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Environmentally-compatible alkyd paints stabilized by wood hemicelluloses

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ABSTRACT

Wood biorefining currently involves large-scale industrial processes where a notable portion of raw materials, namely hemicelluloses and lignin, are either lost with the process water, degraded, or burnt for energy. Value-added utilization of polymeric hemicelluloses is challenging due to their intermediate molar mass and the presence of other wood components, such as phenolic residues or wood extractives. Oil-in-water (O/W) emulsions represent a diverse and abundant class of applications in which the natural properties of wood hemicelluloses are beneficial. In the current work, we present highly promising new technical alkyd paint emulsion systems stabilized with hardwood glucuronoxylans (GX) and softwood galactoglucomannans (GGM). Samples from three isolation methods and their further fractionation by ethanol precipitation were systematically compared with regard to hemicellulose composition, interfacial activity, and functionality in emulsions. Emulsification of alkyd resins was successful with both GX and GGM obtained by various biorefining strategies. The highest emulsion stability over storage was achieved using crude non-purified GX and GGM fractions, and was correlated with the presence of phenolic compounds and extractives, interfacial activity, and small droplet size. Hardwood GX and softwood GGM are envisioned as natural emulsifiers of alkyd O/W emulsions, which are examples of diverse and abundantly-used technical dispersions. This study can be utilized as a guideline for targeted extraction of hemicelluloses with desired functionality, and as a protocol for developing environmentally-compatible industrial dispersions.

1. Introduction

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

The predominant hemicelluloses in hardwoods are glucuronoxylans (GX), which comprise almost 25% of the wood mass. GX consist of backbones β-D-xylopyranosyl (Xyl*p*) units, linked by (1→4)-bonds, and (1→2)-linked 4-*O*-methyl-α-D-glucopyranosyl uronic acid (MeGlc*p*A) and *O*-acetyl side groups (Sjöström, 1993). Hardwoods also contain 2–5% glucomannans. Softwoods, on the other hand, are rich in galactoglucomannans (GGM), comprising roughly 20% of the wood mass. GGM have a backbone with alternating β-D(1→4)-glucopyranosyl (Glc*p*) and β-D(1→4)-mannopyranosyl (Man*p*) units, with α-D(1→6)-galactopyranosyl (Gal*p*) units linked to the backbone Man*p* units. The Man*p* units also carry *O*-acetyl groups at the C-2 and C-3 positions. Softwoods also contain 5–10% arabinoglucuronoxylans. The

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polysaccharide-rich GX and GGM extracts also often contain co-components, such as phenolic residues or other wood-derived extractives (Giummarella and Lawoko, 2017). The extraction conditions, such as temperature and time, affect the extract composition and yield: increase of extraction time and temperature increases the release of hemicelluloses, but concomitantly, the content of co-components in the extracts increase (Song et al., 2011; Pranovich et al., 2016). Covalent bonding between the polysaccharide chains and other structures may occur, and researchers argue whether the origin of such bonds are native structures in wood, or if they result from reactions occurring during the extraction process. For exploitation of hemicelluloses in industrial products, understanding of their structure-dependent functionality arising from different isolation methods is crucial. Molar mass and purity of hemicelluloses is expected to determine their interfacial properties and behavior in dispersed systems (Lehtonen et al., 2018).

Aqueous paints are an example of dispersed systems, and they are environmentally advantageous due to the use of water as the continuous phase, instead of organic solvents. Water is also preferred due to health and safety aspects during paint formulation, storage, and use. Alkyd resins are a group of binders that are increasingly exploited in water-borne dispersions due to their good coating-formation ability, in combination with the advantages of solvent-free coatings (Beetsma, 1998). Alkyd resins are polyesters made by condensation polymerization of polyols, polybasic acids, and fatty acids or triglyceride oils. Alkyd resins have low glass transition temperatures (T_g), which makes them viscous and tacky materials that are difficult to handle (Jones, 2016). Emulsification of alkyd resins (Weissenborn and Motiejauskaite, 2000; Watson and Mackley, 2002) facilitates their handling, such as pouring, pumping, and applying on surfaces for coating or paint layer formation. However, the intrinsic nature of emulsions results in thermodynamic instability and tendency for structural breakdown during storage. To stabilize alkyd resin emulsions, the droplet interface is usually covered by compounds that fulfill two basic requirements: they have to be anchored onto the droplet surface and they have to dissolve in the continuous phase, i.e., water (Beetsma, 1998).

