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Novel Xylan Gels Prepared from Oat Spelts

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Summary: Gels and pastes are used in many areas including application in the cosmetic, pharmaceutical and medical industries. A xylan derivative with pasty consistency was prepared in addition to the synthesis of xylan ethers and esters. The water content of the gel can be widely varied. The gel is formed although the xylan contains no cross-linking group. The hydrophobic and hydrophilic nature of the xylan gel can be adjusted by modifying the xylan. All of the gels can be dried using different methods (air drying, solvent exchange as well as freeze drying) and the dried gels can again disperse in water. The gels were characterised by porosity measurements (mercury intrusion), dynamic vapour sorption (DVS), scanning electron microscopy (SEM) and dispersion stability investigation respectively.

Keywords: dynamic vapour sorption; gels; hemicellulose; mercury intrusion; xylan

Introduction

Xylan is a predominantly hemicellulose component found in plants and in some algae. Xylan makes up about 10-15% of softwoods, about 10-35% of hardwoods and about 35-40% of the total mass in the residues of annual plants, such as oat hulls or spelts.

The structure of xylan is more complex than that of cellulose, and has been summarised in several reviews.[1-6] A proposed structure of hemicellulose in annual plants is shown in Figure 1. The repeating units are linked by β-(1-4) glycosidic bonds. Typical examples of side chains or groups in xylan are arabinofuranose, xylopyranose, rhamnose, glucuronic acid and acetyl groups.

Despite its prevalence xylan's application areas in industry and technology are very few. One of the reasons may be the lack of availability.[7] Xylan is accessible for various reactions in order to obtain anionic, cationic, hydrophilic or hydrophobic derivatives.[8-10] However gels, hydrogels and pastes are formed after treating the hemicellulose with cross-linking agents or by adding to another gel-forming polymer. Mixtures of xylan and chitosan were investigated by Gabrielii et al.[11,12] The resulting films showed a high swelling capacity at a certain composition. The gel formation of arabinoxylan can be detected if the polysaccharide mixture contains ferulic acid.[13] This hydroxycinnamic acid serves as a cross-linker between the polysaccharides chains. Hoseney and Faubion studied the oxidative gelation of wheat flour water-soluble pentosans with viscosimetry.[14] Different oxidation agents were tested. Its potential as a barrier material of hemicellulose films was studied by Hartman et al.[15] The authors used O-acetyl-galactoglucomannan as their hemicellulose component and different plasticizers were used to prevent brittleness. Furthermore, films were tested containing hemicellulose and other polymers like alginate or carboxymethylcellulose. The various mixtures investigated showed that a compromise between low O_2 permeability, high mechanical toughness and flexibility must be found. For arabinoxylan-based films, mechanical properties, moisture content and water vapour permeability were considered as a function of plasticizer concentration in a further study.[16] The plasticised arabinoxylan films produced in this study are characterised by a lower water vapour permeability than that of unplasti-

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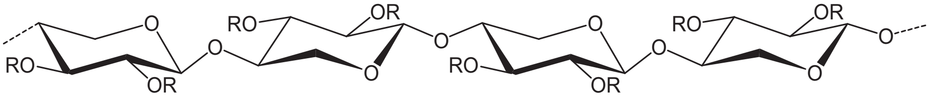

Figure 1.
Structure of xylan in annual plants with R = arabinofuranose, xylopyranose, rhamnose, glucuronic acid and acetyl groups.

cised films. The arabinoxylan used here was taken from corn hulls. In another study glucuronoxylan-based free films isolated from aspen wood were prepared by casting from aqueous solutions and drying in a controlled environment.[17,18] Adding xylitol or sorbitol facilitated film formation and thus the examination of the material properties of these films. The mechanical properties as well as the oxygen barrier properties of the films were evaluated. These films are also formed after varying the arabinose / xylan ratio.[19] A detailed review of sustainable films and coatings made from hemicellulose is given by Hansen and Plackett.[20]

