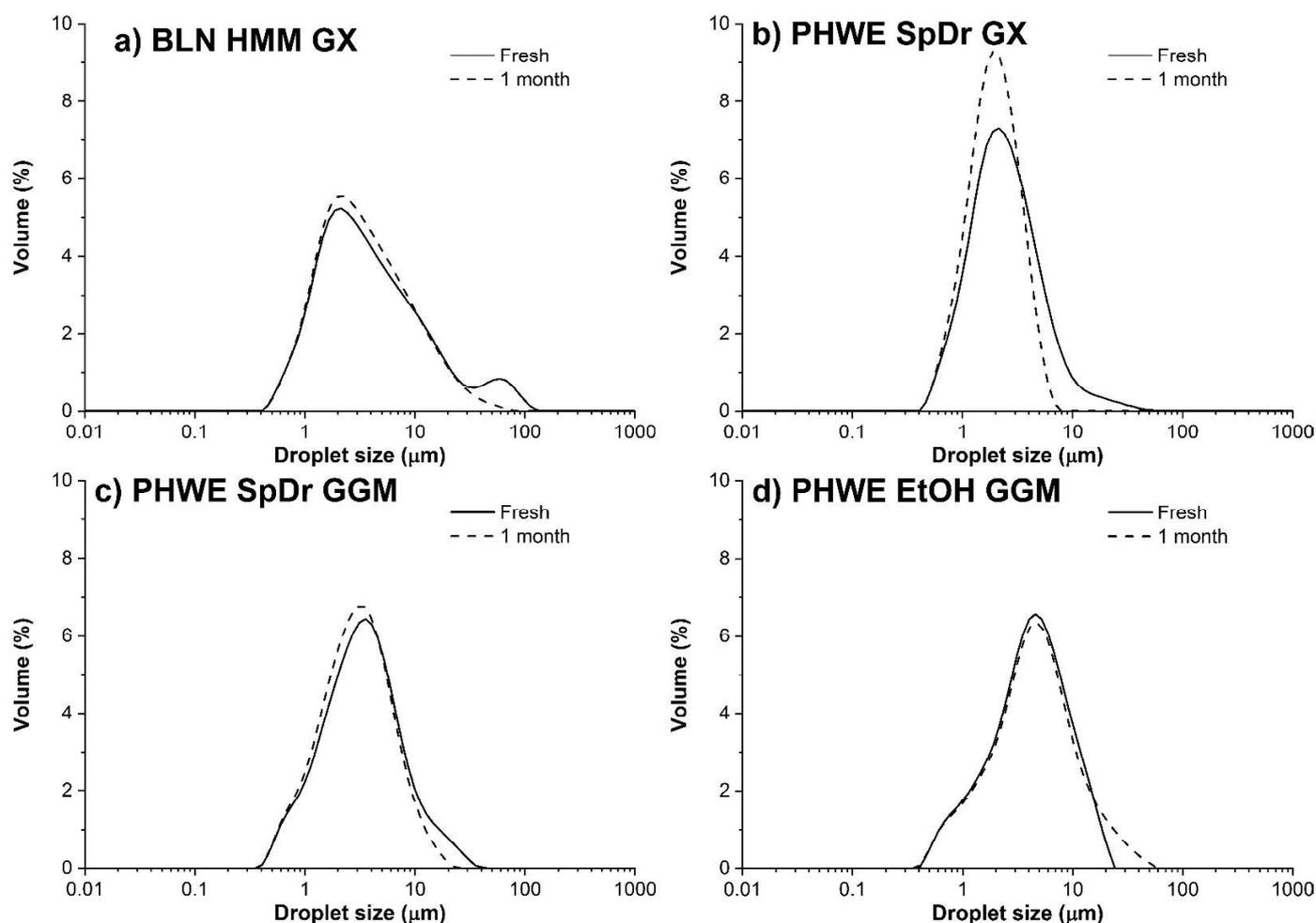
Hemicellulose	Storage time	D[3,2] (μm)	D[4,3] (μm)	D(10) (μm)	D(50) (μm)	D(90) (μm)	Syneresis (%)	Sedime ntation (%)
BLN GX	Fresh	3.2 ± 0.1	13.0 ± 1.9	1.3 ± 0.0	5.3 ± 0.2	38 ± 3	0	0
	1 w	2.9	10.9	1.2	4.3	31	0	0
	1 m	3.0 ± 0.0	10.7 ± 1.6	1.3 ± 0.0	4.6 ± 0.2	28 ± 7	5	0
BLN HMM GX	Fresh	2.7 ± 0.0	8.0 ± 1.5	1.2 ± 0.0	3.7 ± 0.2	18 ± 3	0	0
	1 w	2.6 ± 0.1	6.4 ± 0.3	1.2 ± 0.0	3.6 ± 0.4	15 ± 2	1	0
	1 m	2.8 ± 0.3	7.7 ± 2.6	1.2 ± 0.0	4.0 ± 0.9	18 ± 6	2	0
PHWE SpDr GX	Fresh	2.5 ± 0.4	5.3 ± 1.7	1.2 ± 0.1	3.5 ± 1.0	10.9 ± 4.3	0	0
	1 w	2.3 ± 0.3	3.8 ± 0.7	1.1 ± 0.1	3.0 ± 0.6	7.3 ± 1.5	5	8
	1 m	2.0 ± 0.3	3.9 ± 2.1	1.1 ± 0.1	2.6 ± 0.5	5.3 ± 1.2	16	11
PHWE EtOH GX	Fresh	2.6 ± 0.4	8.9 ± 4.5	1.2 ± 0.1	3.6 ± 1.0	18.0 ± 6.9	0	0
	1 w	2.5 ± 0.3	7.0 ± 3.3	1.2 ± 0.1	3.4 ± 0.7	13.2 ± 2.6	4	0
	1 m	2.2 ± 0.1	7.0 ± 4.9	1.1 ± 0.0	2.7 ± 0.3	7.6 ± 0.2	6	0
BLN HMM GGM	Fresh	3.5 ± 0.4	14 ± 5	1.4 ± 0.1	6.2 ± 1.2	41 ± 18	0	0
	1 w	3.3	12	1.3	5.7	31	1	0
	1 m	3.3 ± 0.1	13 ± 2	1.3 ± 0.0	5.5 ± 0.3	29 ± 3	2	0
PHWE SpDr GGM	Fresh	2.7 ± 0.7	5.7 ± 0.7	1.2 ± 0.0	3.9 ± 0.4	11.6 ± 1.5	0	0
	1 w	2.7 ± 0.8	5.4 ± 0.8	1.2 ± 0.0	3.9 ± 0.5	11.1 ± 1.6	5	0
	1 m	2.6 ± 1.2	5.3 ± 1.2	1.2 ± 0.1	3.8 ± 0.6	10.6 ± 2.4	10	1
PHWE EtOH GGM	Fresh	2.7 ± 0.3	5.4 ± 1.1	1.2 ± 0.1	4.1 ± 0.8	10.8 ± 2.0	0	0
	1 w	2.7 ± 0.3	5.3 ± 1.0	1.2 ± 0.1	4.0 ± 0.8	10.7 ± 1.9	3	0
	1 m	2.9 ± 0.1	6.2 ± 0.8	1.3 ± 0.1	4.5 ± 0.2	12.5 ± 2.4	5	0
TMP SpDr GGM	Fresh	3.1 ± 0.2	9.3 ± 1.3	1.3 ± 0.0	5.1 ± 0.8	21 ± 4	0	0
	1 w	3.1 ± 0.2	8.7 ± 1.3	1.3 ± 0.0	5.0 ± 0.8	20 ± 3	3	0
	1 m	3.1 ± 0.3	8.7 ± 1.9	1.3 ± 0.0	5.0 ± 0.9	20 ± 4.4	8	0