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

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

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 dessicator 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.

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.

2.2. Methods

2.2.1. Characterization of hemicelluloses

2.2.1.1. Monosaccharide composition. Sugar analysis was performed to quantify free monomeric sugars and the total carbohydrate composition of the hemicellulose samples. Monosaccharides were determined with a GC-FID on a 25 m × 0.2 mm i.d. column coated with cross-linked methyl polysiloxane (HP-1) after direct silylation of freeze-dried sample. Total carbohydrates in the hemicellulose samples and the isolated fractions were analyzed with a GC after the samples were freeze-dried, subjected to acid methanolysis, and silylated (Sundberg et al., 1996). Minor contents of free monomeric sugars, mainly pentoses, were detected in BLN GGM and GX concentrates as well as in low molar mass BLN GX fraction, PHWE SpDr GX, PHWE EtOH GX, and PHWE SpDr GGM. The carbohydrate composition of hemicelluloses is reported as mg/g of the sample, after subtracting the content of free monosaccharides. The analysis was performed in duplicate.

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

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

2.2.1.4. Degree of acetylation. Acetyl groups in hemicelluloses were released by alkaline treatment in 2.35 mg/mL sodium hydroxide solutions at 70 °C for 20 h. Hydrolyzed acetic acid was analyzed by HPLC (Agilent Technologies 1269, Waldbronn, Germany) with a Synergi Hydro-RP 80R HPLC Column (250 mm x 4.6 mm, 4 µm, Phenomenex, Torrance, CA, USA). The pH of samples was adjusted to 2.6 with 30% ortho-phosphoric acid. The eluent contained 20 mM KH2PO4 in deionized water and pH was adjusted to 2.5 with ortho-phosphoric acid. The eluent was filtered with a 0.1-µm filter (Anodisc 47, Whatman International, Maidstone, UK). The flow rate of eluent was 1.0 mL/min and the injection volume was 20 µl. Degree of acetylation (DA) was calculated as mol-% of backbone carbohydrates (Xyl*p* in GX samples and Man*p* and Glc*p* in GGM samples).

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

2.2.2. Emulsion preparation

O/W emulsions were prepared using 40 wt.-% alkyd resins and 8 wt.-% hemicelluloses, to test the capacity of hemicelluloses to emulsify and stabilize technical dispersions. Alkyd resins were heated up to 62 °C to improve their flowability before the desired amount was weighed. Hemicelluloses were dissolved in reverse osmosis purified water at room temperature (RT) for 2 h using a magnetic stirrer with the lowest possible speed in order to avoid foaming. They were then heated up to 62 °C prior to emulsification. Emulsification was done in water bath at 62 °C, using an Ultra Turrax (T-18 basic, IKA, Staufen, Germany) equipped with an emulsification mixing blade (diameter 25 mm), at mixing speed of 11,000–13,000 rpm for 15 min. Emulsification experiments of all studied hemicellulose samples with LA were made as duplicates. Furthermore, the most interesting hemicellulose samples: PHWE SpDr GGM, PHWE EtOH GGM, PHWE SpDr GX, and BLN EtOH HMM GX, were selected for emulsion testing with TA.

2.2.3. Emulsion characterization

2.2.3.1. Droplet size distribution. Droplet size distribution of emulsions was measured directly after preparation and after one week and one month of storage to evaluate emulsion stability. The droplet size distribution was characterized by static light scattering using a Mastersizer Hydro 3000 SM (Malvern Instruments Ltd, Worcestershire, UK) using refractive index of 1.59, absorption index of 0.1 and density value of 1 g/cm^3. Due to high viscosity and turbidity of the emulsion samples, they were diluted in deionized water for the analysis. Furthermore, selected emulsions were diluted ten-fold, stored, and characterized for droplet size distribution. Droplet size distribution was reported as an average of three replicate measurements.

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

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

3. Results

3.1. Composition of hemicellulose isolates

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

The main carbohydrates comprising the isolated GX samples were Xyl*p* units, which accounted for about 80% of the carbohydrates. Secondly, the MeGlc*p*A content of different GX samples varied between 5 and 9%, and other carbohydrates were present at minor quantities (Fig. 1A). The GGM samples were mainly composed of Man*p*, Glc*p*, and Gal*p* units, with some Xyl*p* units, especially in the PHWE GGM and BLN GGM samples (Fig. 1B). The characterized carbohydrates summed up to about 600–800 mg/g of the samples, the BLN GGM concentrate showing the highest content of carbohydrates. In general, the carbohydrate content of EtOH precipitated hemicelluloses was higher than that of SpDr hemicelluloses, as expected (Fig. 1).

