

Research Paper

Microcellular foaming of arabinoxylan and PEGylated arabinoxylan with supercritical CO₂Linda Härdelin^a, Anna Ström^a, Ernesto Di Maio^b, Salvatore Iannace^c, Anette Larsson^{a,*}^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41296 Gothenburg, Sweden^b Department of Chemical, Materials and Production Engineering, University of Naples, Federico II P.le Tecchio 80, 80125 Naples, Italy^c Institute for Macromolecular Studies (ISM-CNR), Via Bassini 15, 20133 Milano, Italy

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ABSTRACT

In this study, arabinoxylan extracted from barley husks was reacted with polyethylene glycol (PEG) of various molecular weights to introduce an internal plasticizer into the polymer matrix. A successful PEGylation reaction was identified using FTIR and elemental analysis. Thermal and mechanical properties were studied using dynamic mechanical analysis, which revealed that the attachment of PEG chains reduced the glass transition temperature by up to 25 °C. Foaming experiments were conducted under different test conditions in a batch foaming process with supercritical CO₂ in a thermoregulated and pressurized cylinder. The foams were evaluated using SEM by studying the morphology of the samples foamed at different temperatures. The unmodified arabinoxylan sample was found to produce the best foam morphology, though the PEGylated samples could be produced at lower temperatures than could the unmodified arabinoxylan. This was interpreted as due to the decrease in the glass transition temperature.

1. Introduction

The three main components of trees and agricultural crop residues are cellulose, lignin, and hemicellulose. Cellulose and lignin have been extensively studied over the years with a view to developing new chemicals and materials (Calvo-Flores, Dobado, Isac-García, & Martín-Martínez, 2015; Rojas, 2016). Research on hemicellulose has so far mostly focused on packaging films and food coatings (Hansen & Plackett, 2008). Barley husks are an agricultural crop residue that contains approximately 30–35% cellulose, 30–33% hemicellulose, 17–25% lignin, with the remainder being other components, such as ash and extractives (Glasser, Kaar, Jain, & Sealey, 2000; Höjje, Gröndahl, Tømmeraaas, & Gatenholm, 2005; Krawczyk, Persson, Andersson, & Jönsson, 2008; Köhnke, Brelid, & Westman, 2009; Persson, Dinh, & Jönsson, 2009; Pitkänen, Tuomainen, Virkki, Aseyev, & Tenkanen, 2008; Roos, Persson, Krawczyk, Zacchi, & Stålbrand, 2009). The hemicellulose arabinoxylan can be extracted from barley husks using various techniques, such as alkaline extraction (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Höjje et al., 2005), water extraction (Bengtsson & Åman, 1990; Glasser et al., 2000), dimethyl sulphoxide extraction (Saake, Kruse, & Puls, 2001), microwave treatment (Roos et al., 2009), enzymatic-aided treatment (Figuerola-Espinoza, Poulsen, Søre, Zargahi, & Rouau, 2004), and

extrusion (Vaidya, Gaugler, & Smith, 2016). Arabinoxylan has a backbone of xylose units to which L-arabinofuranose and D-glucuronic acid (or its 4-O-methyl derivative) are attached at positions C-2 or C-3 or both (Spiridon & Popa, 2008). Its structural features depend on origin as well as extraction method (da Silva et al., 2012; Doner & Hicks, 1997; Ebringerová & Heinze, 2000; Eda et al., 1976; Gruppen, Hamer, & Voragen, 1992; Höjje et al., 2006; Saha & Bothast, 1999; Saulnier, Marot, Chanliaud, & Thibault, 1995; Schooneveld-Bergmans, Beldman, & Voragen, 1999; Shibuya & Iwasaki, 1985).

The action of attaching polyethylene glycol (PEG) to various molecules is termed PEGylation and has been used extensively in pharmaceutical production (Harris & Chess, 2003; Pasut & Veronese, 2012). Hydrophilic PEG has also been used to plasticize several compounds, such as chitosan films (Suyatma, Tighzert, Copinet, & Coma, 2005), poly(lactic acid) films (Sungsanit, Kao, & Bhattacharya, 2012), and poly(vinyl alcohol) membranes (Li, Wu, Lin, & Xiang, 2012) in order to alter material properties such as hydrophilicity, elasticity, and ductility.

Synthetic polymer foams have been widely used and were developed in the 1930s and 1940s (Frisch, 1981). Today they are found everywhere in our daily lives, for example, in disposable packaging, wound care products, furniture, and insulation (Klempner & Sendjarevic, 2004). In recent years, interest in biodegradable foams has increased along with awareness of the finiteness of