The term gel is often used randomly and many definitions exist. A gel is defined as a disperse system that is dimensionally stable, slightly deformable, high in liquid and gas and made of at least two components. If the interspace between the particles is filled with liquids, the system is considered a lyogel. If the liquid is water it is called a hydrogel. There is no precise definition for the term paste. Normally a paste is a solid dispersion in liquids of a doughy consistency. If the above definition is used, a paste is described as a lyogel or a hydrogel with a doughy consistency. Further definitions and the differences between macrogels, microgels and reversible gels in regards to polymers are discussed by Burchard.[21] The gel formation of the xylan we used occurred through rheological measurement.[8] Frequency sweep testing of the sample produced higher storage shear modulus G' values than the loss modulus G'' (Figure 2).

Experimental Part

Xylan Gel

The preparation of the gel is carried out as recently described.[8] For a typical procedure, a dispersion of 35.25 g (0.267 mol) of xylan in 311.7 g of sodium hydroxide solution (5%, w/w) was prepared and stirred for 1 h at 80 °C. Subsequently 5.7 g of H_2O_2 (35%) was added to the solution heated and stirred for 2 h. A further 4.3 g of H_2O_2 (35%) was added to the solution and stirred for 1 h. The product was precipitated by adjusting the pH to 4.5 with aqueous citric acid. The product was separated by centrifugation for 45 min at 15000 rpm. The liquid was decanted and a further centrifugation at 15000 rpm for 30 min followed. The dry content of the resulting xylan gel was 22.7%.

The samples were dried by lyophilisation (freeze drying), solvent exchange or air drying for further characterisation. Solvent exchange occurred by adding methanol. 100 ml of methanol was added to 58 g of the prepared gel and subsequently centrifuged. The procedure was repeated four times with methanol and one time with acetone. Finally, the gel was dried in a vacuum drying oven.

Dynamic Vapour Sorption

The moisture absorption was measured in a Dynamic Vapour Sorption, Automated Water Sorption Analyser from Surface Measurement Systems LTD which is an automated instrument for measuring the water sorption properties of materials. It is a rapidly user-friendly gravimetric system and operates at between 0% and 98% relative humidity and from 5 °C to 40 °C. The most sensitive configuration has a resolution of just 0.1 μg. In the Dynamic Vapour Sorption approach, the sample being investigated is placed on a microbalance, which is exposed to a continuous flow of air, with a predetermined and constant relative humidity. As the humid air passes over the sample, a

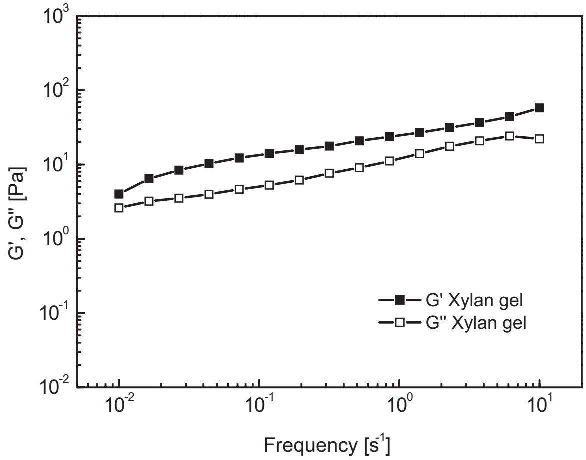

Figure 2.
Frequency sweep testing of the typical unmodified xylan gel (sample Xyl12).

zone of constant moisture concentration and relative humidity is established closely around the sample. This zone allows for the rapid establishment of equilibrium by maximising the mass transport of water vapour into and out of the sample. Combined with an ultra sensitive microbalance, sample sizes can be very small which also speeds up the equilibration process. About 20 mg of the sample was weighed in the equipment's special weighing bottle. The measurements were run with water vapour as humidity component.