Compared to the total content of carbohydrates, the content of

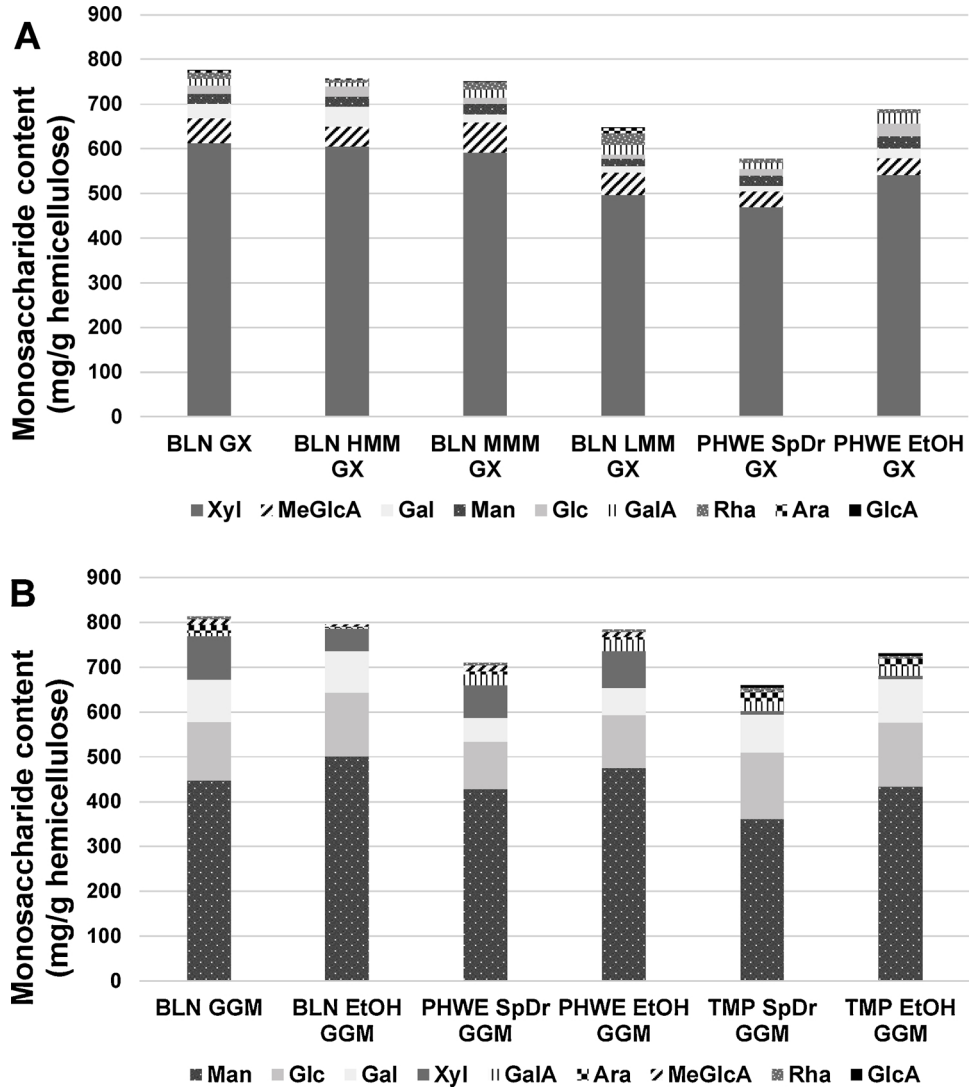

Fig. 1. Carbohydrate composition of A) glucuronoxylan (GX) and B) galactoglucomannan (GGM) samples after subtracting the content of free monosaccharides. Please refer to Table 1 for the sample codes.

phenolic compounds and extractives in the hemicellulose samples followed an opposite trend. The results showed relatively large amounts of phenolic compounds from the Folin-Ciocalteau assay (Table 2) and GC analysis identified extractives (Table 3) in all three SpDr hemicelluloses. Notably, these hemicelluloses also contained some relatively high molar mass co-components that are hypothesized as oligolignols or oligolignans. The "monomeric" components that dominated among the extractives were lignin fragments (phenolics), lignans, and (oxidized) resin acids.