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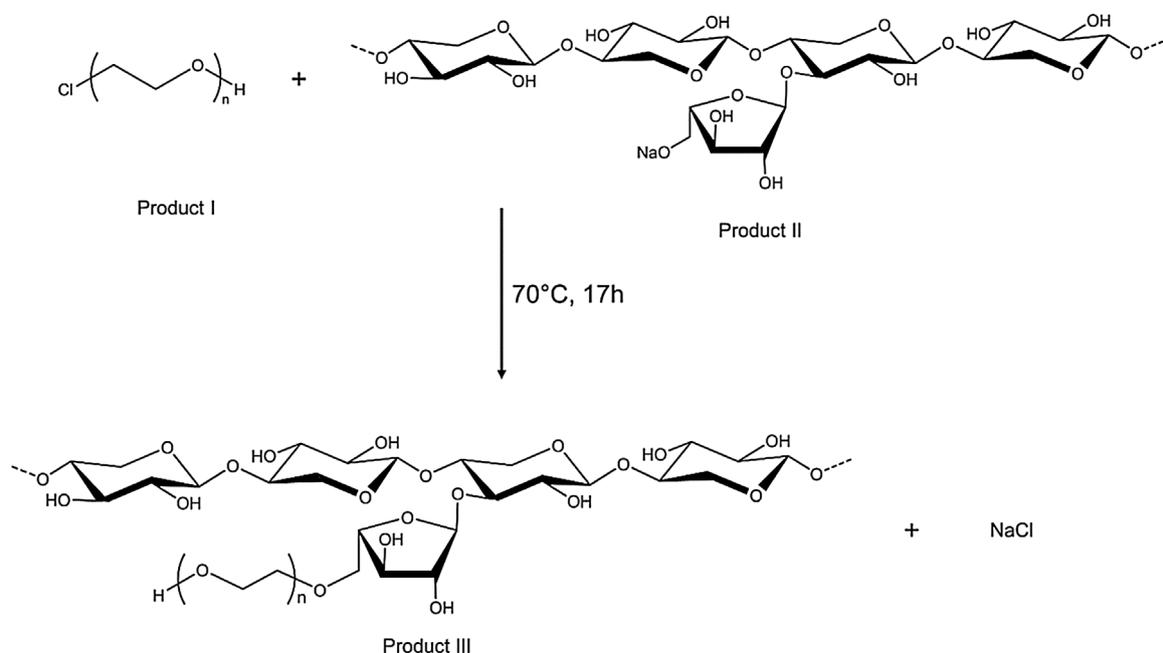


Fig. 1. Proposed reaction scheme of the PEGylation procedure.

our planet's resources (Jeon et al., 2013). Hemicelluloses crosslinked with chitosan have previously been foamed (Ayoub, Venditti, Pawlak, Salam, & Hubbe, 2013; Salam, Venditti, Pawlak, & El-Tahawy, 2011).

The microcellular batch foaming process has been developed over the last three to four decades. In principle, the solid sample is placed inside a high-pressure vessel and exposed to CO_2 at the saturation pressure and temperature, whereupon the gas diffuses into the polymer. The CO_2 plasticizes the polymer and reduces the glass transition temperature (T_g) as the polymer viscosity is reduced due to an increase in free volume (Jeon et al., 2013; Nalawade, Picchioni, & Janssen, 2006; Park & Suh, 1996). Foaming occurs as the pressure is released and thermodynamic instability causes the gas to separate and nucleation sites to form (Nalawade et al., 2006; Park & Suh, 1996). Several biodegradable polymers have been foamed using the microcellular batch foaming process (Fujimoto et al., 2003; Hao, Geng, Xu, Lu, & Yu, 2008; Jeon et al., 2013; Matuana, 2008; Salerno, Oliviero, Di Maio, & Iannace, 2007; Xu et al., 2004); however, to our knowledge, hemicellulose have not previously been foamed using microcellular foaming or any other foaming techniques. In the present study, polyethylene glycol molecules were coupled to the hemicellulose arabinosulfate to introduce an internal plasticizer into the material and to lower the T_g . The samples were then foamed with supercritical CO_2 (scCO_2) and the foamability was evaluated using SEM.

2. Experimental procedure

2.1. Materials

The hemicellulose arabinosulfate (AX) was extracted from milled barley husks (waxy locus of *Hordeum vulgare* L.), received from Lyckeby Starch AB (Kristianstad, Sweden). First a pre-treatment using 0.05 M HCl solution, 20 mL g^{-1} of barley husk (BH), was performed to remove extractives from the husks (Glasser et al., 2000). Then delignification with 0.15 g NaClO_2 g^{-1} BH, followed by alkali extraction with 1 M NaOH containing NaBH_4 as reducing agent (0.1 g g^{-1} BH) were performed. The hemicellulose precipitated in ethanol at a 2:1 ratio and was dried at room temperature.

Chemicals used in the PEGylation reaction were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. These chemicals were polyethylene glycol 400 (PEG 400), polyethylene glycol

1500 (PEG 1500), zinc chloride, glacial acetic acid, ethanol 95%, HCl, and NaOH. For carbohydrate analysis, sulphuric acid, and trifluoroacetic acid as well as the sugar monomers L-arabinose (Ara), D-galactose (Gal), D-glucose (Glc), D-xylose (Xyl), and D-mannose (Man) were purchased from Sigma-Aldrich.