Pore Characterisation

According to the IUPAC definition, pores are classified into three groups: macro pores with diameter >50 nm, meso pores with diameter between 50 and 2 nm and micro pores with diameter <2 nm.[22] The large range of pore diameters requires multiple, complementary methods to characterise the whole variety of pores necessary for elucidating structure-property relations and to get an idea of the influence of different parameters of preparation or processing on the structure and properties of the samples. To this end Hg-intrusion is used.

Mercury Intrusion

Generally, mercury intrusion is a suitable method for characterising accessible macro and meso pores. This method was primarily used to determine the specific volume and to calculate the specific surface of the pores, the porosity and bulk density of the samples. Hg-intrusion was carried out combining the macro and meso pore units "Pascal 140" and "Pascal 440" (Thermo-electron Cooperation, Milano, Italy) respectively, and merging the data of both units into one distribution. To ensure the reproducibility of measurements, the samples with a maximum volume of 2 cm^3 space were thoroughly dried and conditioned for 1 h in the recipient of the equipment (pressure 10 Pa) prior to Hg intrusion to completely remove moisture from the sample. The parameters of the pore size distribution were calculated from the curve of the cumulative pore volume, where the pore radius is related to the pressure applied on mercury by Washborn's equation assuming cylindrical pore geometry.[23]

Measurements of the Dispersion Stability

The dispersion stability was determined using a Turbisan^{TM} device from Quantochrome GmbH. The samples are filled in optical cells. Afterwards the whole cell is scanned vertically with a resolution of 40 μm. Thus the migration of the particles is recorded in upwards direction (creaming) as well as in a downwards direction (sedimentation). If a phase separation or a change of the phase equilibrium is observed, the concentration of the dispersed phase changes locally accompanied by a change of the transmission and/or the backscattering depending on the height in the cell. The principle is to determine the intensity of the transmission and backscattering in relation of the irradiated light. The Mie theory forms the basis of the data analysis in the case of backscattering and the Lambert-Beer-Law in the case of transmission.

Results

The xylan gel was prepared accordingly as described above. The formation of the gel isn't based on a cross-linker. Hemicelluloses can contain phenolic esters, e.g. ferulic acid or other derivatives of hydroxycinnamic acid. Such phenol esters can support the formation of hemicellulose gels.[24] However, the investigation of the used xylan could not detect any amount of hydroxy cinnamic acid.

The gel is formed after dispersion in alkaline media by adding the hydrogen peroxide. It can be assumed that the oxidation leads to a formation of a keto-group in C2 or C3 position or, in the case of a ring opening, a dialdehyde or a dicarboxyl group respectively (Figure 3). The content of the carbonyl-group is determined through a reaction with hydroxyl amine following the determination of the nitrogen content by elemental analysis.[25] Carbonyl content between 88 and 143 mmol/100 g was detected.

The xylan gels were prepared from raw xylan as well as xylan derivatives (Table 1). The modified xylans were prepared as described in a recent paper.[8] The hydrophobic and hydrophilic nature of the xylan gels can be varied by using different substituents.

Porosity Measurement

Selected sample were characterised using porosity measurements. The porosity measurement supplies results of the pore size distribution and cumulative pore volume. Five dried and variously treated gels were compared with the raw xylan. One gel was prepared from hydrophobic modified xylan (Xyl4). The gels were dried by lyophilisation (GT), by solvent exchange (LM) or by air drying (AD). Three of the dried samples were ground. Figure 4 presents the comparison of the resulting pore volumes. The largest pore volume in the macro pores range is detected with the dried hydrophobic xylan gel (sample Xyl4, Figure 4 left). The raw xylan indicates a higher cumulative pore volume than the other four dried gel samples. No significant differences in the range of the meso and macro pores are found in connection with the drying methods. All four samples show a similar cumulative pore volume. Grinding of the dried sample also has no influence on the porosity. If the meso pore range is considered the Xyl12LM sample and the raw xylan show the largest pore volume (Figure 4 right).

