Flame retarded composite panels from sugar beet residues

Ivan Šimkovic

Abstract Sugar beet residues and various additives were used to prepare panels by forming the semi-dry or wet mixtures and pressing the composites at a temperature of 150 °C and pressures of 100–5410 kPa for up to 105 min. The highest panel density and second highest thickness were observed when a combination of calcium hydroxide and boric acid were used as additives using the semi-dry procedure. SEM images revealed that at pressures over 1000 kPa the cell wall structure of sugar beet was completely unrecognizable. The FTIR results indicated that the non-cellulosic polysaccharides contributed significantly to the properties of the panels by acting as adhesives. The best flame retardant parameters were also obtained with the calcium hydroxide/boric acid formulation. In comparison to composites prepared from recycled paper and mixtures of sugar beet shreds with recycled paper, higher density panels were prepared at lower pressure from sugar beet sources.

Keywords Sugar beet shreds · Recycled paper fiber · Composite · SEM · FTIR · Flammability · Cone calorimeter

Abbreviations

AEHC	Average effective heat of combustion
AHRR60	Heat release rate averaged over 60 s after sustained ignition
AMLR	Average mass loss rate
ASEA	Average specific extinction area
B	Sample made with H_3BO_3
BCa	Sample modified with H_3BO_3 and subsequently with $Ca(OH)_2$
Ca	Sample made with $Ca(OH)_2$
CaB	Sample modified with $Ca(OH)_2$ and subsequently with H_3BO_3
CaP	Sample made with $Ca(OH)_2/H_2O_2$
FR	Fire retardant
FTIR	Fourier Transform Infrared Spectrometry
HRR	Heat release rate
MS	Sample made with $MgSO_4$
MSP	Sample made with $MgSO_4/H_2O_2$
MSSiP	Sample made with $MgSO_4/Na_2SiO_3/H_2O_2$
P	Sample made with H_2O_2
PHRR	Peak heat release rate
PoISP	Total smoke production for period after sample ignition
PrISP	Total smoke production for the period prior to sample ignition
PSiMS	Sample made with $H_2O_2/Na_2SiO_3/MgSO_4$
RH	Relative humidity
RHR	Rate of heat release
RM	Residual mass as percentage of original mass
RP	Sample made with recycled paper
RS	Sample made with sugar beet shreds refined to dimensions less than either 0.254 or 1.27 mm
SBS	Sample made with non-refined sugar beet shreds
SC	Sample made with Na_2CO_3
SCP	Sample made with Na_2CO_3/H_2O_2
SEM	Scanning Electron Microscope
Si	Sample made with Na_2SiO_3
SiP	Sample made with Na_2SiO_3/H_2O_2
SML	Sample mass loss
THR	Total heat released on a per mass basis
TPHRR	Time to PHRR

I. Šimkovic (✉)
Institute of Chemistry, Slovak Academy of Sciences,
Dúbravská cesta 9, 845 38 Bratislava, Slovak Republic
e-mail: chemsimk@savba.sk

TPSEA   Time for peak SEA
TSI   Time to sustained ignition

Introduction

Sugar beets are the sixth most abundantly planted crop on the earth [1]. One by-product of commercial sugar production from the sliced sugar beets is the pulp residue remaining after pressing out the sucrose solution. While dried beet pulp is widely used as animal feed for all types of livestock, large amounts of this agricultural residue remains unused. Besides cellulose and arabinogalactan (a predominant component of sugar beet hemicelluloses), beet pulp residue also contains pectin and lignin [2, 3]. Since a large portion of its hemicelluloses are water soluble, thermal treatment along with high pressure could render it as a self-bonding composite panel [4]. In the present article, we demonstrate this potential by semi-dry and wet-forming sugar beet mixtures to obtain flat sheets, pressing the mixture with a hot-press, modifying fiber-to-water ratios, and adding various additives to obtain desired performance characteristics. The goal was to examine the potential use of these residues for preparing composite panels comparable with fiberboard/hardboard panels and suitable for applications in building construction or packaging. The advantage of this approach for producing composite panels is that no synthetic polymer adhesives are used since the non-cellulose polysaccharide components are acting as an "environmentally sustainable" adhesives. Evaluations included Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectrometry (FTIR), and cone calorimeter tests. The results in this study are compared with similar approaches described in the literature [5–13].

In previous research it was demonstrated that eluents from sugar beet residues could affect the flame retardant properties of impregnated paper sheets [14]. Silva et al. [15] extracted lignin from sugar cane bagasse and examined the characteristics of blends of the lignin with poly(vinyl acetate). In flame retardation studies of wood materials [16, 17], cotton [18], and other materials [19, 20], a cone calorimeter [21] was used to measure the heat release rate (RHR) due to combustion and other parameters related to the flammability of materials including times for ignition [19] and visible smoke [18].

Experimental

Materials

Bags of the sugar beet shreds (SBS) (Midwest-Agri Communities, San Rafael, CA, USA, www.mwagri.com) were

Fig. 1 Image of the refining machine

purchased from a retail farm feed store in Oregon, WI. The shreds from the bags were used either as is without further treatment, by refining to dimensions smaller than 1.27 mm for the samples made from mixture of refined SBS and recycled paper (RS:RP) or sole RP, or by refining to dimensions smaller than 0.254 mm for refined sugar beet shreds (RS) samples. The refining machine consisted of two disks co-rotating in preset distance (Fig. 1). Prior to refining the fiber was mixed with excess of water to achieve reproducible homogenization by passing the mixture through the rotating disks chamber. After the process the excess of water was pressed out. On the basis of known amount of material used and the weight of the product after pressing the water content was estimated to be 90%. All the chemicals were from commercial sources and were used without further purification.

Recycled paper fibers (RP) were obtained from hydropulped recycled corrugated boxes. The boxes were obtained from a local (Negus Container, Madison, WI, USA) packaging company's scrap material. Following hydropulping, the material was dewatered and placed in cold storage until used to make panels. The moisture content of the cold-stored recycled pulp material was approximately 75%.