2.2. Methods

2.2.1. PEGylation

Arabinosulfate was reacted with polyethylene glycol of two molecular weights (400 and 1500). Microcrystalline cellulose has previously been successfully coupled to PEG (Bhalekar, Desale, & Madgulkar, 2010); here the reaction was adapted to couple PEG chains to the arabinosulfate polymer. In the first step, PEG was reacted with HCl at a molar ratio of 1:2 for 2 h at 70°C . Zinc chloride, 0.5 wt% of the amount of PEG, was added as catalyst. Here, the PEG chains were to be converted into their chloride derivative by replacing the terminal hydroxyl groups with chlorine. In the second step, arabinosulfate (at a molar ratio of 1:1 with PEG 400) was dissolved in 30 wt% NaOH for 2 h at ambient temperature to convert arabinosulfate to its sodium salt. This was done to increase the reactivity of the arabinosulfate. In the third step, the products of the first and second steps were mixed overnight at 70°C using a magnetic stirrer; during this time, the two products reacted to form an arabinosulfate-PEG conjugate, leaving NaCl as the side product. The end product was added to 100 mL of hot water (70°C) and neutralized to pH 7 using glacial acetic acid. The neutralized product was precipitated in ethanol at a 2:1 ratio, then centrifuged and air dried. This procedure was repeated with PEG 1500 to yield two different arabinosulfates coupled to PEG of different molecular weights. A proposed reaction mechanism of the PEGylation procedure is shown in Fig. 1 (modified from (Bhalekar et al., 2010)). Due to practical lab limitations, the PEG 1500 was added at a molar ratio of 1:2 to arabinosulfate. A sample was also prepared in which PEG 400 was physically mixed with arabinosulfate, yielding 20 wt% PEG. Unmodified arabinosulfate was used as a reference sample. To produce test specimens, the polymer samples were compression moulded at 130°C for 3 min at a pressure of 10 MPa. Table 1 summarizes the various samples studied.

2.2.2. Characterization

The unmodified arabinosulfate was hydrolysed using sulphuric acid

Table 1
Investigated samples with abbreviations.

Samples	Abbreviations
Reference sample (unmodified arabinoxylan)	AX
Arabinoxylan coupled with PEG 400	AX-PEG400
Arabinoxylan coupled with PEG 1500	AX-PEG1500
Arabinoxylan physically mixed with 20 wt% PEG 400	AX + PEG400

(Theander & Westerlund, 1986): 3 mL of 72% H₂SO₄ was added to a 200-mg sample and put under vacuum for 15 min before being placed in a water bath at 30 °C for 1 h. Then 84 mL of distilled water was added and the samples were put in an autoclave for 1 h at 125 °C and 20 bar. The hydrolysate was filtered and the solid residue, i.e. the Klason lignin, was analyzed gravimetrically. The amount of acid-soluble lignin was measured using UV spectroscopy (Cary 60 UV-vis spectrophotometer; Agilent Technologies, CA, USA) at 205 nm, with an absorptivity coefficient of 128 dm³g⁻¹ (Köhnke et al., 2009; Schöning & Johansson, 1965). To analyze the carbohydrate content, the hydrolysed samples were diluted with distilled water to a concentration of 200 mg L⁻¹.

The neutral carbohydrate composition was analyzed on acid-hydrolysed hemicellulose samples using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD), using an ICS 3000 ion chromatography system (Dionex, Sunnyvale, CA, USA) equipped with a CarboPac PA1 (4 × 250 mm) analytical column, gradient pump, isocratic post column pump, column oven, and auto sampler. The various sugars detected using the system were L-arabinose (Ara), D-galactose (Gal), D-glucose (Glc), D-xylose (Xyl), and D-mannose (Man).

Fourier-transform infrared (FTIR) spectroscopy was recorded on a PerkinElmer Frontier FT-IR Spectrometer (PerkinElmer, Waltham, MA, USA) equipped with an attenuated total reflection (ATR) device. Samples were analyzed using FTIR spectroscopy using 32 scans between 4000 and 400 cm⁻¹. The elemental analysis measurements were made by Mikrolab Kolbe in Germany.

Size exclusion chromatography (SEC) with multi-angle laser light scattering (SEC-RI-MALLS) was used to evaluate the molecular weight. This method employs a SEC system consisting of an HPLC pump (Waters, Milford, MA, USA), a Dawn HELEOS II multi-angle laser light scattering detector (Wyatt Technology Co., Goleta, CA, USA), an Optilab T-rEX refractometer (Wyatt Technology Co., Goleta, CA, USA), and one TSKgel GMPWXL column (Tosoh Bioscience, Tokyo, Japan). In this procedure, a solvent of 0.10 mM NaCl and 0.02% sodium azide was used as the mobile phase and the samples were dissolved in the mobile phase at a concentration of 0.5 mg mL⁻¹ at 80 °C. Before analysis, the samples were filtered through a 0.45-µm syringe filter. The injection volume, flow rate, and temperature were 100 µL, 0.5 mL min⁻¹, and 25 °C, respectively. The specific refractive index, dn/dc, was measured using a manual injector with the Optilab T-rEX refractometer. The arabinoxylan dn/dc value of 0.135 was calculated using solutions of different concentrations.

Dynamic mechanical analysis (DMA) was used to measure the thermal and mechanical properties of arabinoxylan and the PEGylated arabinoxylans. The measurements were made using a Q800 DMA instrument (TA Instruments, New Castle, DA, USA). The samples were compression moulded into films then cut into samples using a parallel razor blade cutter with an inner distance of 5.90 mm. The thickness of

Table 2
Relative carbohydrate composition of arabinoxylan (% of carbohydrates, n = 3).