TMP EtOH	Fresh	2.5 ± 0.1	6.7 ± 0.6	1.2 ± 0.1	3.4 ± 0.1	14.9 ± 3.5	0	0
GGM	1 w	2.5 ± 0.0	6.2 ± 1.8	1.2 ± 0.1	3.4 ± 0.0	13.9 ± 4.7	0	0
	1 m	2.7 ± 0.2	11.7 ± 6.2	1.2 ± 0.1	3.6 ± 0.3	22.9 ± 8.7	0	0

287

288 The best performing LA emulsions, namely those stabilized with BLN HMM GX, PHWE SpDr GX, PHWE
 289 SpDr GGM, and PHWE EtOH GGM showed generally unimodal droplet size distributions (Figure 2). The
 290 droplet size distribution of PHWE SpDr GX –stabilized LA emulsions slightly shifted towards larger droplets
 291 during one month storage. The emulsions stabilized with BLN HMM GX, PHWE SpDr GGM and PHWE
 292 EtOH GGM did not considerably change during storage with regard to their droplet size distribution.

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295 Figure 2. Droplet size distributions of LA emulsions stabilized with (A) BLN HMM GX, (B) PHWE SpDr GX, (C)
 296 PHWE SpDr GGM and (D) PHWE EtOH GGM as fresh and after storage of one month at RT. Please refer to Table 1 for
 297 the sample codes.

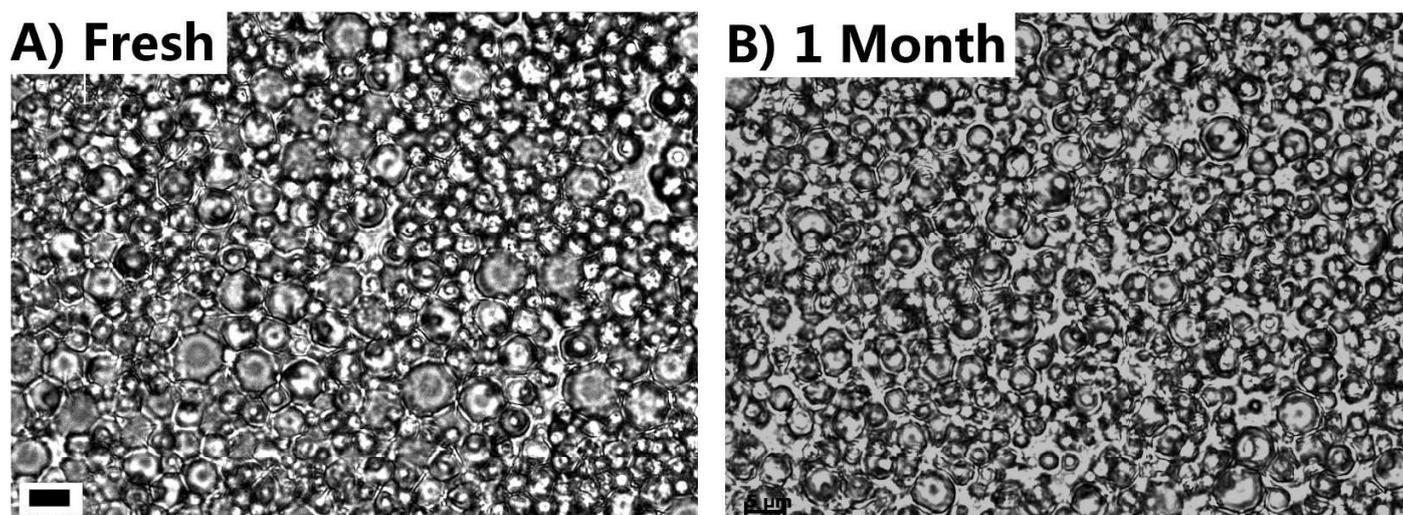
298 The alkyd resin emulsification capacity of selected hemicelluloses, namely, BLN HMM GX, PHWE SpDr GX, PHWE
 299 SpDr GGM and PHWE EtOH GGM, was further tested using TA, which contains more polar lipids than LA and was
 300 thus expected to be more challenging to emulsify. The average droplet size of TA emulsions (Table 6) was similar to
 301 that of LA emulsions (Table 6), and did not significantly change during one month of storage.

302 Table 6. Average droplet size, syneresis, and sedimentation of TA emulsions as fresh and after one week (1 w) and one
 303 month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

Hemicellulose	Storage time	D[3,2] (μm)	D[4,3] (μm)	D(10) (μm)	D(50) (μm)	D(90) (μm)	Syneresis (%)	Sedimentat ion (%)
BLN HMM GX	Fresh	2.5	10.5	1.0	4.0	30	0	0
	1 w	2.6	10.7	1.0	4.2	30	10	0
	1 m	2.5	9.3	1.0	3.8	25	5	0
PHWE SpDr GX	Fresh	2.4	6.3	1.2	2.9	14.9	0	0
	1 w	2.2	4.2	1.1	2.5	9.6	5	2
	1 m	1.9	2.5	1.1	2.1	4.5	11	5
PHWE SpDr GGM	Fresh	2.3	6.2	1.1	2.8	13.6	0	0
	1 w	2.3	5.1	1.1	2.7	12.0	2	0
	1 m	2.3	5.0	1.1	2.7	11.6	5	10
PHWE EtOH GGM	Fresh	2.4	8.7	1.1	2.9	18.6	0	0
	1 w	2.4	6.1	1.1	2.8	14.1	2	0
	1 m	2.2	4.4	1.1	2.6	9.9	5	0

304

305 Microscopic observation supported the results obtained by droplet size measurement. Typical microscopic
 306 images of emulsions are presented in Figure 3, showing that the droplet size corresponded with the average
 307 droplet diameter measured by static light scattering (Table 5 and 6). Notable changes during one month storage
 308 were not observed by microscopy.