Preparation of composite panels

In the preparation of the panels, the SBS were processed by a semi-dry method and the RS were processed by a wet method in triplicate. In the semi-dry method, the dry SBS (300 g) were mixed with water (300 ml) and homogenized for 1 h by mixing in zip-locked plastic bags. For panels with chemical additives, the chemicals were mixed with the water in quantitative based on dry weight (Table 1). For SBS samples with combined additives they were added in the order listed in Table 1. The water amount was divided to equal parts according to the number of additives. Sample panels were formed as circular sheets (240 mm in diameter). The material was placed between four copper screens

Table 1 Uptake of chemicals in samples treated with additives

Abbreviation	Additive	Uptake of additive % of original mass
SBS	None	0
SBS-B	H_3BO_3	1
SBS-Ca	$Ca(OH)_2$	1
SBS-BCa	$H_3BO_3/Ca(OH)_2$	1
SBS-CaB	$Ca(OH)_2/H_3BO_3$	1
SBS-PSiMS	$H_2O_2/Na_2SiO_3/MgSO_4$	1
RS	None	0
RS-B	H_3BO_3	10
RS-Ca	$Ca(OH)_2$	10
RS-CaB	$Ca(OH)_2/H_3BO_3$	10
RS-Si	Na_2SiO_3	10
RS-SC	Na_2CO_3	10
RS-P	H_2O_2	10
RS-SiP	Na_2SiO_3/H_2O_2	10
RS-CaP	$Ca(OH)_2/H_2O_2$	10
RS-SCP	Na_2CO_3/H_2O_2	10
RS-MS	$MgSO_4$	10
RS-MSP	$MgSO_4/H_2O_2$	20
RS-MSSiP	$MgSO_4/Na_2SiO_3/H_2O_2$	30
RP	None	0
RS:RP	None	0

SBS Non-refined sugar beet shreds, *RS* sugar beet shreds refined to dimensions either smaller than 0.254 mm or 1.27 mm; *RP* recycled paper

and two aluminum plates (310 × 310 mm) and put into a Fred Carver Laboratory Press (Subdivision of Sterling Inc., Menomonee Falls, WI, USA) set at 150 °C. Panels were hot-pressed with board pressures ranging from 100 to 5410 kPa (Tables 1, 2). After completion of the pressing process, the circular panel sheets were separated from the screens and cut to the 100 × 100 mm samples for cone calorimeter testing. In this way multiple sample specimen were available for testing.

In the wet method, the SBS (1 kg; particle size <1.27 mm; 90% water content), no refined recycled paper (RP; 1 kg; 75% water content), mixture of SBS/RP (0.5 kg SBS; particle size <0.254 mm and 0.4 kg of no refined RP; 25% water content) was wet-formed into 205 mm diameter sheets and hot-pressed at 150 °C under pressure conditions listed in Table 2. The chemicals were added in a same way as for semi-dry method (Table 1). After the pressing process, the panels were cut as previously described for the semi-dry method samples.

Instrumentation

SEM images of the samples were taken on 1 × 1 mm samples that were mounted on aluminum sample holders using silver paste. Samples were sputter-coated with gold using a Denton Desk-1 sputter coater (Cherry Hill, NJ) and examined and photographed with LEO EVO 40 SEM (Carl Zeiss SMT, Inc., Thornwood, NY) at 10 kV. All of the pressed samples were cleaved in-plane to expose the internally bonded surface for imaging. The boards were also fractured in the transverse direction so that the cross-section could be imaged. However, in some cases the transversely fractured surfaces were too rough with many loose fibers; therefore, the cross-section surfaces of the panels were cut using a razor blade and subsequently imaged.

FTIR spectra were obtained using a Nicolet iN10 FTIR spectrometer with OMNIC Specta software (Thermo Scientific, Verona, WI). The spectra were acquired using a single bounce ATR accessory with a diamond crystal. A total of 64 scans were obtained with a resolution of 4 cm^{-1}. The resulting spectra were corrected for baseline drift and the peak heights were recorded using (Thermo Scientific).

A cone calorimeter (Combustion Analysis System (AutoCal), Model No.: Cone 2A Atlas Electric Devices Company of Chicago, IL) was used to test the samples in accordance with ASTM International Standard method E 1354 [22]. Before testing, samples were conditioned to the equilibrium moisture content at 50% R.H. and 23 °C. Samples were tested in the horizontal orientation using a 25 mm distance from the heat source and data acquisition was 1 Hz. The optional standard retainer frame was used without any grid. The samples were tested using a 50 kW/m^2 heat flux. The 57 mm orifice plate was used and the exhaust flow was 0.024 m^3/s.

The following data were recorded as specified in ASTM standard E1354-09 [22] or the corresponding ISO 5660-1 and ISO 5660-2 standards [23, 24]. The data reported in this article include the following measurements: *HRR* (the heat evolved from the sample due to combustion, expressed per unit of exposed sample area, per unit of time, kW/m^2) including the initial *peak heat release rate* (PHRR, kW/m^2), *time to PHRR* (TPHRR, s); *heat release rate averaged over 60 s after sustained ignition* (AHRR60, kW/m^2), and the *total heat released* (THR, total heat evolved per sample mass over the entire test period calculated by integrating the curve of HRR versus time and dividing by the initial sample mass, MJ/kg). THR is normally expressed in terms of the surface area (MJ/m^2). Due to variations in thickness and initial mass of the samples, results in this article are expressed in terms of initial sample mass; *average effective heat of combustion* (AEHC, the measured THR divided by the mass loss for the test duration, MJ/kg); *average mass-loss rate* (AMLR, mass lost per time averaged for the period of 10–90% mass loss, g/s-m^2), and *residual mass* (RM, residual mass as percentage of the initial mass, %);