Sample	Ara ^a (%)	Gal ^a (%)	Glc ^a (%)	Xyl ^a (%)	Man ^a (%)
AX	26.2 ± 0.04	0.80 ± 0.01	10.5 ± 0.03	62.1 ± 0.03	0.30 ± 0.04

^a Ara, arabinose; Gal, galactose; Glc, glucose; Xyl, xylose; Man, mannose.

the films (average of three measurements) was measured using a micrometer (Mitutoyo, Kanagawa, Japan). The samples were mounted in the test chamber with an approximate distance between the clamps of 1.5 cm. The samples were tested at a frequency of 1 Hz and at a strain of 0.1%. The preload force was set to 0.001 N. The temperature was swept from 50 °C to 250 °C at a ramp rate of 3 °C min⁻¹. Before measurement, the samples were conditioned at 23 °C and 50% RH for 24 h.

Scanning electron microscopy (SEM) was used to study the morphology of the foamed hemicellulose samples. Before the SEM analyses, the samples were coated with an approximately 10-nm-thick gold coating to prevent electrostatic accumulation. A LEO Ultra 55 FEG SEM (Zeiss, Oberkochen, Germany) operated at an acceleration voltage of 3 kV was used for the analysis.

2.2.3. Foaming

The foaming experiments were conducted using a batch foaming process with supercritical CO₂ (scCO₂) in a thermoregulated and pressurized cylinder, described elsewhere (Marrazzo, Di Maio, Iannace, & Nicolais, 2008). Samples were measured with an electronic calliper (Mitutoyo) before and after foaming to determine volume expansion. Foaming was performed at foaming temperatures of 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, and 170 °C, and the solubilization time was 2 h with a CO₂ pressure of 10 MPa. The pressure drop rate at the time of foaming was 15 MPa s⁻¹.

3. Results and discussion

3.1. Characterization of arabinoxylan

For the neutral carbohydrate analysis, the unmodified arabinoxylan was hydrolysed with sulphuric acid according to the method developed by Theander and Westerlund (Theander & Westerlund, 1986). For comparison, trifluoroacetic acid (TFA) was also used to hydrolyse samples for carbohydrate analysis (Albersheim, Nevins, English, & Karr, 1967). The arabinoxylan mainly comprised 62% xylose, 26% arabinose, and 11% glucose, giving an Ara/Xyl ratio of 0.42 (see Table 2). The relative carbohydrate composition of arabinoxylan obtained using both methods indicated no significant difference, so only the results of the sulphuric acid method are shown in Table 2. Relative carbohydrate composition has been suggested to be less sensitive to variations in instrument calibration than is absolute carbohydrate amount (Jacobs, Laine, & Syverud, 2003). Carbohydrate amount and composition are presented in the Supplementary Information. The arabinoxylan also contains 5.8 wt% Klason lignin and 3.2 wt% acid-soluble lignin, giving a total lignin content of 9 wt%.

3.2. Characterization of PEGylated material

FTIR analysis of the samples (Fig. 2) revealed structural changes in the PEGylated material. The absorption bands at 2922 and 2853 cm⁻¹ correspond to CH₂ stretching, and the intensity increases as the number of CH₂ linkages increases in the different samples. The AX (Fig. 2d) has the least pronounced absorption bands at 2922 and 2853 cm⁻¹ and the absorption bands intensify in the following order: AX + PEG400 (Fig. 2c), AX-PEG1500 (Fig. 2a), and AX-PEG400 (Fig. 2b). The increased numbers of CH₂ linkages are due to the increased numbers of PEG molecules in the samples. For the three PEGylated samples, there is an absorption band at 1733 cm⁻¹ attributed to carbonyl groups, and it

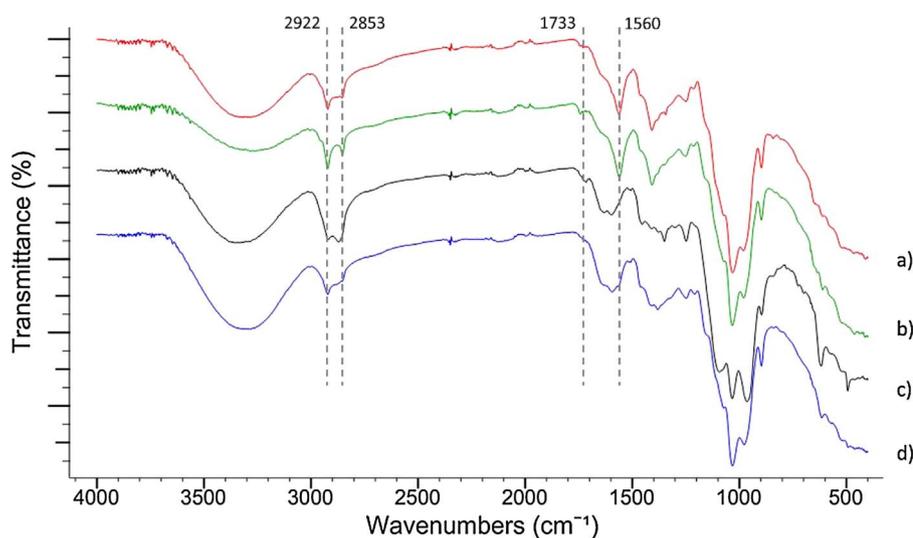


Fig. 2. FTIR spectra of a) AX-PEG1500, b) AX-PEG400, c) AX + PEG400, and d) AX.

is related to oxidation of the OH group at the end of the PEG molecule into an aldehyde (Han, Kim, & Kwon, 1997). This absorption band is not seen in the AX sample, which contains no PEG molecules. The absorption band at 1560 cm^{-1} corresponds to ether bonds and is clearly seen for the two samples with PEG coupled to arabinoxylan, indicating several new ether bonds. In the physically mixed sample, no new ether bonds are formed, which is as expected and is shown in Fig. 2, where the spectrum of AX + PEG400 follows the spectrum of AX.