309
310 Figure 3. Microscopy images of typical structures of LA emulsions stabilized with PHWE SpDr GX as A) fresh and B)

311 after one month of storage at RT. The scale bar in A is 5 μm and both images are at the same magnification.

312

313 The viscosity of selected LA emulsions, namely, those stabilized with BLN HMM GX, PHWE SpDr GX,
314 PHWE SpDr GGM and PHWE EtOH GGM, was determined to understand their flow properties and correlate
315 that with the emulsion stability. The LA emulsion with PHWE SpDr GX exhibited the lowest viscosity values,
316 roughly 30 $\text{mPa}\cdot\text{s}$ at 50 l s^{-1} , while the viscosity of other studied samples was between 56 and 85 $\text{mPa}\cdot\text{s}$ (Table
317 7). The difference in viscosity between fresh and stored samples was minor; however, increase in the standard
318 deviation between replicate samples was observed after storage with the PHWE SpDr GX and PHWE EtOH
319 GGM –stabilized emulsions.

320 Table 7. Apparent viscosity ($\text{mPa}\cdot\text{s}$) of the LA emulsions as fresh and after one month storage (1 m) at RT, with shear
321 rate of 50 l s^{-1} . Please refer to Table 1 for the sample codes.

Storage time	BLN HMM GX	PHWE SpDr GX	PHWE SpDr GGM	PHWE EtOH GGM
Fresh	85 ± 10	30 ± 1	67 ± 1	71 ± 8
1 m	84 ± 3	26 ± 24	56 ± 14	62 ± 1

322

323 4 Discussion

324 **4.1 Effect of hemicellulose characteristics on emulsification**

325 Various different wood-derived hemicellulose samples were compared for their capacity to emulsify and
326 stabilize alkyd resins in water, to characterize them in novel, sustainable paint formulations. The studied
327 hemicelluloses were derived from hardwood (GX) or softwood (GGM) and recovered using three different
328 isolation methods, namely, the BLN, PHWE, and TMP processes that all produce water-soluble hemicelluloses
329 with the major part of the native acetyl groups remaining (Table 2). Furthermore, the hemicellulose samples
330 were either used as concentrates or after spray drying, containing all solid compounds originating from the
331 wood extract, or fractionated after precipitation with EtOH. Consequently, the carbohydrate composition,
332 content of phenolic residues and extractives, and molar mass of the hemicellulose samples varied.

333 Evidently, the wood species determined the carbohydrate composition of hemicellulose samples (Figure 1).
334 The isolation and fractionation methods mainly affected the purity of hemicelluloses, which was observed in
335 the total content of carbohydrates, molar mass of recovered hemicelluloses, as well as adversely in the content
336 of phenolic compounds and extractives, especially lignans (Figure 1; Table 2 and Table 3). The BLN method,
337 where the extraction is performed in the absence of oxygen, yielded hemicelluloses with high purity, whereas
338 the TMP and PHWE methods produced hemicelluloses that contained more of phenolic residues and
339 extractives as co-components. The GX and GGM obtained from the hot water extraction of wood chips or saw
340 meal (BLN and PHWE methods) had lower molar mass than the TMP GGMs obtained from the thermo-
341 mechanical process, in which wood pulp is mechanically ground in the presence of hot water. The differences
342 in the hemicellulose purity and molar mass are expected to be due to differences in extraction temperature,
343 wood material particle size (pulp vs. saw meal), availability of oxygen during the isolation process for potential
344 cross-linking reactions between phenolic compounds and carbohydrates, and the time of contact between water
345 and the woody biomass during processing (Willför et al., 2003a; Xu et al., 2007; Kilpeläinen et al., 2014, von
346 Schoultz, 2015). Short extraction time at low temperature is expected to release a low yield of hemicelluloses
347 with high molar mass and a small amount of co-components, and vice versa (Song et al., 2011). In the TMP

348 process, low yield of GGM is accessible for dissolution in hot water without essential chemical changes, i.e.
349 the polysaccharide backbone length and acetyl groups attached with GGM are preserved (Willför et al., 2003a),
350 while major part of high-molar-mass GGM remains with the TMP cellulose fibers. The extraction temperature
351 in PHWE and BLN processes is much higher, which causes hydrolysis of polysaccharides. Small
352 polysaccharides are more easily extractable from wood cell walls than large ones, and therefore the yield of
353 PHWE and BLN extraction is high. The pH of aqueous BLN samples was lower than that of other studied
354 hemicelluloses, but could not be clearly correlated with the other properties or functionality of the extracts.

355 The major part of the co-components (lignans and other extractives) was removed through ethanol precipitation
356 of TMP GGM and the PHWE hemicelluloses. Correspondingly, the ethanol-soluble LMM BLN GX sample
357 was rich in extractives compared to the other BLN GX samples, and contained low molar mass carbohydrates.
358 Thus ethanol precipitation could be used to purify and concentrate the high molar mass fractions of
359 hemicellulose samples. In order to make the process economically feasible, the ethanol should be recycled.

360 Both GX and GGM functioned very well as alkyd resin emulsifiers, as the BLN GX, BLN HMM GX, BLN
361 HMM GGM, both TMP GGMs, and all PHWE hemicelluloses produced and stabilized alkyd emulsions with
362 small average droplet size after straightforward mechanical mixing. Both two tested alkyd resin types could be
363 emulsified with GX and GGM, which illustrates the versatility of the concept. On the other hand, the medium
364 and low molar mass BLN GX fractions and the BLN GGM did not emulsify alkyd resins. In general, the least
365 pure hemicellulose samples yielded emulsions with smallest average droplet size and high stability over
366 storage, with the exception of the BLN LMM GX (Table 5). Of the fractionated BLN GX hemicelluloses, only
367 the HMM functioned as alkyd resin emulsifier, indicating that molar mass of GX played a crucial role in its
368 functionality. However, the PHWE GXs showed capacity to emulsify alkyd resins, even though their molar
369 mass was similar to that of BLN MMM GX (Table 2). Thus the molar mass alone did not define the
370 emulsifying capacity of hemicelluloses. There was also no clear correlation between the DA and emulsion
371 stabilizing capacity of the studied hemicellulose samples.