Figure 5 demonstrates the relative pore volume depending on the pore diameter. The maximum value is between 10 and 11 μm except with the Xyl sample (Figure 5d). It must be assumed that the data detected in this range represent the volume between the particles rather than the pore volume. When considering the particle size distribution (Figure 6), the

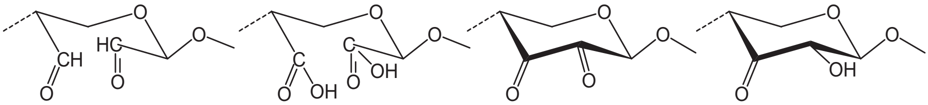

Figure 3.
Possible different structure of oxidized xylose units.

Table 1.

Some examples of prepared gels from xylan and its derivatives; selected samples are additionally dried for DVS and porosity measurements (abbreviation: AD - air drying, GT - lyophilization, LM - solvent exchange). The preparation of xylan derivatives is carried as described in a recent paper.[8]

Sample	Description	Starting material	DS	Dry content of the gel [%]	Drying
Xyl	raw xylan				
Xyl1	hydrophobic gel	caprylxylan	~0.14	31	
Xyl2	hydrophobic gel	laurylxylan	~0.12	33	
Xyl3	hydrophobic gel	octadecylxylan	~ 0.09	32	
Xyl4	hydrophobic gel	octadecylxylan	~ 0.05	35	GT
Xyl5	anionic gel	xylansulfat	0.04	32	
Xyl6	anionic gel	xylansulfat	0.15	34	
Xyl7	anionic gel	carboxymethylxylan	0.07	30	
Xyl8	xylan gel	xylan		31	GT
Xyl9	xylan gel	xylan		30	AD
Xyl10	cationic gel	2-hydroxy-3-trimethylammoniumpropylxylan	0.11	27	
Xyl11	cationic gel	2-hydroxy-3-dimethyllaurylammoniumpropylxylan	0.13	36	
Xyl12	xylan gel	xylan		31	GT, LM
Xyl13	no gel formation	2-hydroxy-3-trimethylammoniumpropylxylan	0.35	97	
Xyl14	xylan gel	xylan		32	

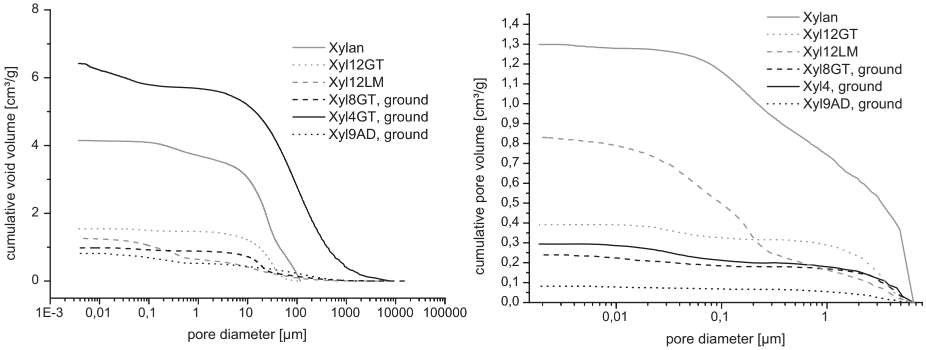

Figure 4.

Cumulative pore volume of dried xylan gel in comparison with raw xylan: left - the whole pore range, right: the meso pore range.

pore volume must be less than 0.5 µm. The ground samples Xyl8GT and Xyl9 are characterised by a very small pore volume in the range of meso pores (50 - 2 nm). Apparently the grinding process leads to agglomeration and decomposition of the meso pore structure. The hydrophobic sample Xyl4GT is regarded as an exception in the case of the ground samples. However, obvious pore volumes in the meso range are detected with the raw xylan sample, Xyl12GT, Xyl12LM and even Xyl4GT, whereby the solvent exchange dried sample (Xyl12LM) clearly shows the largest meso pore volume.