Table 2 Pressure conditions used for preparation of composite panels

Sample	SW[a]/g	WC[b]/%	Applied pressure/kPa at various times/min								Density/kg m^{-3}	Thickness/mm
			Initial	15	30	45	60	75	90	105		
SBS	300	9	840	1130	265	1930	1755[c]	–	–	–	1000	6.15
SBS-B	300	9	770	250	2220	2100	2290[c]	–	–	–	866	4.91
SBS-Ca	300	9	915	1060	1785	695[c]	–	–	–	–	1015	5.64
SBS-BCa	300	9	250	870	1120	230	160[a]	–	–	–	877	5.17
SBS-CaB	300	9	115	595	785	335	220[c]	–	–	–	1058	7.17
SBS-SiMS	300	9	175	800	450	190	115[c]	–	–	–	967	8.29
RS	1000	90	215	215	160	840	770[c]	–	–	–	773	2.12
RS	1500	90	130	115	160	190	365	870	770[c]	–	887	2.37
RS	2000	90	130	145	160	160	200	220	275	465[c]	1015	3.53
RS-B	1000	90	115	160	175	365	725	985	1130[c]	–	779	2.65
RS-Ca	1000	90	100	130	145	160	175	1320	840[c]	–	911	3.97
RS-CaB	1000	90	115	100	115	160	189	495	840[c]	–	927	4.19
RS-Si	1000	90	115	115	115	160	290	945	680[c]	–	897	2.59
RS-SC	1000	90	115	145	145	220	770	1262	1030[c]	–	872	2.32
RS-P	1000	90	115	160	175	175	479	986	825[c]	–	835	2.69
RS-SiP	1000	90	100	100	100	115	100	145	435	595[c]	759	3.21
RS-CaP	1000	90	100	116	130	245	680	800[c]	–	–	937	2.83
RSS-CP	1000	90	100	125	115	115	145	320	885[c]	–	903	2.79
RS-MS	1000	90	100	130	160	580	610	1000[c]	–	–	937	2.83
RS-MSP	1000	90	100	100	100	130	160	510[c]	–	–	984	3.14
RS-MSSiP	1000	90	100	100	100	100	145	335	725[c]	–	876	3.04
RP	1000	90	335	3235	1000	5410	3450[c]	–	–	–	996	6.03
RS:RP	1000	90	5410	4300	3200	1740	1640[c]	–	–	–	1022	4.50

See Table 1 for abbreviations

[a] Initial sample weight

[b] Water content

[c] Pressure at the end of the process

average specific extinction area (ASEA; a measure of smoke obscuration averaged over the entire test period, m^2/kg), and total smoke production (PrISP, for the period before sample ignition and PoISP, for period after sample ignition, m^2/m^2); and time for sustained ignition [TSI, determined visually and taken as the period required for most of the surface of the sample to have sustained (4 s criteria) flames, s]. For many of the results, the measurements are expressed per surface area of the opening of the sample holder (0.008836 m^2).

Results and discussion

Sample preparation

Samples made from the non-refined SBS were thicker and had slightly higher density than the respective samples made from the refined materials (Table 2). The non-refined SBS sample with the additive consisting of H_2O_2/Na_2SiO_3/

$MgSO_4$ was the thickest sample at 8.29 mm. The thickness of the pressed panel sheets of refined samples without additives increased from 2.12 to 3.53 mm when doubling the amount of the starting material (i.e., from 1 to 2 kg). This increasing amount of starting material also required an increased pressure and prolonged pressing time (Table 2). The thicknesses of refined samples (2.12–4.19 mm) were less than the non-refined SBS samples (4.81–8.29 mm) with the exception of recycled paper and refined sugar beet: recycled paper samples with thickness of 6.03 and 4.50 mm and densities of 996 and 1022 kg/m^3. The recycled paper material contains long softwood fibers that might act to enhance the network strength of the formed mat. For the refined samples, the optimal pressure cycle to reduce flow required lower pressures for longer times, while panels from non-refined SBS material were made using slightly higher pressures for shorter time periods.

The sugar beet sample containing $Ca(OH)_2$/H_3BO_3 displayed the best properties with regards to the combination of time, pressure, density, and thickness. For this sample,

only 1% of combined additives were used in contrast to the refined samples where, in the presence of 10–30% of additives, lower pressures for longer time periods were used to prevent degradation due to the much higher amount of additive (Table 1). The sugar beet sample containing $Ca(OH)_2$ was pressed at higher pressure and for a shorter time than sample containing $Ca(OH)_2/H_3BO_3$ and had the second highest density. This might be due to the fact that $Ca(OH)_2$ was not solubilized and not washed out from the sample. In the samples containing $Ca(OH)_2/H_3BO_3$ and $H_3BO_3/Ca(OH)_2$, $Ca(OH)_2$ was neutralized with boric acid to form $Ca_3(BO_3)_2$. When boric acid was added before calcium hydroxide (SBS-BCa), some of the hemicelluloses may have been solubilized, resulting in lower density of the resulting panel than for SBS-CaB. The obtained densities for all the samples were higher than those reported on maize husk, maize cob, groundnut shell, coconut pith, or paddy straw under comparable pressing conditions and bigger particle size [5]. These higher densities might be related to the type of hemicellulose present in individual species and their behavior during pressing as well as the fiber thermal softening that occurs in the presence of water and high temperature. In the majority of the experiments from this study the applied pressure was lower than that of fiberboards made from tree-top residues with comparable product densities [8].

FTIR study

According to FTIR results, the spectra of dark and light spots on the prepared composite surfaces were similar with intensities of bands at: 668 [–OH out of plane bending]; 1020 [v (CC)(CO) stretching and –C–OH banding]; 1050 [v (CC)(CO) stretching]; 1096 [v (CO) + δ (OH)]; 1140 [v (C–O–C) glycosidic bond]; 1236 [v (COC) ester]; 1318 [–C–H banding and wagging and OH banding]; 1371 [–C–H banding]; 1428 [–COO$^-$ symmetric stretching]; 1615 [–COO$^-$ anti-symmetric stretching (salt)]; 1733 [C=O stretch in carbonyl and ester groups, acid]; 2900–2938 [–CH stretching, CH_2 anti-symmetric stretching of methyl and methylene groups]; 3272–3344 cm^{-1} [–OH stretching] fluctuating from sample to sample.

On the recycled paper sample new bands at 897 [γ (C–OH) ring], 1200 [C–O–C stretching mode of the pyranose ring], and 1260–1280 cm^{-1}, which are typical for cellulose and related to the degree of crystallinity were observed [25]. These samples also did not have the spectral bands typical for non-cellulosic polysaccharides at 1236, 1428, and 1615 cm^{-1}, as the hemicelluloses were washed out during the delignification process.