The TMP GGM samples had the highest molar mass of the studied hemicelluloses (Table 2). The molar mass of the other hemicelluloses decreased in the following order: BLN HMM GGM, PHWE GGM samples

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[a]	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

[nd] = not detected.
[a] Based on unidentified peaks in the same retention time region as identified lignans.

and BLM GX HMM, followed by the PHWE GX samples and the other BLN GGM and BLN GX samples. As expected, the BLN GX LMM exhibited the lowest molar mass.

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

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

3.2. Emulsion formation and stability

Alkyd resins and the aqueous hemicellulose solutions were mixed directly through a straightforward one-step process to prepare finely dispersed alkyd resin droplets in water. Emulsification was successful with all TMP and PHWE hemicelluloses and with the BLN GX, BLN HMM GX, and BLN HMM GGM. The BLN GGM, BLN LMM GX, and BLN MMM GX did not form emulsions, as the alkyd resins and hemicellulose solutions separated into liquid and semi-solid phases during mixing.

The surface average droplet size D[3,2] of all LA emulsions was about 3 µm (Table 5). Because the D[3,2] value considers the ratio of surface area to the volume of droplets, it emphasizes the numerous small droplets present in the emulsions. Larger differences between the studied emulsion types were detected in the volume average droplet size D[4,3] values, which varied between 5–14 µm. The D[4,3] is more sensitive to the presence of few large droplets in emulsions, and thus the values were higher than the D[3,2] values. Correspondingly, the D (10) values (meaning that 10% of lipid droplets were smaller than the D (10)), were similar (˜1 µm) for all emulsions. The D(50) (median size) varied between 2.7 and 5.1 µm. Largest differences were observed in the D(90) values of emulsions (meaning that 90% of lipid droplets were smaller than the D(90)). The most promising emulsions, namely, those stabilized by PHWE SpDr GGM, PHWE EtOH GGM, and PHWE SpDr GX, showed D(90) values of about 10 µm. The BLN HMM GX –stabilized emulsions also showed D(90) values lower than 20 µm. The average droplet size of all emulsions was generally maintained at the initial level throughout the one-month storage time. Furthermore, ten-fold dilution of emulsions did not change the droplet size during storage (data not shown). Syneresis of 2–16 % of the emulsion volume (i.e., separation of an aqueous layer on top of emulsions) was monitored in some samples during storage (Table 5). In emulsions stabilized with the PHWE SpDr GX, sedimentation was also observed, which could be due to LA droplets and/ or non-dissolved GX (Table 5).

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

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

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

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

The viscosity of selected LA emulsions, namely, those stabilized with BLN HMM GX, PHWE SpDr GX, PHWE SpDr GGM and PHWE EtOH GGM, was determined to understand their flow properties and

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 ± 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 GGM	Fresh	2.5 ± 0.1	6.7 ± 0.6	1.2 ± 0.1	3.4 ± 0.1	14.9 ± 3.5	0	0
	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