Dynamic Vapour Absorption (DVS)

Virtually all materials are sensitive to the presence of water vapour or moisture. They may retain water by bulk absorption, surface adsorption capillary condensation, chemical reaction or complexation, formation of solution or a combination of these

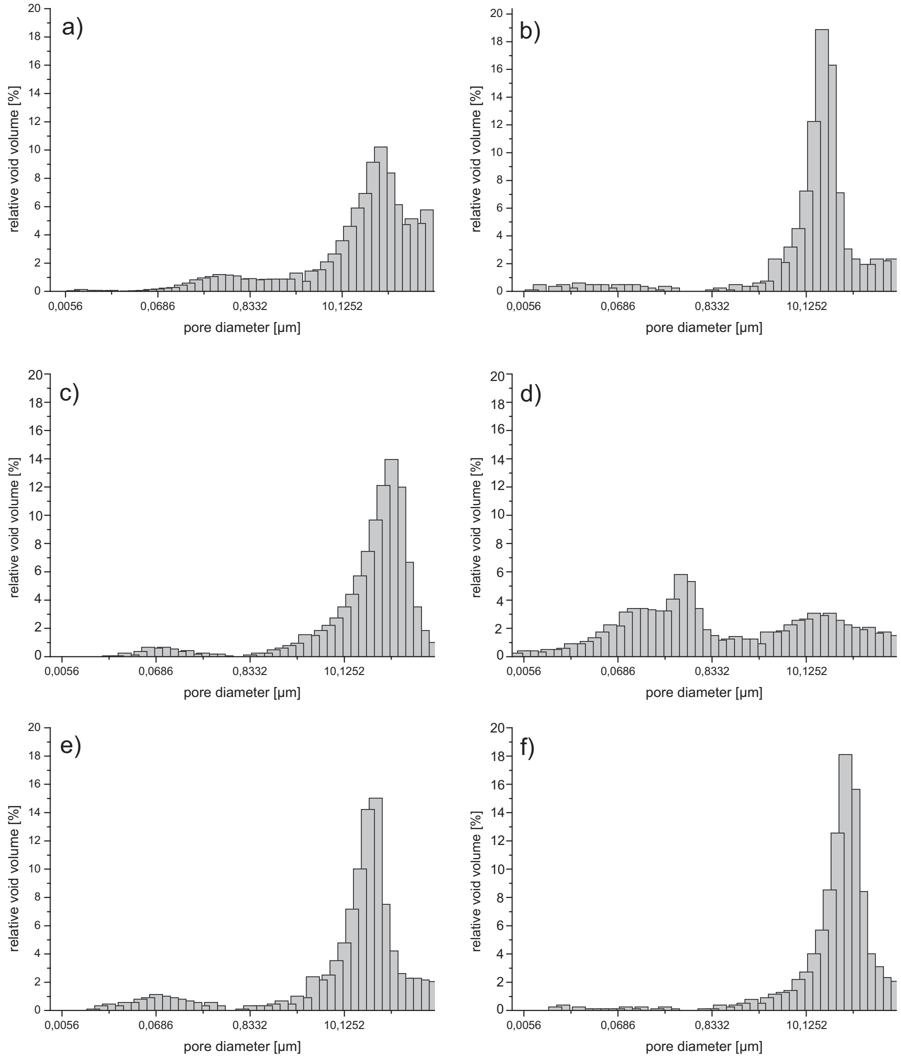

Figure 5.
The relative pore volume of the dried xylan gels: a) raw xylan, b) Xyl8GT, c) Xyl12GT, d) Xyl12LM, e) Xyl4, f) Xyl9.

mechanisms. In any case, knowledge of water material interactions is critical for improving our understanding of virtually all types of materials.

Many of the water sorption problems commonly encountered are associated with the storage, processing, and/or the chemical or biological activity of these material types. The percentage of moisture content is the simplest and most important single parameter for describing the water content of a material. However, a material's moisture content is directly dependent on the partial vapour pressure of water, commonly referred to as the relative humidity (RH), in the sample environment. An important fundamental relationship which provides a more meaningful description of the water sorption process is the water sorption isotherm - the dependency of the equilibrium moisture content of a material and % relative humidity.