However, during pressing, the pectin and arabinogalactans present in sugar beet [2] were partially eluted from the sample and dried as film on surface of the pressing machine.

The FTIR spectrum of the film contained all the bands of sugar beet samples. For further analysis, the ratio of peak heights of 1615 and 1733 cm^{-1} were calculated for all samples. The ratio of those peak heights on the eluted film spectra was 1.65, while on the light spot of sugar beet samples it was 1.23 and on the dark spot the value was 1.60. The maximum ratio was observed at the surface edge of a sugar beet sample modified with $H_3BO_3/Ca(OH)_2$ sample and was 2.14. For sugar beet sample when $Ca(OH)_2/H_3BO_3$ was used, the carboxyl peak shifted to 1619 cm^{-1} and the ratio was 1.89. This indicates that non-cellulosic polysaccharides are eluted out of sugar beet cell walls and are taking part in the adhesion process during the pressing. This is happening by intermolecular dehydration of the solubilized/displaced and subsequently dried arabinan. Similarly, it is evident that intermolecular dehydration of cellulose is also contributing to the process of panel formation as on recycled paper comparable panels were produced. This process takes part at higher pressures as seen from conditions used when panels from recycled paper were prepared.

SEM study

The SEM image of the sugar beet sample surface of untreated starting material is shown in Fig. 2a. It is less compact, but similar to the surface of the sugar beet panel sample (Fig. 2b). Upon fracture, some preserved parts of the sugar beet cell wall could be observed acting like tubing at the cross-section (Fig. 2c). The refined sample (Fig. 2d), refined to particles smaller than 0.0127 mm, have a less preserved structure with less and smaller tubing upon fracture when compared with the non-refined sample. In the presence of calcium hydroxide the internal surface of panels from the sample was less homogeneous, indicating the presence of insoluble or precipitated additive (Fig. 3a), which was not observed on sample without additive. Upon fracture of the sugar beet sample treated with calcium hydroxide, the original structure of the root of sugar beet could be observed, but the cell lumina were more compressed (Fig. 3b) than analogical image of sugar beet sample without additive. On the sample from refined sugar beet and recycled paper mixture, the anatomical structures of sugar beet fibers completely disappeared on the cleaved surface of sample (Fig. 3c). With samples containing recycled paper the fracture experiment could not be performed. Instead, the sample was sectioned with a razor blade and the SEM images (Fig. 3d, e) showed the paper fibers along the cut surface. This was compared with image of the cleaved surface of the recycled paper sample (Fig. 3e) which looked similar to that of the RS:RP sample. Also the image of the cut profile of recycled paper (Fig. 3f) was similar to the image of the mixture of refined sample and recycled paper (Fig. 3d).