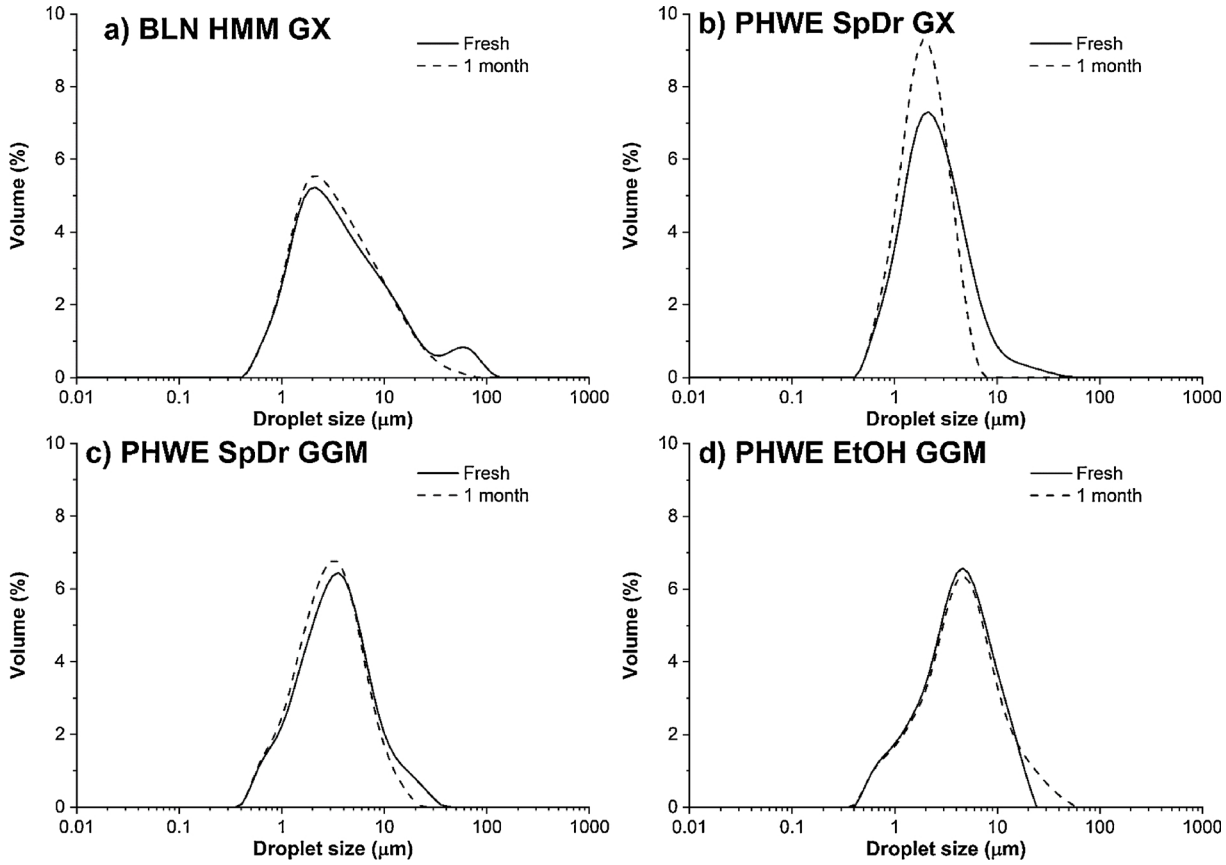

Fig. 2. Droplet size distributions of LA emulsions stabilized with (A) BLN HMM GX, (B) PHWE SpDr GX, (C) PHWE SpDr GGM and (D) PHWE EtOH GGM as fresh and after storage of one month at RT. Please refer to Table 1 for the sample codes.

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

correlate that with the emulsion stability. The LA emulsion with PHWE SpDr GX exhibited the lowest viscosity values, roughly 30 mPa·s at 50 1 s^{-1}, while the viscosity of other studied samples was between 56 and 85 mPa·s (Table 7). The difference in viscosity between fresh and stored samples was minor; however, increase in the standard deviation between replicate samples was observed after storage with the PHWE SpDr GX and PHWE EtOH GGM –stabilized emulsions.

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 1 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

4. Discussion

4.1. Effect of hemicellulose characteristics on emulsification

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

Evidently, the wood species determined the carbohydrate composition of hemicellulose samples (Fig. 1). The isolation and fractionation methods mainly affected the purity of hemicelluloses, which was observed in the total content of carbohydrates, molar mass of recovered hemicelluloses, as well as adversely in the content of phenolic compounds and extractives, especially lignans (Fig. 1; Tables 2 and 3). The BLN method, where the extraction is performed in the absence of oxygen, yielded hemicelluloses with high purity, whereas the TMP and PHWE methods produced hemicelluloses that contained more of phenolic residues and extractives as co-components. The GX and GGM obtained from the hot water extraction of wood chips or saw meal (BLN and PHWE methods) had lower molar mass than the TMP GGMs obtained from the thermo-mechanical process, in which wood pulp is mechanically ground in the presence of hot water. The differences in the hemicellulose purity and molar mass are expected to be due to differences in extraction temperature, wood material particle size (pulp vs. saw meal), availability of oxygen during the isolation process for potential cross-linking reactions between phenolic compounds and carbohydrates, and the time of contact between water and the woody biomass during processing (Willför et al., 2003a; Xu et al., 2007: Kilpeläinen et al., 2014; Von Schoultz, 2015). Short extraction time at low temperature is expected to release a low yield of hemicelluloses with high molar mass and a small amount of co-components, and vice versa (Song et al., 2011). In the TMP process, low yield of GGM is accessible for dissolution in hot water without essential chemical changes, i.e. the polysaccharide backbone length and acetyl groups attached with GGM are preserved (Willför et al., 2003a), while major part of high-molar-mass GGM remains with the TMP cellulose fibers. The extraction temperature in PHWE and BLN processes is much higher, which causes hydrolysis of polysaccharides. Small polysaccharides are more easily extractable from wood cell walls than large ones, and