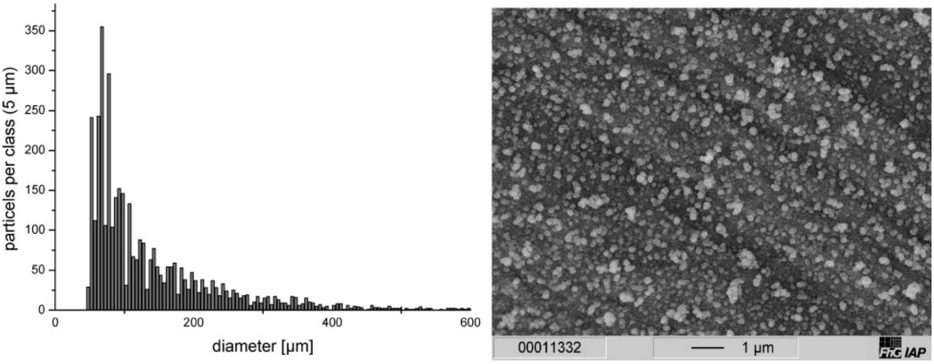

Figure 6.
The particle size distribution of a xylan gel. The distribution is obtained through a pattern analysis of SEM images.

The behaviour of three samples at different moisture levels was investigated by DVS. The adjustment of the moisture occurs depending on the establishment of the equilibrium. If the weight increase or decrease is less than a certain limit variation of the weight, the moisture is adjusted. The Xyl12 sample was dried by lyophilisation and by solvent exchange and compared with a pure xylan sample. At first the water sorption and desorption are measured at different relative moistures (10, 30, 50, 70 and 80%) at 25 °C. The vapour sorption and desorption of the samples is performed in a similar way in all cases. The samples absorb water until a relative moisture of 50% linearly is reached, whereas the Xyl12LM sample absorbs less than both of the other samples (Figure 7 left). However, the sorption of the lyophilised sample (Xyl12GT) increases significantly at higher moisture. The Xyl12LM sample's clearly lowest sorption in comparison with the other samples was surprising. Therefore a kinetic measurement of the sample was added. Kinetic measurement means the maintenance of the relative moisture and the determination of the weight increase. The vapour sorption and desorption of the samples were measured at a relative humidity of 70% (Figure 7 right). The xylan sample attained the quickest weight increase. A constant weight is observed after 5 hours for the lyophilised dried xylan gel sample Xyl12GT. No mass weight change is observed after two hours in the case of the Xyl12LM sample, which was dried by solvent exchange. But the absorbed water vapour amount is higher as in the dynamic measurement. This means that the establishment of equilibrium is very slow. However, the order of the measured samples doesn't change but the absorbed water vapour amount at relative moisture of 70% changes significantly (Figure 7). The sorption of water takes time during the dispersion process and should be supported by strong agitating.

Dispersion Stability

Three samples with different dry content (15, 25 and 32%) are measured using the described method. The sample with a dry content of 32% couldn't be measured because the viscosity was too high. Figure 8 shows the transmission and backscattering curves of the Xyl14 sample with a dry content of 15%. The x-axis shows the local resolution of the cell and the y-axis on the left shows the values of transmission and backscattering. The temporal course of the measurement is shown on the right. The backscattering curve changes significantly because the light scattering particles drop

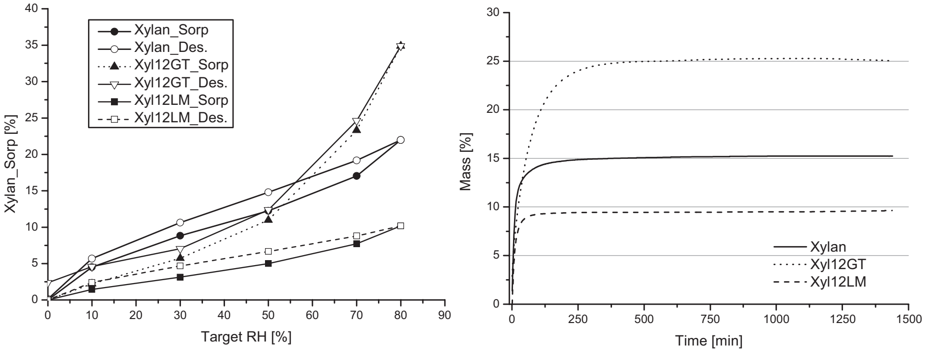

Figure 7.
Dynamic vapour sorption of dried xylan gels (left) and kinetic measurement at constant relative moisture (70%) and 25°C (right).