372 4.2 Key factors affecting alkyd emulsion stability

373 The total content of carbohydrates (Figure 1), phenolic compounds (Table 2), and extractives (Table 3) of the
374 studied hemicelluloses correlated with their capacity of decreasing the surface tension of water (Table 4). The
375 least pure, spray dried GX and GGM samples were the most surface active. This can be attributed to the
376 hydrophobic character of phenolic structures and extractives compared to pure polysaccharides. Some of the
377 phenolic compounds may be bound with hemicelluloses by glycosidic or ester linkages (Lehtonen et al., 2018).
378 Our hypothesis is that the associations of phenolic groups with hemicellulose tails induce an amphiphilic
379 character to the assembly, and that the phenolic structures deliver and anchor hemicelluloses at the O/W
380 interface (Lehtonen et al., 2018). Anchoring at the interface could explain the decrease in surface tension,
381 which could aid in oil droplet breakup and size reduction (Dickinson, 2009). Hemicelluloses anchored at the
382 droplet interface by the phenolic structures could also induce steric stabilization and prevent droplets from
383 colliding (Mikkonen et al., 2016a; Mikkonen et al., 2016b). The LMM BLN GX sample showed that the
384 hemicellulose tail should be of certain size to act at the interface, as emulsification was not successful with the
385 LMM BLN GX, even though it contained more phenolic co-components than the other BLN GX samples. On
386 the other hand, the HMM BLN GX showed high emulsification and stabilization capacity, even though its
387 effect on surface tension of water was minor (Table 4).

388 Viscosity, which is correlated with molar mass, may also contribute to emulsion stability by reducing droplet
389 mobility and probability for collision (Dickinson, 2009). The viscosity of PHWE EtOH GGM continuous
390 phase, at the same concentration as used presently, was studied earlier to be 6.9 mPa·s (Mikkonen et al.,
391 2016a). Due to their relatively low molar mass, wood hemicelluloses increase the viscosity of aqueous systems
392 significantly at only very high concentrations when there is a sufficient amount of molecules present to cause
393 coil overlapping (Xu et al., 2009; Mikkonen et al., 2016a). On the other hand, the studied dispersed phase,
394 namely alkyd resins, are highly viscous, which was apparent during their handling, although it was not
395 determined by rheology due to their sticky character, which makes their handling difficult. Emulsion viscosity

396 is affected by the viscosity of the continuous phase, the volume fraction, droplet size, packing of the dispersed
397 phase (Krieger and Dougherty, 1959), and steric stabilization (De Kruif et al., 1985). Emulsification of alkyd
398 resins using hemicelluloses enabled decreasing the viscosity of the system to almost as low as that of rapeseed
399 O/W emulsions with similar volume fraction (Mikkonen et al., 2016a). Thus, the hemicellulose-based alkyd
400 emulsions fulfilled the requirements for technical emulsions, by facilitating the handling of alkyd resins. The
401 viscosity analysis can also be used to measure the emulsion stability over storage. In the present work, the flow
402 properties of emulsions remained similar during one month storage, indicating high stability (Table 7).

403 **4.3 Prospects of wood hemicelluloses as technical emulsifiers**

404 Non-toxic, biobased and biodegradable natural polymers are a highly attractive option for stabilizing technical
405 emulsions. Furthermore, wood hemicelluloses have the benefits of being economic, as they are currently
406 treated as low-value side products. Advantages of wood hemicelluloses include the fact that their
407 functionalization does not require chemical derivatization, but can be tailored by adjusting the isolation method
408 to produce hemicelluloses with optimized properties. Sustainable aqueous isolation processes can be designed
409 to produce highly pure hemicelluloses for high-value purposes, and less pure fractions, where the phenolic
410 residues introduce interfacial activity and functionality. Hemicelluloses also show capacity to inhibit lipid
411 oxidation in emulsions (Lehtonen et al., 2016; Lehtonen et al., 2018), which may protect alkyd resins from
412 oxidation and polymerization during the paint shelf-life and storage, but the inhibition capacity is not expected
413 to hinder paint drying when applied to surfaces, where the drying emulsion is accessible to oxygen and light.

414 **Conclusions**

415 Environmentally compatible, aqueous alkyd paint formulations were successfully emulsified and stabilized
416 using natural, hemicellulose-rich wood extracts. Alternative wood biorefining strategies can be exploited to
417 produce hemicelluloses with desired purity and functionality for designed end use. The BLN hemicelluloses
418 were of high purity, whereas PHWE and TMP processes resulted in fractions containing more of co-
419 components, namely, phenolic residues and extractives. The crude technical hemicellulose fractions showed

420 interfacial activity and were the most efficient ones in emulsification and stabilization, indicating that pure
421 fractions are not needed for optimized hemicellulose functionality as emulsion stabilizers. The proposed
422 concept is straightforward, exploits the natural characteristics of hemicellulose isolates, and is versatile,
423 functioning with different alkyd resins, including in diluted emulsions. Notable breakdown of the emulsions'
424 physical structure was not observed during one month storage. The function mechanisms of wood-derived
425 hemicelluloses are between those of classical surfactants and macromolecular hydrocolloids. We expect that
426 the emulsion stabilizing properties of wood hemicelluloses can be exploited in numerous value-added
427 industrial processes, and may contribute to shifting of the industries towards circular (bio)economy.

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436 **Competing interests**

437 The authors have no competing interests to declare.

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499

500 Table titles:

501 Table 1. Hemicellulose samples.

502 Table 2. Total content of phenolic compounds and molar mass of hemicelluloses and pH of aqueous
503 hemicellulose solutions. Please refer to Table 1 for the sample codes.