The arabinoxylan polymer chain contains five carbon atoms and four oxygen atoms in the arabinose and xylose units, giving a carbon to oxygen (C:O) ratio of 5:4; in the PEG units, the ratio is 2:1, since there are twice as many carbon as oxygen atoms in each PEG segment. This means that when PEG molecules are attached to the arabinoxylan, the number of carbon atoms in the sample should increase relative to the number of oxygen atoms, which was confirmed by elemental analysis (Table 3). The AX sample is assumed to consist of 100% arabinoxylan. The theoretical carbon/oxygen relationship of arabinoxylan would be 1.25 if the sample consisted of 100% arabinoxylan. However, as indicated by the characterization of the reference sample, arabinoxylan instead consists of up to 30 wt% of lignin, glucose, and water. The water content in the sample also greatly influences the results, and water from the surrounding environment when the elemental analysis is performed can greatly affect the results. However, these results indicate that the PEGylation reaction was successful and that PEG molecules are attached to the arabinoxylan, since the carbon amount has increased and the oxygen amount decreased in the PEGylated samples relative to the reference arabinoxylan. The larger increase in AX-PEG1500 than the AX-PEG400 is due to its higher molecular weight, i.e. the average PEG 1500 chain consists of 34 PEG units versus 9 PEG units in the average PEG 400 chain.

3.3. Molecular weight distribution

The molecular weight of arabinoxylan extracted from barley depends on whether it is extracted from barley husk (Köhnke, Pujolras, Roubroeks, & Gatenholm, 2008; Roos et al., 2009) or hull-less barley (Comino, Shelat, Collins, Lahnstein, & Gidley, 2013; Storsley,

Table 3
Results of elemental analysis.

Samples	C wt%	O wt%	C:O molar ratio
AX	34	59	0.78
AX-PEG400	36	57	0.84
AX-PEG1500	40	52	1.03

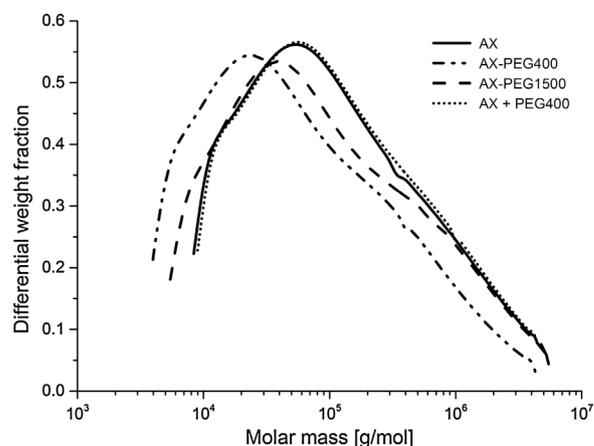


Fig. 3. Molecular weight distribution of arabinoxylan and PEGylated arabinoxylans.

Table 4
SEC results of arabinoxylan and PEGylated arabinoxylans (Standard deviation in brackets, $n = 3$).

Sample	M_w (kDa)	M_n (kDa)	PDI
AX	373 (± 5)	45 (± 1)	8.3 (± 0.3)
AX-PEG400	245 (± 1)	22 (± 1)	11.0 (± 0.3)
AX-PEG1500	382 (± 4)	33 (± 1)	11.6 (± 0.4)
AX + PEG400	385 (± 4)	48 (± 2)	8.1 (± 0.2)

Izydorczyk, You, Biliaderis, & Rossnagel, 2003). The arabinoxylan used in this study was extracted from barley husk therefore a low molecular weight around 20 kDa was expected (Köhnke et al., 2008). However the molecular weights obtained (Fig. 3 and Table 4) were considerably larger, similar to molecular weights reported for arabinoxylan extracted from hull-less barley bran (Zheng, Li, & Wang, 2011).

Whether the high molecular weight obtained was related to starch was tested by treating the extracted arabinoxylan with α -amylase (Teramyl 120) (see Supplementary Information). Carbohydrate analysis showed that the glucose content was reduced by 77% (unpublished results), however, the molecular weight was not reduced considerably. It is known that arabinoxylan with low arabinose content has a tendency to aggregate in water (Blake & Richards, 1971; Pitkänen, Virkki, Tenkanen, & Tuomainen, 2009) therefore the high molecular weight of the arabinoxylan obtained here could be related to aggregates of arabinoxylan chains.