to the bottom. The backscattering signal decreases near the meniscus whereas the signal near the bottom increases. The transmission curve hardly changes due to the opacity of the sample. Less change is observed with the Xyl14 sample that has a dry content of 25% (Figure 9). The dispersion of this sample is essentially more stable. It obviously makes the stability index is smaller (Table 2). Figure 10 shows the periodic variance on the bottom of the cell. The sample with the lower concentration shows a continuous increase in the thickness of the sediment (up to 11 mm).

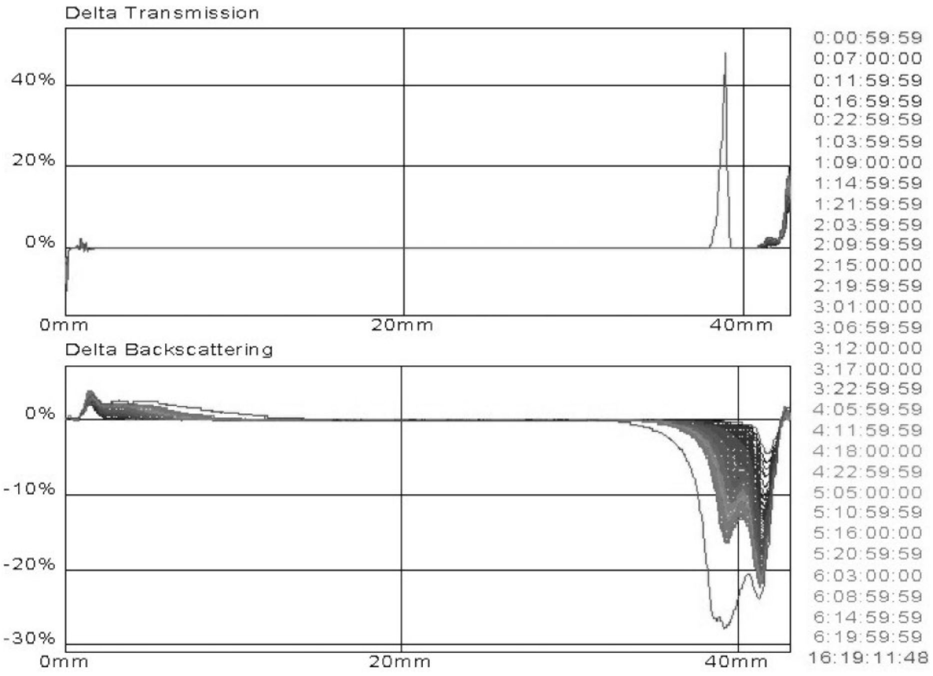

Figure 8.
Investigation of dispersion stability - transmission and backscattering of the Xyl14 sample (15%) in the reference mode (reference: first scan, time scale: dd:hh:mm:ss).