504 Table 3. Extractives in hemicelluloses (mg/g). Please refer to Table 1 for the sample codes.

505 Table 4. Surface tensions of GX- and GGM-water solutions. Please refer to Table 1 for the sample codes.

506 Surface tension of ion exchanged water was 71.1 ± 0.3 mN/m ($T=23$ °C).

507 Table 5. Average droplet size and standard deviation, syneresis, and sedimentation of LA emulsions as fresh
508 and after one week (1 w) and one month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

509 Table 6. Average droplet size, syneresis, and sedimentation of TA emulsions as fresh and after one week (1 w)
510 and one month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

511 Table 7. Apparent viscosity (mPa·s) of the LA emulsions as fresh and after one month storage (1 m) at RT,
512 with shear rate of 50 1 s⁻¹. Please refer to Table 1 for the sample codes.

513

514

515 Figure captions:

516 Figure 1. Carbohydrate composition of A) glucuronoxylan (GX) and B) galactoglucomannan (GGM) samples
517 after subtracting the content of free monosaccharides. Please refer to Table 1 for the sample codes.

518 Figure 2. Droplet size distributions of LA emulsions stabilized with (A) BLN HMM GX, (B) PHWE SpDr GX,
519 (C) PHWE SpDr GGM and (D) PHWE EtOH GGM as fresh and after storage of one month at RT. Please refer
520 to Table 1 for the sample codes.

521 Figure 3. Microscopy images of typical structures of LA emulsions stabilized with PHWE SpDr GX as A)
522 fresh and B) after one month of storage at RT. The scale bar in A is 5 μm and both images are at the same
523 magnification.

Table 1. Hemicellulose samples.

Abbreviation	Production method	Supplier
BLN GX	Concentrated BLN, solids 40%	CH-Bioforce
BLN HMM GX	Ethanol precipitated ^a BLN, high molar mass	CH-Bioforce
BLN MMM GX	Ethanol precipitated ^b BLN, medium molar mass	CH-Bioforce
BLN LMM GX	Ethanol soluble BLN, low molar mass	CH-Bioforce
PHWE SpDr GX	Spray dried pressurized hot water extract	Luke
PHWE EtOH GX	Ethanol precipitated ^c pressurized hot water extract	Luke
BLN GGM	Concentrated BLN, solids 53%	CH-Bioforce
BLN HMM GGM	Ethanol precipitated ^a BLN	CH-Bioforce
PHWE SpDr GGM	Spray dried pressurized hot water extract	Luke
PHWE EtOH GGM	Ethanol precipitated pressurized hot water extract	Luke
TMP SpDr GGM	Spray dried purified thermomechanical pulp process water	Åbo Akademi
TMP EtOH GGM	Ethanol precipitated ^d and freeze dried, purified thermomechanical pulp process water	Åbo Akademi

a) precipitated with water/ethanol at ratio 25/75 v/v.

b) precipitated with water/ethanol at ratio 10/90 v/v

c) precipitated with water/ethanol at ratio 10/80 v/v

d) precipitated with water/ethanol at ratio 10/90 v/v

Table 2. Total content of phenolic compounds and molar mass of hemicelluloses and pH of aqueous hemicellulose solutions. Please refer to Table 1 for the sample codes.

Sample	Total phenolic compounds, mg Gallic acid equivalent / g hemicelluloses	Molar mass, g/mol	Degree of acetylation, mol-%	pH
BLN GX	4.2	4700	51	3.6
BLN HMM GX	4.1	8300	49	3.9
BLN MMM GX	6.1	3000	53	3.7
BLN LMM GX	22.2	1900	63	3.5
PHWE SpDr GX	71.1	4000	55	6.2
PHWE EtOH GX	10.8	4300	58	3.4
BLN GGM	nd	5300	28	2.7
BLN HMM GGM	2.3	10000	30	2.8
PHWE SpDr GGM	48.7	8200	36	5.3
PHWE EtOH GGM	15.8	8200	38	4.9
TMP SpDr GGM	19.4	48 000	35	4.4
TMP EtOH GGM	5.1	27 600	39	4.9

nd = not detected

Table 3. Extractives in hemicelluloses (mg/g). Please refer to Table 1 for the sample codes.

Sample	Dioic acids (C5–C10)	Fatty acids (C14–C22)	Resin acids	Oxidized resin acids	Simple phenolics	Lignans (identified)	Unknown lignans*	Total extractives
BLN GX	nd	0.04	0.03	0.005	0.008	0.03	0.04	0.17
BLN HMM GX	0.005	0.03	0.03	0.008	0.002	0.01	0.06	0.16
BLN MMM GX	0.006	0.04	0.006	nd	0.04	0.02	0.03	0.15
BLN LMM GX	0.08	0.04	0.01	0.009	0.4	0.2	0.3	1.1
PHWE SpDr GX	0.06	0.2	0.01	0.03	2.4	4.2	3.4	10.5
PHWE EtOH GX	0.02	0.03	nd	nd	0.2	0.3	0.2	0.83
BLN GGM	0.004	0.03	0.003	nd	0.005	0.01	0.03	0.11
BLN HMM GGM	nd	0.03	0.03	0.01	nd	0.02	0.04	0.14
PHWE SpDr GGM	0.08	0.05	0.3	0.3	1	1	2	5.1
PHWE EtOH GGM	0.02	0.04	0.04	0.005	0.07	0.07	0.1	0.36
TMP SpDr GGM	0.7	0.09	0.2	1.4	0.7	3.2	2.4	9.1
TMP EtOH GGM	0.1	0.04	0.03	0.1	0.2	0.1	0.1	0.89

*Based on unidentified peaks in the same retention time region as identified lignans.

nd = not detected

Table 4. Surface tensions of GX- and GGM-water solutions. Please refer to Table 1 for the sample codes.

Surface tension of ion exchanged water was 71.1 ± 0.3 mN/m ($T=23$ °C).

Sample	Content (weight %)		
	0.5	1.0	5.0
BLN GX	60.5 ± 0.2	60.2 ± 0.2	56.9 ± 0.4
BLN HMM GX	62.6 ± 0.1	61.9 ± 0.1	60.3 ± 0.2
BLN MMM GX	58.9 ± 0.3	60.6 ± 0.1	57.6 ± 0.1
BLN LMM GX	58.9 ± 0.3	60.6 ± 0.1	57.6 ± 0.1
PHWE SpDr GX	57.3 ± 0.3	53.9 ± 0.4	38.6 ± 0.5
PHWE EtOH GX	59.6 ± 0.3	57.9 ± 0.3	55.0 ± 0.3
BLN GGM	64.6 ± 0.2	63.3 ± 0.2	65.6 ± 0.1
BLN HMM GGM	67.1 ± 0.3	69.3 ± 0.2	64.4 ± 0.3
PHWE SpDr GGM	59.5 ± 0.3	57.6 ± 0.3	49.5 ± 0.3
PHWE EtOH GGM	66.0 ± 0.1	65.1 ± 0.3	59.3 ± 0.4
TMP SpDr GGM	48.4 ± 0.3	46.1 ± 0.2	41.7 ± 0.2
TMP EtOH GGM	63.4 ± 0.2	55.1 ± 0.3	49.1 ± 0.2