Foaming of the PEGylated arabinoxylan and the unmodified

arabinoxylan in this study was performed largely in the absence of water why further investigations of the molecular weight of the arabinoxylan e.g. in DMSO, a solvent in which the arabinoxylan aggregates less, was out of scope of this study.

As seen in Fig. 3, the reference sample, arabinoxylan, and the arabinoxylan sample physically mixed with PEG 400 exhibit similar molecular weight distributions. This is to be expected, since the addition of the plasticizer, PEG, is only physically mixed with the arabinoxylan and therefore does not alter the characteristics of the polymer. The PEG 400 molecules, which has an average molecular weight of 400 Da, have too low molecular weight to be detected here. For the other two samples the plasticizer is chemically bound to the arabinoxylan, which alters the polymer characteristics. The AX-PEG400 sample shows a larger change compared to the AX-PEG1500 sample. This is most likely related to a larger amount of substitution of the PEG400 compared to the PEG1500 arabinoxylan, contributing to reduced aggregation tendency of the AX, hence reducing molecular weight.

3.4. Thermal and mechanical properties of arabinoxylan and PEGylated arabinoxylans

The thermal and mechanical properties of the compression-moulded samples are shown in Fig. 4. The glass transition temperature (T_g) is defined as the temperature at which $\tan \delta$ reaches a maximum. The average T_g values of all samples were determined from three measurements. For AX, the T_g was 217 ± 5 °C, but when PEG 400 had been covalently bonded to arabinoxylan, the T_g dropped by 25 °C to 192 ± 7 °C. For AX-PEG1500, the T_g was 205 ± 5 °C, which, compared with the unmodified sample, is a 12 °C decrease. The T_g of the sample in which PEG 400 was only physically mixed into the arabinoxylan, and not covalently bonded, was unchanged compared with that of the unmodified arabinoxylan, i.e. the T_g was 223 ± 2 °C. Thus, AX-PEG400 displayed the greatest decrease in T_g (25 °C), followed by AX-PEG1500 (12 °C), indicating that it is insufficient to physically mix PEG400 with AX to reduce the T_g . The difference in T_g between the reference sample and the two samples with PEG coupled to

arabinoxylan confirms the IR results as it also indicates that the polymers are modified. The decrease in T_g is the largest for AX-PEG400, probably because this PEGylation reaction was conducted at a molar ratio of 1:1 (arabinoxylan:PEG), so more PEG molecules could theoretically be attached to the arabinoxylan. The AX and AX-PEG1500 samples have a storage modulus of approximately 2000 MPa and a loss modulus of 200–300 MPa. Compared with the typically used polylactic acid (PLA), they are similar in strength but differ in $\tan \delta$ (Gårdebjer, Larsson, Löfgren, & Ström, 2015; Martin & Avérous, 2001). For the AX-PEG400, the storage modulus is somewhat lower, approximately 1000 MPa, and the loss modulus is 200–300 MPa. For the sample with PEG physically mixed with arabinoxylan, the storage and loss moduli are lower than for the other samples, so the incorporation of physically mixed PEG molecules weakens the material at the composition tested. This was also seen when PLA was plasticized with 20 wt% PEG 400, causing the storage modulus to decrease from 2000 MPa to 976 MPa (Martin & Avérous, 2001). All investigated samples display no influence of temperature until approximately 160–180 °C. When the materials are handled at room temperature during testing, the specimens are soft and formable, with the AX-PEG400 material being the softest compared with the unmodified AX material, indicating efficient plasticization. This is somewhat in contrast to the DMA results, which indicate a glass transition temperature of approximately 200 °C, which would give a brittle and stiff material at room temperature. However, polysaccharides are known to be hygroscopic (Wu, Stokke, Stevens, & Han, 2013) and the unmodified arabinoxylan has a water content of 11 wt% (measured using thermogravimetric analysis). Therefore, the water molecules presumably plasticize the materials at ambient conditions, and when the DMA measurements are conducted, the water evaporates as the temperature increases during the experiment, resulting in the DMA measurement being made on dry samples.