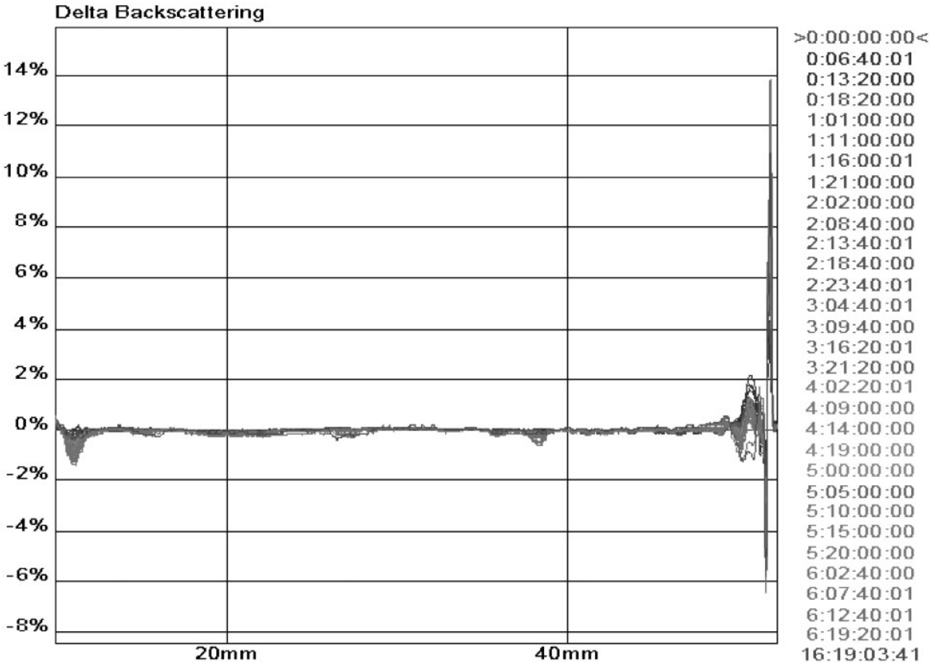

Figure 9.
Investigation of dispersion stability - backscattering of the Xyl14 sample (25%) in the reference mode (reference: first scan, time scale: dd:hh:mm:ss).

The thickness of the sample with the higher concentration is stagnates after three days. The decrease of the thickness after about 7 days is due to the packing effect of the sediment.

Conclusion

The focus of our study was to characterize gels prepared from xylan of oat spelts. The water content of the gel varies widely. The gel is formed even though the xylan used contains no cross-linking group. The hydrophobic and hydrophilic properties of the xylan gels can be varied by using different substituents. The gels were dried and characterised by porosity measurement and dynamic vapour sorption. The porosity showed differences depending on the drying method. The gels can be drying by different methods and afterwards they can be dispersed again. But the sorption of water takes time until the equilibrium is adjusted. The prepared gels are stable whereas the dispersion stability of the gel is influenced by the water content and dry content, respectively.

Table 2.
Results of the dispersion stability; the samples were measured at 28°C and with a measurement interval of 100 min.

Sample	Dry content	Measurement period	Stability index after 1 day	Predominant instability mechanism
	[%]	[dd:hh:mm]		
Xyl14	15	16:19:11	0.40	Sedimentation
Xyl14	25	16:19:03	0.20	

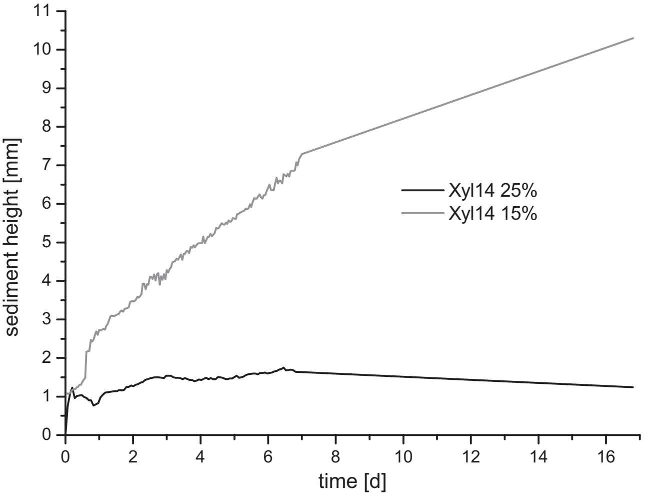

Figure 10.
Comparison of the temporary change of backscattering of both concentrations (15% and 25%) in the middle of the cell between 10.1 and 12.8 mm.

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