Table 5. Average droplet size and standard deviation, syneresis, and sedimentation of LA emulsions as fresh and after one week (1 w) and one month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

Hemicellulose	Storage time	D[3,2] (μm)	D[4,3] (μm)	D(10) (μm)	D(50) (μm)	D(90) (μm)	Syneresis (%)	Sedimentation (%)
BLN GX	Fresh	3.2 \pm 0.1	13.0 \pm 1.9	1.3 \pm 0.0	5.3 \pm 0.2	38 \pm 3	0	0
	1 w	2.9	10.9	1.2	4.3	31	0	0
	1 m	3.0 \pm 0.0	10.7 \pm 1.6	1.3 \pm 0.0	4.6 \pm 0.2	28 \pm 7	5	0
BLN HMM GX	Fresh	2.7 \pm 0.0	8.0 \pm 1.5	1.2 \pm 0.0	3.7 \pm 0.2	18 \pm 3	0	0
	1 w	2.6 \pm 0.1	6.4 \pm 0.3	1.2 \pm 0.0	3.6 \pm 0.4	15 \pm 2	1	0
	1 m	2.8 \pm 0.3	7.7 \pm 2.6	1.2 \pm 0.0	4.0 \pm 0.9	18 \pm 6	2	0
PHWE SpDr GX	Fresh	2.5 \pm 0.4	5.3 \pm 1.7	1.2 \pm 0.1	3.5 \pm 1.0	10.9 \pm 4.3	0	0
	1 w	2.3 \pm 0.3	3.8 \pm 0.7	1.1 \pm 0.1	3.0 \pm 0.6	7.3 \pm 1.5	5	8
	1 m	2.0 \pm 0.3	3.9 \pm 2.1	1.1 \pm 0.1	2.6 \pm 0.5	5.3 \pm 1.2	16	11
PHWE EtOH GX	Fresh	2.6 \pm 0.4	8.9 \pm 4.5	1.2 \pm 0.1	3.6 \pm 1.0	18.0 \pm 6.9	0	0
	1 w	2.5 \pm 0.3	7.0 \pm 3.3	1.2 \pm 0.1	3.4 \pm 0.7	13.2 \pm 2.6	4	0
	1 m	2.2 \pm 0.1	7.0 \pm 4.9	1.1 \pm 0.0	2.7 \pm 0.3	7.6 \pm 0.2	6	0
BLN HMM GGM	Fresh	3.5 \pm 0.4	14 \pm 5	1.4 \pm 0.1	6.2 \pm 1.2	41 \pm 18	0	0
	1 w	3.3	12	1.3	5.7	31	1	0
	1 m	3.3 \pm 0.1	13 \pm 2	1.3 \pm 0.0	5.5 \pm 0.3	29 \pm 3	2	0
PHWE SpDr GGM	Fresh	2.7 \pm 0.7	5.7 \pm 0.7	1.2 \pm 0.0	3.9 \pm 0.4	11.6 \pm 1.5	0	0
	1 w	2.7 \pm 0.8	5.4 \pm 0.8	1.2 \pm 0.0	3.9 \pm 0.5	11.1 \pm 1.6	5	0
	1 m	2.6 \pm 1.2	5.3 \pm 1.2	1.2 \pm 0.1	3.8 \pm 0.6	10.6 \pm 2.4	10	1
PHWE EtOH GGM	Fresh	2.7 \pm 0.3	5.4 \pm 1.1	1.2 \pm 0.1	4.1 \pm 0.8	10.8 \pm 2.0	0	0
	1 w	2.7 \pm 0.3	5.3 \pm 1.0	1.2 \pm 0.1	4.0 \pm 0.8	10.7 \pm 1.9	3	0
	1 m	2.9 \pm 0.1	6.2 \pm 0.8	1.3 \pm 0.1	4.5 \pm 0.2	12.5 \pm 2.4	5	0
TMP SpDr GGM	Fresh	3.1 \pm 0.2	9.3 \pm 1.3	1.3 \pm 0.0	5.1 \pm 0.8	21 \pm 4	0	0
	1 w	3.1 \pm 0.2	8.7 \pm 1.3	1.3 \pm 0.0	5.0 \pm 0.8	20 \pm 3	3	0
	1 m	3.1 \pm 0.3	8.7 \pm 1.9	1.3 \pm 0.0	5.0 \pm 0.9	20 \pm 4.4	8	0
TMP EtOH GGM	Fresh	2.5 \pm 0.1	6.7 \pm 0.6	1.2 \pm 0.1	3.4 \pm 0.1	14.9 \pm 3.5	0	0
	1 w	2.5 \pm 0.0	6.2 \pm 1.8	1.2 \pm 0.1	3.4 \pm 0.0	13.9 \pm 4.7	0	0
	1 m	2.7 \pm 0.2	11.7 \pm 6.2	1.2 \pm 0.1	3.6 \pm 0.3	22.9 \pm 8.7	0	0

Table 6. Average droplet size, syneresis, and sedimentation of TA emulsions as fresh and after one week (1 w) and one month (1 m) storage at RT. Please refer to Table 1 for the sample codes.

Hemicellulose	Storage time	D[3,2] (μm)	D[4,3] (μm)	D(10) (μm)	D(50) (μm)	D(90) (μm)	Syneresis (%)	Sedimentation (%)
BLN HMM GX	Fresh	2.5	10.5	1.0	4.0	30	0	0
	1 w	2.6	10.7	1.0	4.2	30	10	0
	1 m	2.5	9.3	1.0	3.8	25	5	0
PHWE SpDr GX	Fresh	2.4	6.3	1.2	2.9	14.9	0	0
	1 w	2.2	4.2	1.1	2.5	9.6	5	2
	1 m	1.9	2.5	1.1	2.1	4.5	11	5
PHWE SpDr GGM	Fresh	2.3	6.2	1.1	2.8	13.6	0	0
	1 w	2.3	5.1	1.1	2.7	12.0	2	0
	1 m	2.3	5.0	1.1	2.7	11.6	5	10
PHWE EtOH GGM	Fresh	2.4	8.7	1.1	2.9	18.6	0	0
	1 w	2.4	6.1	1.1	2.8	14.1	2	0
	1 m	2.2	4.4	1.1	2.6	9.9	5	0

Table 7. Apparent viscosity (mPa·s) of the LA emulsions as fresh and after one month storage (1 m) at RT, with shear rate of 50 l s^{-1} . Please refer to Table 1 for the sample codes.