3.5. Foamability of arabinoxylan and PEGylated arabinoxylans at different temperatures

The foamability of arabinoxylan was studied by analyzing the

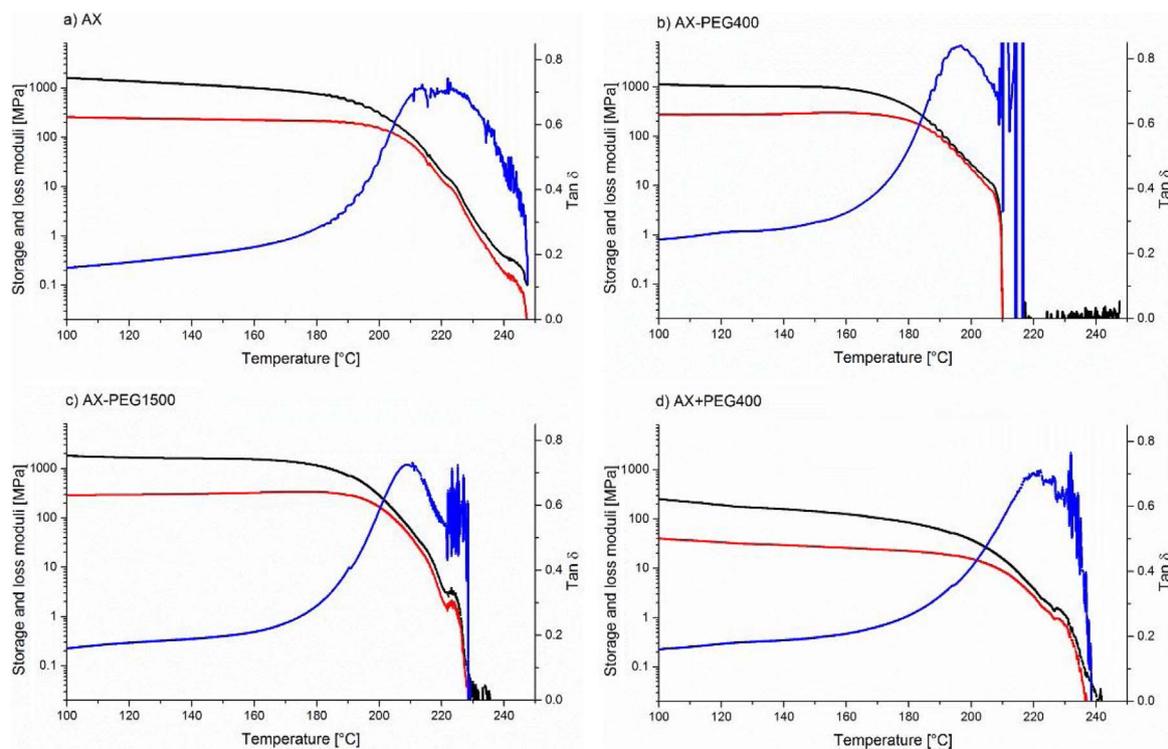


Fig. 4. Thermal and mechanical properties of a) AX, b) AX-PEG400, c) AX-PEG1500, and d) AX + PEG400. Storage modulus (black line), loss modulus (red line), and $\tan \delta$ (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5
Foamability and volume expansion (in per cent) of foamed samples.

Sample	Glass transition temperature	Foaming temperature					
		120°C	130°C	140°C	150°C	160°C	170°C
AX	217°C ± 5°C	0	10	0	50*	170**	300***
AX-PEG400	192°C ± 7°C	130**	10	0	80	120**	50
AX-PEG1500	205°C ± 5°C	0	5	0	0	40*	20
AX + PEG400	223°C ± 2°C	0	10	0	30	30	50

*1 initial bubble in centre of sample.