Fig. 2 SEM images of no refined sugar beet sample (SBS; **a**), opened surface of panel made from SBS (**b**), fracture of the SBS panel (**c**), and fracture of panel made from recycled paper (**d**)
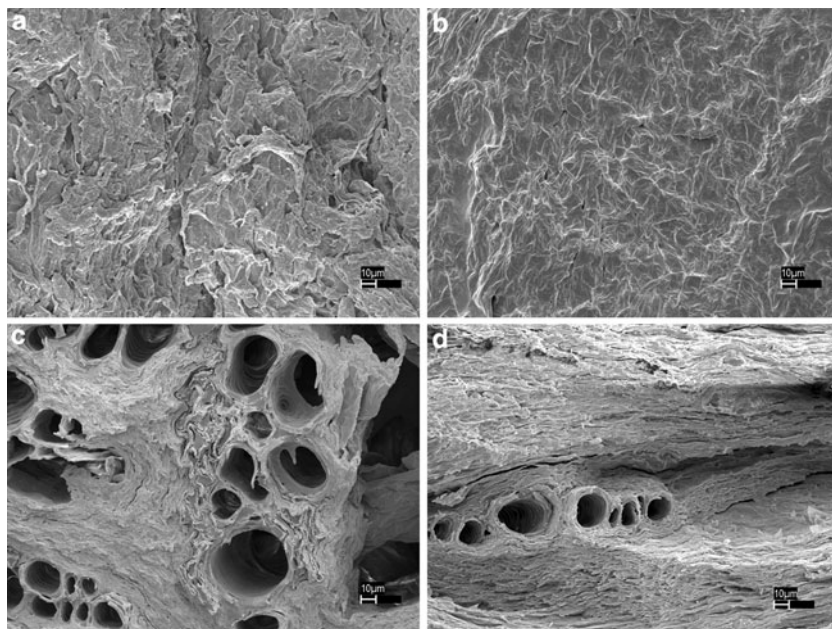
Fig. 3 SEM images of a surface of no refined sample treated with calcium hydroxide (SBS-Ca) sample (**a**), fracture surface of a SBS-Ca sample (**b**), splitted surface of a refined sugar beet/recycled paper sample (RSB/RP; **c**), section image on the razor blade cut of RS/RP (**d**), cleaved surface of a RP sample (**e**), and section image on the razor blade cut of a RP sample (**f**)
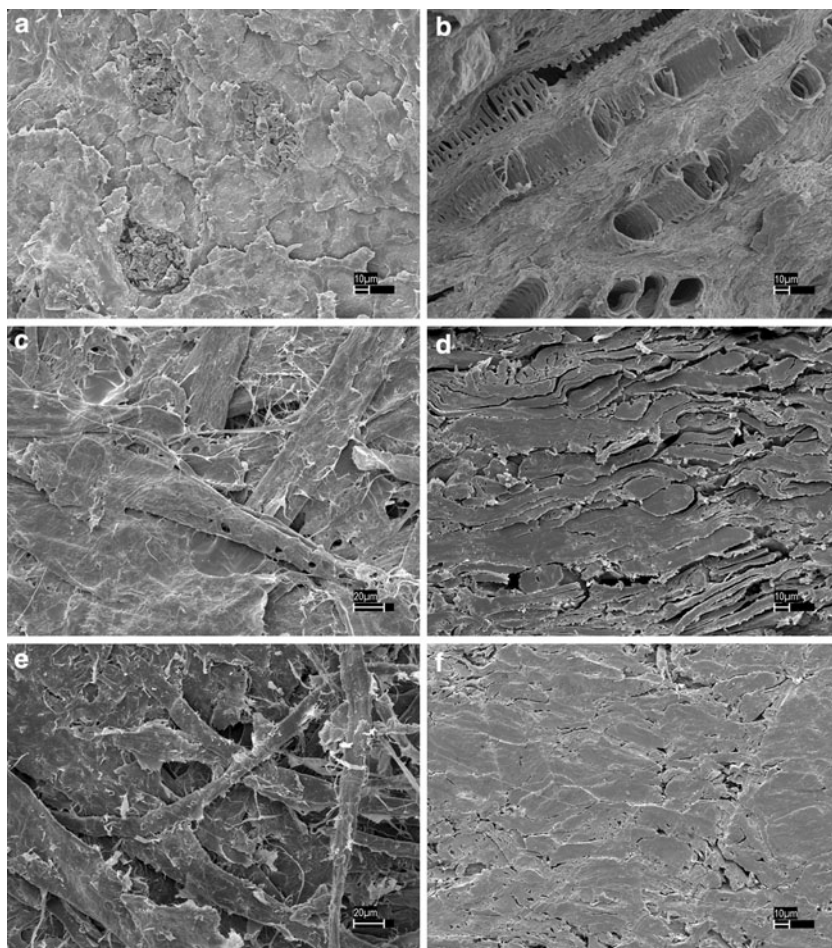
Fig. 4 SEM images of no refined sugar beet sample modified with H_2O_2/Na_2SiO_3/$MgSO_4$ combination (**a**); refined sugar beet sample with Na_2SiO_3 (**b**); H_2O_2/Na_2SiO_3 (**c**); and H_2O_2/Na_2SiO_3/$MgSO_4$ treatments at the splitted surfaces (**d**)
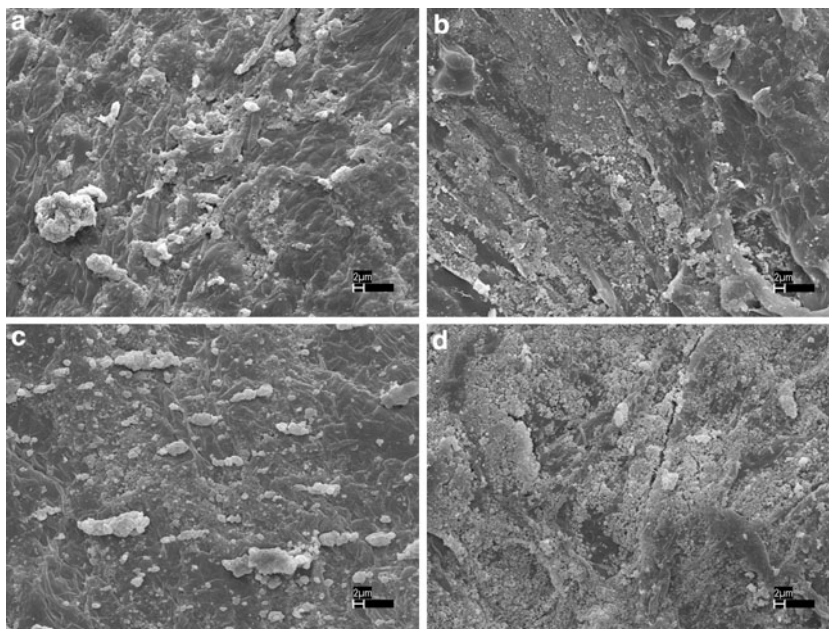

On samples where $NaSiO_3$ was added, small white particles were observed on the fracture surface (Fig. 4a–d). These particles probably originated from precipitated silicates, since all three images where $NaSiO_3$ was used looked similar. Additionally, the film that dried on the surface of the pressing platens during first periods of the pressing process of refined or non-refined sugar beet samples gave a similar image (Fig. 5) as films obtained from xylan [26].

Cone calorimetry study

The results from the cone calorimeter tests included those associated with heat released, mass loss, ignition, and visible smoke observations are listed in Table 3. It was shown that in most cases the results of multiple analysis were close and representative results could be obtained from single experiment. This was in agreement with results obtained on wood and paper sheet samples [14, 16, 17].

Initial peak of the heat release rate (PHRR) value (146 kW/m^2) for untreated sugar beet sample was close to most of the treated samples. The smallest value from this group of samples was obtained on the sample modified with calcium hydroxide and boric acid (119 kW/m^2). The shape of the chart of heat releasing rate (HRR) versus time was affected by the shrinkage, surface deformation, and charring processes during flaming, resulting in a much broader second peak than the first one and several waves between them (Fig. 6). Reported PHRR values are for the initial peak which maybe less than the value for the second peak. We also listed a HRR averaged for 60 s time interval after sustained ignition (AHRR60) for all the samples.
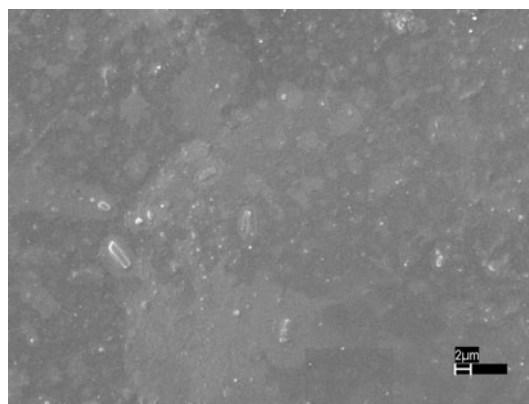
Fig. 5 SEM image of film surface dried from eluted water solution during pressing of refined and no refined samples

HRR data averaged over a time period typically have less variability than PHRR data. Only for sugar beet sample treated with mixture of calcium hydroxide and boric acid AHRR60 was smaller than for unmodified sample, which correlated with PHRR values. The bigger difference between these two variables (PHRR and AHRR60) was observed for sugar beet sample modified with calcium hydroxide, which also had the highest AEHC.