Storage time	BLN HMM GX	PHWE SpDr GX	PHWE SpDr GGM	PHWE EtOH GGM
Fresh	85 ± 10	30 ± 1	67 ± 1	71 ± 8
1 m	84 ± 3	26 ± 24	56 ± 14	62 ± 1

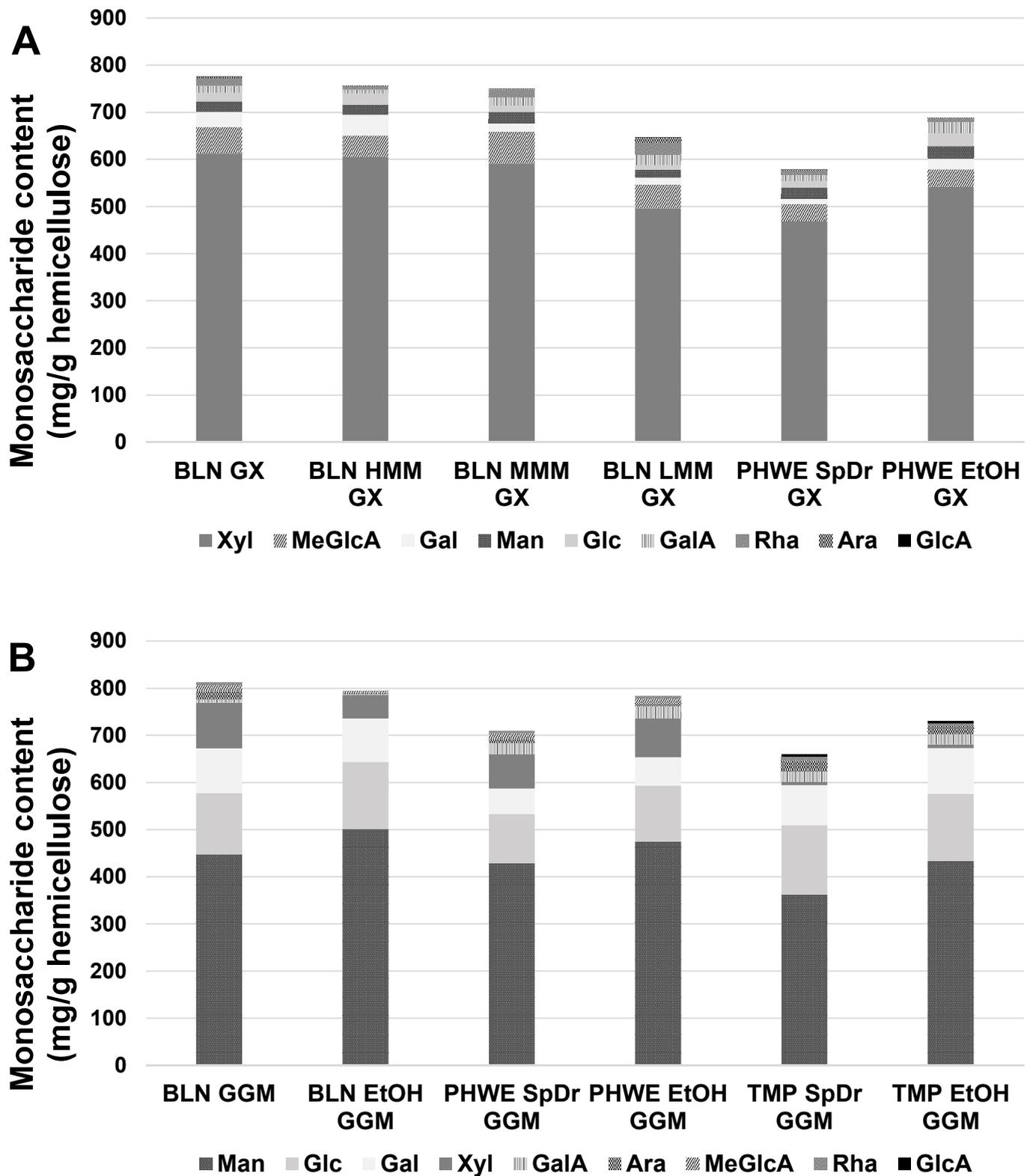


Figure 1. Carbohydrate composition of A) glucuronoxylan (GX) and B) galactoglucomannan (GGM) samples after subtracting the content of free monosaccharides. Please refer to Table 1 for the sample codes.