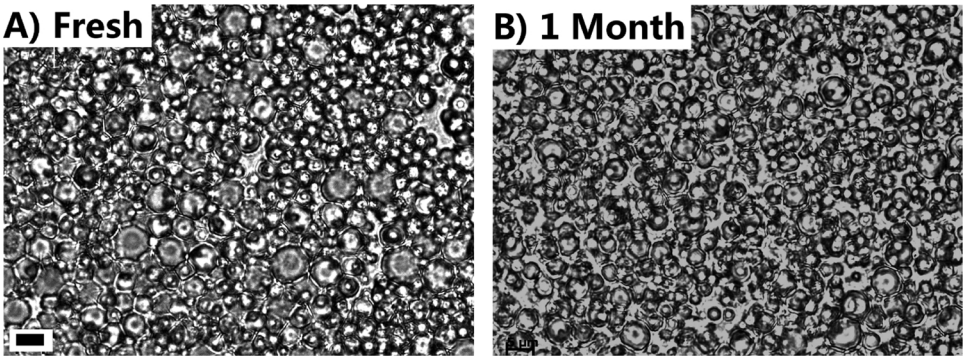

Fig. 3. Microscopy images of typical structures of LA emulsions stabilized with PHWE SpDr GX as A) fresh and B) after one month of storage at RT. The scale bar in A is 5 μm and both images are at the same magnification.

therefore the yield of PHWE and BLN extraction is high. The pH of aqueous BLN samples was lower than that of other studied hemicelluloses, but could not be clearly correlated with the other properties or functionality of the extracts.

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

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

4.2. Key factors affecting alkyd emulsion stability

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

Viscosity, which is correlated with molar mass, may also contribute to emulsion stability by reducing droplet mobility and probability for collision (Dickinson, 2009). The viscosity of PHWE EtOH GGM continuous phase, at the same concentration as used presently, was studied earlier to be 6.9 mPa·s (Mikkonen et al., 2016a). Due to their relatively low molar mass, wood hemicelluloses increase the viscosity of aqueous systems significantly at only very high concentrations when there is a sufficient amount of molecules present to cause coil overlapping (Xu et al., 2009; Mikkonen et al., 2016a). On the other hand, the studied dispersed phase, namely alkyd resins, are highly viscous, which was apparent during their handling, although it was not determined by rheology due to their sticky character, which makes their handling difficult. Emulsion viscosity is affected by the viscosity of the continuous phase, the volume fraction, droplet size, packing of the dispersed phase (Krieger and Dougherty, 1959), and steric stabilization (De Kruif et al., 1985). Emulsification of alkyd resins using hemicelluloses enabled decreasing the viscosity of the system to almost as low as that of rapeseed O/W emulsions with similar volume fraction (Mikkonen et al., 2016a). Thus, the hemicellulose-based alkyd emulsions fulfilled the requirements for technical emulsions, by facilitating the handling of alkyd resins. The viscosity analysis can also be used to measure the emulsion stability over storage. In the present work, the flow properties of emulsions remained similar during one month storage, indicating high stability (Table 7).

4.3. Prospects of wood hemicelluloses as technical emulsifiers

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

5. Conclusions

Environmentally compatible, aqueous alkyd paint formulations were successfully emulsified and stabilized using natural, hemicellulose-rich wood extracts. Alternative wood biorefining strategies can be exploited to produce hemicelluloses with desired purity and functionality for designed end use. The BLN hemicelluloses were of high purity, whereas PHWE and TMP processes resulted in fractions containing more of co-components, namely, phenolic residues and extractives. The crude technical hemicellulose fractions showed interfacial activity and were the most efficient ones in emulsification and stabilization, indicating that pure fractions are not needed for optimized hemicellulose functionality as emulsion stabilizers. The proposed concept is straightforward, exploits the natural characteristics of hemicellulose isolates, and is versatile, functioning with different alkyd resins, including in diluted emulsions. Notable breakdown of the emulsions' physical structure was not observed during one month storage. The function mechanisms of wood-derived hemicelluloses are between those of classical surfactants and macromolecular hydrocolloids. We expect that the emulsion stabilizing properties of wood hemicelluloses can be exploited in numerous value-added industrial processes, and may contribute to shifting of the industries towards circular (bio)economy.

Competing interests

The authors have no competing interests to declare.

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