The values of AEHC were similar for the whole group of SBS samples (Table 3). Only the sample treated with calcium hydroxide in combination with boric acid had a lower value of AEHC (10.43 MJ/kg) than untreated sample (10.68 MJ/kg). Likewise, the sample treated with calcium hydroxide in combination with boric acid, it had the lowest THR (MJ/kg) value from the no refined samples.

Table 3 Cone calorimeter data on sugar beet composite panels

Sample[a]	Heat released				Mass			Smoke		Ignition
	PHRR[b]/ kW m^{-2}	AHRR60[c]/ kW m^{-2}	AEHC[d]/ MJ kg^{-1}	THR[e]/ MJ kg^{-1}	IM[f]/ g	AMLR[g]/ g m^{-2} s^{-1}	RM[h]/ %	ASEA[i]/m^2 kg^{-1}	PrISP/ PoISP[j]/m^2 m^{-2}	TSI[l] TPHRR[k]/s
SBS	146	114	10.68	7.99	60.7	12.5	25	19	6/89	29/23
SBS-B	145	124	10.72	7.79	42.5	12.4	27	4	7/9	24/18
SBS-Ca	173	118	11.28	7.92	57.2	11.7	30	22	6/93	32/27
SBS-BCa	140	114	10.94	7.70	59.0	11.7	30	51	7/233	27/19
SBS-CaB	119	103	10.43	6.87	75.9	10.8	34	18	2/97	28/21
SBS-PSiMS	149	120	10.49	7.02	80.2	10.2	33	25	7/144	32/24
RS	189	208	12.54	10.09	16.4	16.5	20	48	6/67	32/22
RS-B	164	167	11.03	7.96	20.6	17.0	28	45	11/64	29/22
RS-Ca	113	108	12.30	8.75	36.2	14.2	29	54	6/152	34/28
RS-CaB	113	104	10.91	7.78	38.9	14.8	29	56	16/160	39/34
RS-Si	132	128	11.87	8.52	23.2	13.3	28	101	5/186	24/20
RS-SC	143	134	11.66	8.60	20.2	13.5	26	124	6/204	23/19
RS-P	170	135	12.37	9.63	22.5	14.0	22	60	8/111	24/20
RS-SiP	150	123	11.40	8.64	24.4	12.2	24	51	9/97	26/21
RS-CaP	133	117	11.88	8.77	30.0	13.6	26	45	10/104	35/30
RSS-CP	153	111	11.59	8.63	25.2	12.5	25	109	10/222	19/19
RS-MS	190	150	11.65	9.57	26.5	17.6	22	27	4/62	25/21
RS-MSP	197	152	11.74	8.92	30.9	17.3	24	30	4/76	25/23
RS-MSSiP	192	113	11.25	7.83	26.6	12.4	30	41	5/81	24/22
RP	173	163	12.84	10.60	64.2	19.3	17	76	21/433	65/41
RS/RP	168	160	12.61	9.91	46.0	15.7	21	77	2/315	73/26

[a] Refer to Table 1

[b] Initial peak heat release rate

[c] Heat release rate averaged over 60 s after sustained ignition

[d] Average effective heat of combustion

[e] Total heat released per kg of initial mass

[f] Initial sample mass

[g] Average mass loss rate (10–90%)

[h] Residual mass

[i] Average specific extinction area

[j] Pre- and post-ignition smoke production

[k] Time to peak of RHR/sustained ignition

[l] Time of sustainable ignition

For all the samples with additives lower average mass loss rate (AMLR) values were observed, than for the untreated sample (12.5 g/m²s). Except for the slightly lower value for $MgSO_4/Na_2SiO_3/H_2O_2$ and $Ca(OH)_2/H_3BO_3$ treated samples, also the lowest AMLR value was observed for the non-refined sugar beet samples. The residual mass (RM) was the lowest for untreated sample and increased from 25 up to 34% for $Ca(OH)_2/H_3BO_3$ treated sample. Higher RM is typically associated with a more effective fire retardant treatment.

The ASEA value was the lowest for boric acid treated sample (SBS-B) (4 m²/kg). Also the pre- and post-ignition smoke production values were low for SBS-B

sample (7 and 9 m²/m², respectively). For the boric acid in combination with calcium hydroxide the post-ignition smoke production (PoISP) value depended upon the order of adding of boric acid and calcium hydroxide. Much higher PoISP values were observed for sugar beet modified with boric acid and calcium hydroxide combination (SBS-BCa; 233 m²/m²) than for sample where calcium hydroxide was added before boric acid (SBS-CaB) (97 m²/m²) in the process of activation (see Experimental section). The values of time at the peak of heat release rate (TPHRR) and times of spontaneous ignition (TSI) were similar for most of the sugar beet samples.