**1 large bubble in centre of sample.

***1 very large bubble in centre of sample.

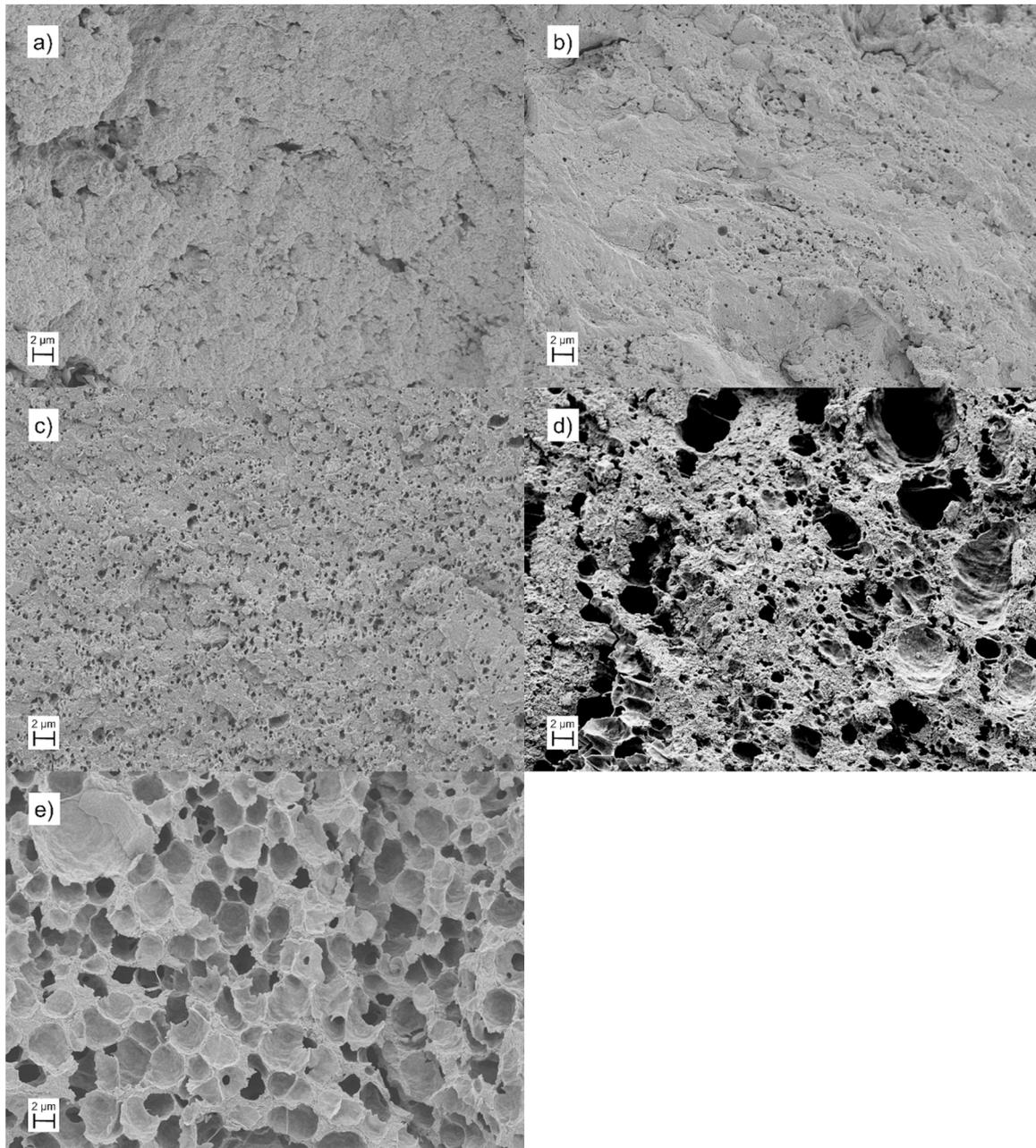


Fig. 5. Classification of foamability: a) Class 1, AX + PEG400, 150 °C; b) Class 2, AX-PEG1500, 150 °C; c) Class 3, AX, 150 °C; d) Class 4, AX + PEG400, 170 °C; and e) Class 5, AX, 170 °C.

effects of different PEGs on foam morphology. The volume expansion of the foamed samples was evaluated and the results are presented in Table 5. The cross-sectional area of the foams was investigated using SEM (see Supplementary Information for micrographs of all foamed samples). Tests were also performed with PEG 6000 coupled to the arabinosyl polymer, and these results are found in the Supplementary Information. The foamability was evaluated by studying the morphology of the foamed samples at different temperatures. Foaming experiments could not be conducted at temperatures higher than 170 °C, as the samples degraded and burned at higher temperatures. The foamability was ranked on a scale of 1–5, where 1 represents samples unable to produce foams (represented by the grey background in Table 5). A representative sample of class 1 is shown in Fig. 5a. These samples displayed no signs of foamability, instead exhibiting a compact structure and very low to negligible volume expansion. Class 2 is represented by the red background in Table 5, and a representative sample is shown in Fig. 5b. These samples started to display some initial small pores, but with low volume expansion. In Class 3, represented by the orange background in Table 5, a foamed structure is observed in which small pores appear in the samples, as illustrated in Fig. 5c. In Class 4, represented by the yellow background in Table 5, more and larger pores are seen, as illustrated in Fig. 5d. The sample that produced the best foam is represented by the green background in Table 5 and Fig. 5e shows a representative sample.

The gas, here scCO₂, dissolves by diffusion into the polymer and when the pressure is released, separates to form bubbles within the polymeric matrix. The morphology of the foams produced is determined by several factors, such as the amount of gas dissolved in the polymer, temperature, and pressure (Jeon et al., 2013).

When comparing the foamability of the unmodified arabinosyl and the physically mixed arabinosyl, the unmodified arabinosyl produces foam at a lower foaming temperature and with a better foam morphology. This could be explained by the fact that the scCO₂ in the materials interacts with the PEG molecules instead of creating nucleation sites within the polymer (Girard, Tassaing, Marty, & Destarac, 2016). This limits the bubble formation since there are fewer scCO₂ molecules in the polymer sample to nucleate when the pressure is lowered. For the PEGylated arabinosyl, in which the PEG molecules are coupled to the arabinosyl polymer, this interaction can also occur, explaining why the PEGylated samples display less foamability than does the unmodified arabinosyl.

Though the material used consists predominantly of arabinosyl, with lignin and starch also present, this study demonstrates that foamed structures can be produced at foaming temperatures above 150 °C. It is worth noting that the foaming temperatures used are lower than the determined glass transition temperatures of the samples. This is often the case when foaming thermoplastic polymers, since scCO₂ acts as a plasticizer and lowers the T_g even more. For the PEGylated samples, especially AX-PEG400, foams with better morphology were produced at lower foaming temperatures than for the unmodified arabinosyl samples. One can speculate that this is because foaming can occur at a lower temperature when PEG chains are coupled to arabinosyl. Future work could focus on improving the foaming process parameters at lower temperatures for arabinosyl coupled to PEG 400.

4. Conclusions

Polyethylene glycol was successfully coupled to arabinosyl via a modified synthesis route previously used for microcrystalline cellulose (Bhalekar et al., 2010). The covalently linked PEG chains act as an internal plasticizer, as indicated by a reduction in the glass transition temperature, which could enable lower processing temperatures than those currently used.

Both unmodified arabinosyl and the PEGylated arabinosyls were able to produce foams in a microcellular batch foaming process using scCO₂ as the blowing agent. Foamability was evaluated using

SEM, which indicated that unmodified arabinosyl produced the best foams under the evaluated test conditions (i.e. temperatures of 120–170 °C, a solubilization time of 2 h, a CO₂ pressure of 10 MPa, and a pressure drop rate at the time of foaming of 15 MPa s⁻¹), possibly due to interactions between PEG and scCO₂ that occurred during the foaming process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2017.09.068>.

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