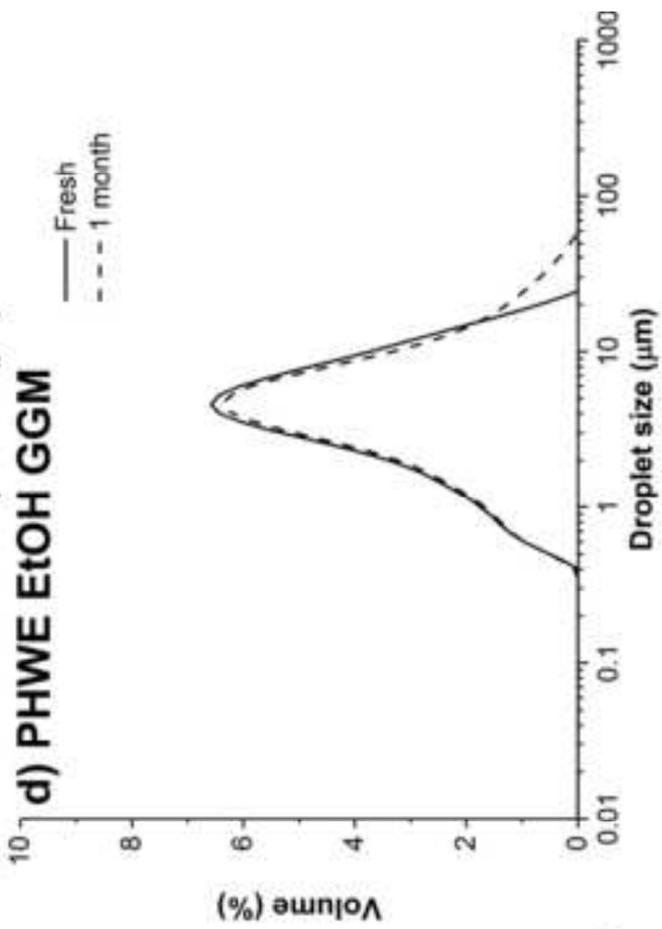
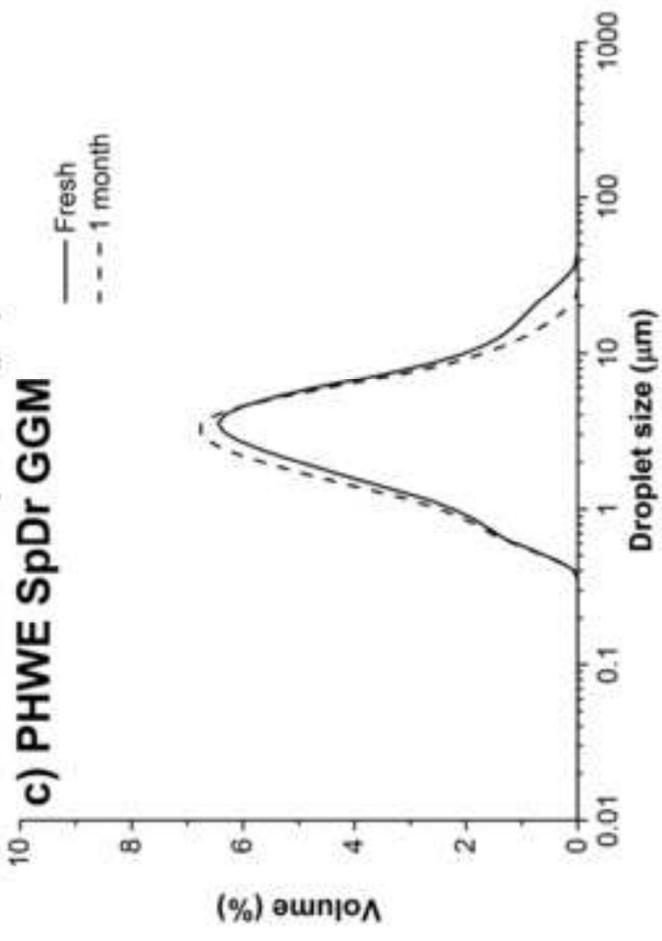
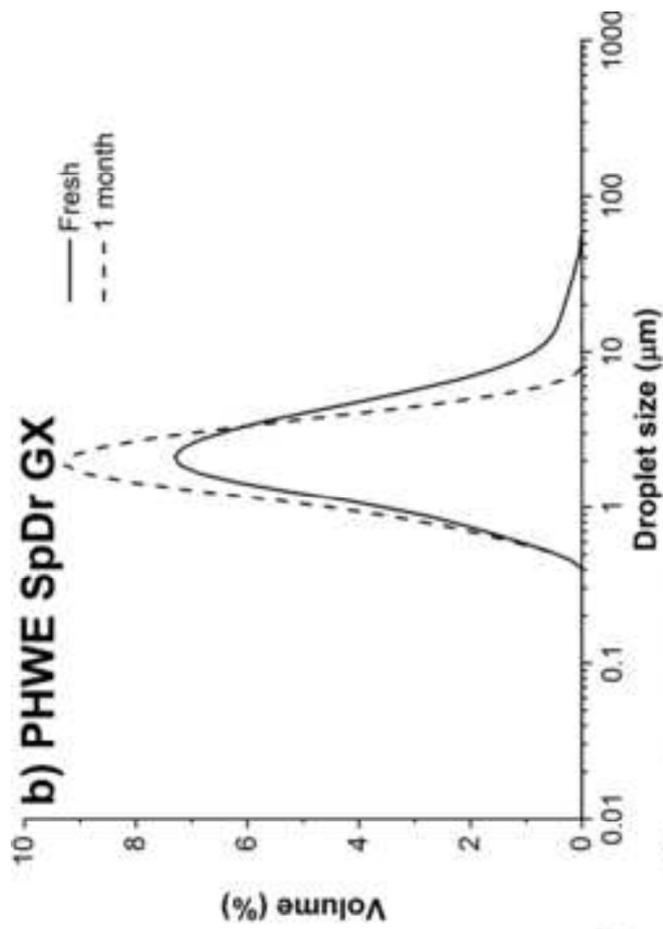
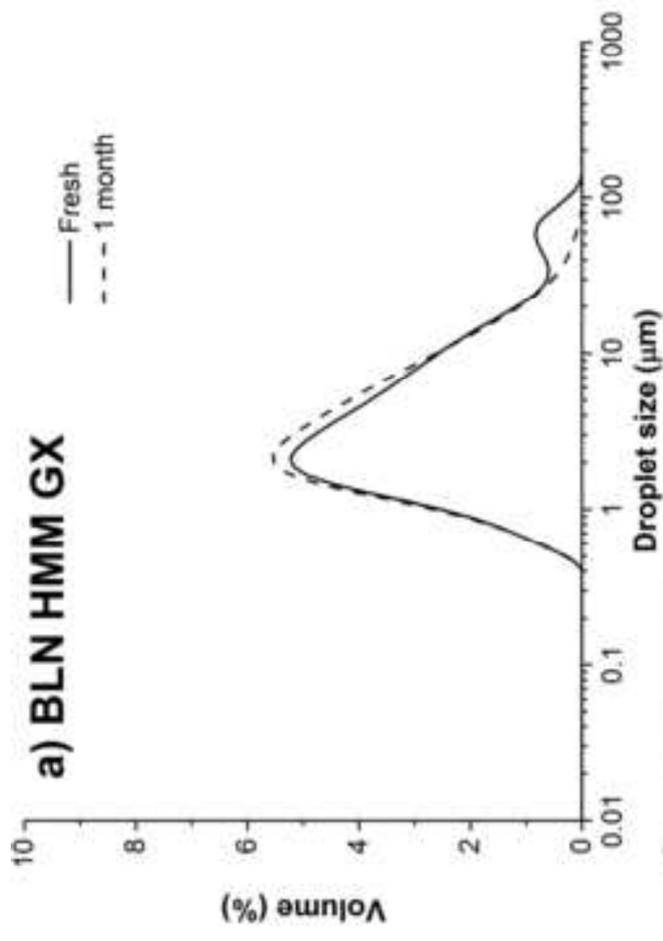


Figure 2

Figure 3