Fig. 6 The charts of HRR
versus time of untreated no
refined sugar beet, boric acid
treated, calcium hydroxide
treated, boric acid/calcium
hydroxide treatment, calcium
hydroxide/boric acid, and H_2O_2/
Na_2SiO_3/$MgSO_4$ combination
samples (the abbreviations in
legends are according to
Table 1)
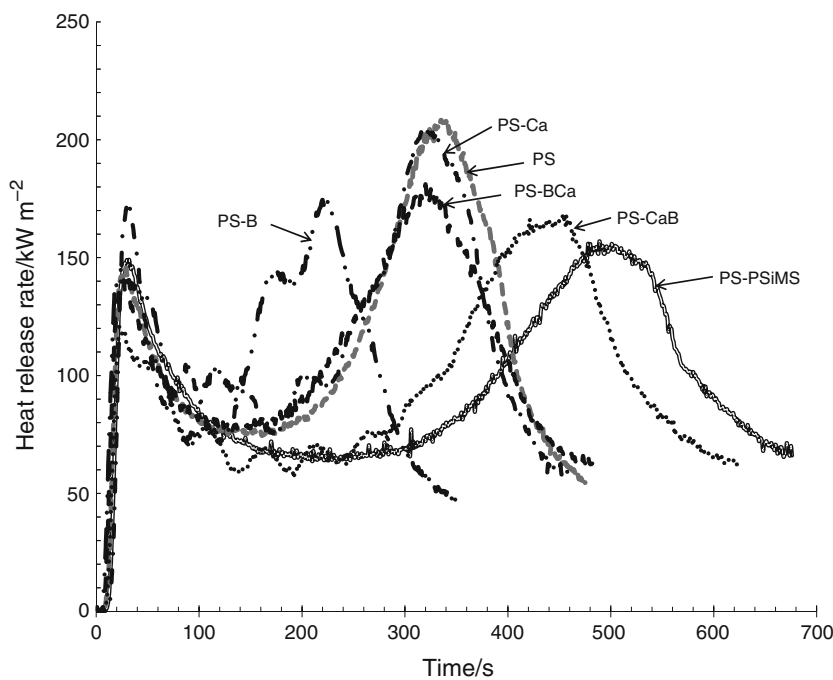
Fig. 7 The charts of HRR
versus time of refined sugar beet
(RS), RS/recycled paper (RP)
mixture, RP, boric acid, calcium
hydroxide, and calcium
hydroxide/boric acid treated
samples (the abbreviations in
legends are according to
Table 1)
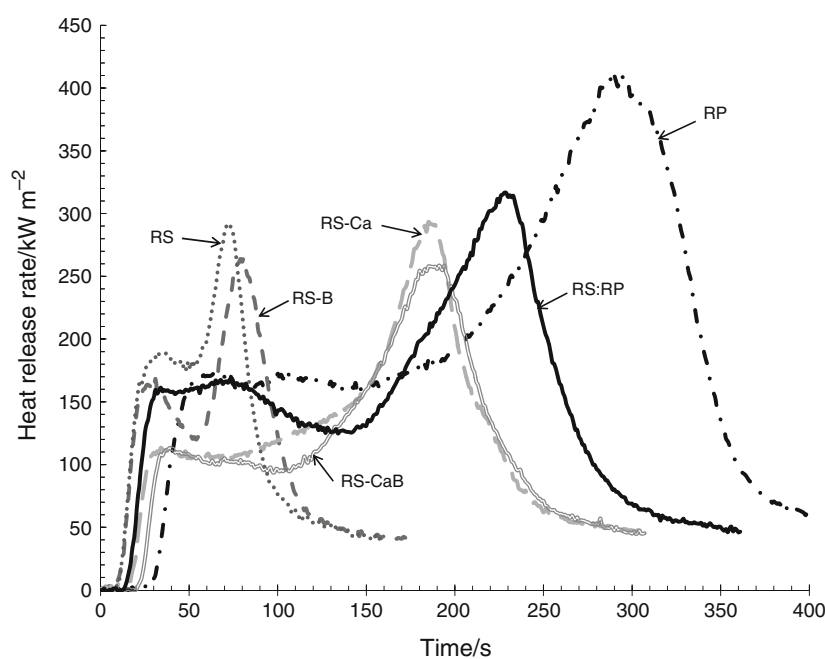
The refined sugar beet sample produced by the wet procedure gave slightly higher PHRR value (189 kW/m²) than untreated sample (146 kW/m²). This result might be due to different amount of air present in the samples and the thinner samples produced in this way. The charts of RHR versus time of same selected samples have much higher second peak (Fig. 7). There were no additional peaks in between. This is probably related to decreased thickness of the panels prepared from refined material which is less deformed during the process. The lowest

PHRR values (113 kW/m²) were obtained for samples treated with calcium hydroxide and $Ca(OH)_2$/H_3BO_3 combination in comparison with other samples prepared from the refined material. Also the values for panels made from recycled paper (173 kW/m²) and mixture of refined sugar beet and recycled paper (168 kW/m²) samples were lower than those of RS (189 kW/m²). This is probably related to the fact that more of the sugar beet material was degraded during the pressing, which resulted in higher PHRR values due to higher cellulose content in those

samples in comparison to samples prepared solely from sugar beet. The absence of a well defined initial peak in the recycled paper test may also reflect the higher cellulose content since lignin is associated with the char layer that reduces the initial rate of degradation. The test durations for these 2–4 mm thick samples did not allow consistent reporting of the average HRR for the longer durations also typically reported. Thin samples also results in less pronounced initial peaks as the back surface quickly heats up and produces the second peak. Even for the 60 s duration, the short durations resulted in the inclusion of a portion of the second peak as evidenced by the PHRR for refined and boric acid treated samples being less than the corresponding result for AHRR60. The values of both PHRR and AHRR60 were bigger for refined than for untreated samples.

The value of AEHC was the lowest for refined sample treated with $Ca(OH)_2/H_3BO_3$ (10.91 MJ/kg). This was also the case for THR (7.78 MJ/kg). The similar AEHC values for the refined sample (12.54 MJ/kg), recycled paper (12.84 MJ/kg), and their mixture (12.61 MJ/kg) indicated that there was not much difference in heat of combustion between these two samples due to content of cellulose, hemicelluloses, and lignin. The AMLR was the highest for recycled paper sample (19.3 g/m²s) and then the next highest for refined sample modified with magnesium sulfate (17.6 g/m²s) and $MgSO_4/H_2O_2$ combination sample (17.3 g/m²s), while the lowest value was obtained for Na_2SiO_3/H_2O_2 combination (12.2 g/m²s), which was greater than the value for the $MgSO_4/Na_2SiO_3/H_2O_2$ combination with the lowest observed AMLR value (10.2 g/m²s). It indicated the potential of sodium silicate as flame retarding additive and was also reflected in similar AMLR values for samples with the Si element. The residual mass (RM) values (20–21%) were again the lowest for samples without added chemicals. The highest RM for the refined sugar beet samples was for $MgSO_4/Na_2SiO_3/H_2O_2$ combination (30%) while the lowest value was observed for recycled paper (17%).

The ASEA value for refined sugar beet samples is the lowest for magnesium sulfate treatment (27 m²/kg) and highest for sodium carbonate treatment (124 m²/kg). From the point of view of total smoke production both samples treated with boric acid (SBS-B and RS-B) seems to be the best due to small values. The highest value was observed on recycled paper sample (433 m²/m² for PoISP).

The time at peak of heat release rate (TPHRR) values were low for refined sodium carbonate treatment (22 s) and analogical Na_2CO_3/H_2O_2 combination (20 s), while the highest value was observed on recycled paper sample (65 s). Also the biggest time of spontaneous ignition (TSI) value was observed for recycled paper (41 s) and the smallest for refined sample with calcium carbonate additive

(19 s) and Na_2CO_3/H_2O_2 combination (19 s) sample. Based on the lowest PHRR and the other variables associated with heat released, the samples with calcium hydroxide added before boric acid (SBS-CaB and RS-CaB), were considered the best flame retarded samples (Table 3). The treatments were more effective resulting in improving performance in the refined sugar beet samples which may reflect more effective treatment of the smaller particles.

Conclusions

Composite panels from the SBS were prepared with or without refining and pressing the material at 150 °C and pressures from 100 to 5410 kPa. The non-refined sugar beet panels required less pressure to produce a suitable panel than required for the refined material. Results from cone calorimeter tests of the samples with calcium hydroxide added before boric acid, were considered as the best flame retarded samples. The no refined sugar beet samples had similar fire performance as the recycled paper sample in terms of heat released (peak heat release rate and average effective heat of combustion), shorter ignition times, and much less visible smoke.

References

1. Mayers N, Kent J. New atlas of plant management. University of California Press, Gaia Books; 2005. p. 164. ISBN 0-520-23879-6.
2. Šimkovic I, Nunez A, Strachan GD, Yadav MP, Mendichi R, Hicks KB. Fractionation of sugar beet pulp by introducing ion-exchanging groups. Carbohydr Polym. 2009;78:06–812.
3. Šimkovic I, Uhliariková I, Yadav MP, Mendichi R. Branched arabinan obtained from sugar beet pulp by quaternization under acidic conditions. Carbohydr Polym. 2010;82:815–21.
4. Šimkovic I, Csomorová K. Thermogravimetric analysis of agricultural residues: oxygen effect and environmental impact. J Appl Polym Sci. 2006;100:1318–22.
5. Sampathrajan A, Vijayaraghavan NC, Swaminathan KR. Mechanical and thermal properties of particle boards made from farm residues. Bioresour Technol. 1992;40:249–51.
6. Panthapulakkal S, Zereshkian A, Sain M. Preparation and characterization of wheat fibers for reinforcing application in injection model thermoplastic composites. Bioresour Technol. 2006;97:265–72.
7. Zheng Y, Pan Z, Zhang R, Jenkins BM, Bluk S. Particleboard quality characteristics of saline jose tall wheatgrass and chemical treatment effect. Bioresour Technol. 2007;98:1304–10.

8. Hunt JF, O'Dell J, Turk C. Fiberboard bending properties as a function of density, thickness, resin, and moisture content. Holzforschung. 2008;62:569–76.

9. Kunaver M, Medved S, Čuk N, Jositukaityté E, Poljanšek I, Strand T. Application of liquefied wood as a new particle adhesive system. Bioresour Technol. 2010;101:1361–8.

10. Xu X, Yao F, Wu Q, Zhou D. The influence of wax-sizing on dimension stability and mechanical properties of bagasse particleboard. Ind Crops Prod. 2009;29:80–5.

11. Ye XP, Julson J, Kuo M, Womac A, Myers D. Properties of medium density fiberboards made renewable biomass. Bioresour Technol. 2007;98:1077–84.

12. Li X, Li Y, Zhikai Z, Wang D, Ratto JA, Sheng K, Sun XS. Mechanical and water soaking properties of medium density fiberboard with wood fiber and soybean protein adhesive. Bioresour Technol. 2009;100:3556–62.

13. deBarros Filho RM, Mendes LM, Novack KM, Aprelini LO, Botaro VR. Hybrid chipboard panels based on sugarcane bagasse, urea formaldehyde and melamine formaldehyde resin. Ind Crops Prod. 2011;33:369–73.

14. Šimkovic I, White RH, Fuller AM. Flammability studies of impregnated paper sheets. J Therm Anal Calorim. 2011. doi: 10.1007/s10973-011-1690-7.

15. Silva MF, Pineda EAG, Hechenleitner AAW, Fernandes DM, Lima MK, Bittencourt PRS. Characterization of poly(vinyl acetate)/sugar cane bagasse lignin blends and their photochemical degradation. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-1475-z.

16. Šimkovic I, Martvoňová H, Maníková D, Grexa O. Flame retardance of insolubilized silica inside of wood material. J Appl Polym Sci. 2005;97(5):1948–52.

17. Šimkovic I, Martvoňová H, Maníková D, Grexa O. Flammability studies of sodium thiosulphate or metabisulphite impregnated wood using cone calorimeter. Fire Mater. 2007;31(1):137–45.

18. Gao M, Wu WH, Wu FS. Thermal degradation and smoke suspension of cotton cellulose modified with THPC and its lanthanide metal complexes. J Therm Anal Calorim. 2009;98:245–51.

19. Morrey EL. Flame retardant composite materials. Measurement and modeling of ignition properties. J Therm Anal Calorim. 2003;72:943–54.

20. Janowska G, Rybinski P, Jantas R. Effect of the modification of silica on thermal properties and flammability of cross-linked butadiene–acrylonitrile rubbers. J Therm Anal Calorim. 2007; 87(2):511–7.

21. Redfern JP. Rate of heat release measurement using the cone calorimeter. J Therm Anal. 1989;35:1861–77.

22. ASTM International. Heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. West Conshohocken: ASTM; 2009. p. E1354-09.

23. ISO. Reaction-to-fire tests, heat release, smoke production, and mass loss rate—part 1: heat release rate (cone calorimeter method). Geneva: ISO; 2002. ISO 5660-1.

24. ISO. Reaction-to-fire tests, heat release, smoke production, and mass loss rate—part 1: smoke production rate (dynamic measurement). Geneva: ISO; 2002. ISO 5660-2.

25. Ilharco LM, Garcia AR, da Silva JL, Ferreira LFV. Infrared approach to the study of adsorption on cellulose: influence of cellulose crystallinity on the adsorption of benzophenone. Langmuir. 1997;13:4126–32.

26. Šimkovic I, Gedeon O, Uhliariková I, Mendichi R, Kirschnerová S. Positively and negatively charged xylan films. Carbohydr Polym. 2011;83:769–75.