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An unconventional approach for improving the integrity and mechanical properties of xylan type hemicellulose based films

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The isolation of xylans from lignocellulosic biomass via alkaline extraction typically involves a neutralization step, which results to salt formation. Usually, these salts are removed from the medium to avoid their presence within the isolated xylans and films made from these polymers. The present work shows that it is not always necessary to do so, since the presence of potassium acetate (KAcO) in the films was found to be beneficial both for the film formation and mechanical properties. While desalted xylans could only form film fragments, presence of KAcO in the films led to intact films with increased toughness by approximately 2 to 5 folds. Increasing KAcO concentration resulted to softer films while the opposite was true for NaCl indicating that the two salts had different effects on the films, which was also verified by the differences in the cross-sectional and surface morphologies of the films containing KAcO and NaCl.

Introduction

Based on renewable resources, environmentally friendly biodegradable polymers provide sustainable alternatives to conventional synthetic polymers for the production of materials intended for a large variety of applications.[1–3] Although not as popular as the biodegradable polymers such as starch and polylactic acid yet, hemicelluloses receive an increasing interest especially in the last decade for the production of biodegradable films and coatings.[4,5] With hemicelluloses being a major constituent of the lignocellulosic biomass structure, one of the core drivers of this interest is the abundance and low cost of lignocellulosic biomass. Furthermore the utilization of lignocellulosic biomass resources for the production of fuels, materials and chemicals do not cause the food vs. fuel competition that occurs due to the utilization of starch.[6]

In the lignocellulosic biomass structure, hemicellulose is found together with cellulose and lignin where these three biopolymers make up the bulk of the plant cell wall. Hemicelluloses are one of the most abundant biopolymers after cellulose and therefore their utilization for the production of various value-added products is a reasonable option.[7] So far, hemicellulose based films have been produced from a large variety of different lignocellulosic feedstocks,[4,5] as well as from mixtures of hemicelluloses with different lignocellulosic biomass origins.[8,9] Due to their low oxygen permeability, hemicellulose based films are good oxygen barriers, which is a crucial property needed in certain food packaging applications.[10,11] The recent review by Mikkonen and Tenkanen provides comparative data on the oxygen and water vapor permeability of hemicellulose based films in addition to the mechanical properties of the films.[5] The production of hemicellulose based films were recently coupled to glucose production from the cellulose fraction of the same lignocellulosic feedstock[12] in order to integrate the hemicellulose based films into a multi-product biorefinery scenario.[13]

Using plasticizers and/or other polymers together with hemicelluloses in order to obtain continuous and self-supporting hemicellulose based films with improved mechanical properties is a common approach in the literature. Various plasticizers including glycerol, sorbitol, xylitol, propylene glycol and polyethylene glycol methyl ether have been used together hemicelluloses up to a concentration of 40% to enhance the mechanical properties of the films.[10,14,15] Polymers such as wheat gluten,[16] polyvinyl alcohol,[9] carboxyl methyl cellulose,[17–19] and chitosan[17,18,20,21] were also included into the hemicellulose based films for the same purpose. Furthermore, it was shown that the incorporation of nanofibrillated cellulose at a loading of 5-10% into the hemicellulose based films prevent the formation of cracks, resulting in a continuous film.[22] The type of the lignocellulosic biomass in which the hemicellulose was isolated from also

Table 1 Explanations of the sample codes used for different hemicellulose based films

Sample Code	Polymer Matrix	Additives (w/w %)		
		KAcO	NaCl	Sorbitol
S-0	Xylan with salt	0	0	0
S-10S	Xylan with salt	0	0	10
DeS-0	Desalted xylan	0	0	0
DeS-10S	Desalted xylan	0	0	10
DeS-5S5K	Desalted xylan	5	0	5
DeS-10K	Desalted xylan	10	0	0
DeS-25K	Desalted xylan	25	0	0
DeS-10N	Desalted xylan	0	10	0
DeS-25N	Desalted xylan	0	25	0

plays an important role in the formation of an intact hemicellulose based film.[23]

Corn (maize) is among the most produced agricultural commodities in the world together with sugar cane, wheat and rice.[24] The high corn production volume eventually leads to the accumulation of huge amounts of corn cob, which can serve as an abundant hemicellulose source. With a backbone consisting of xylose monomers, xylan is the major type of hemicellulose in corn cob where it is typically substituted with arabinose groups.[25,26]

Xylans are often isolated from lignocellulosic biomass by alkaline extraction, which relies on the dissolution of hemicelluloses in the alkaline solution.[27] During xylan isolation from lignocellulosic biomass, the alkaline solution containing the dissolved hemicelluloses is neutralized by the addition of acids. Depending on the type of the base and acid used during the xylan isolation process, different salts are formed at this step, which are removed from the medium via techniques such as dialysis and ultrafiltration. The removal of these salts is an important issue for the xylan based film production process since the presence of the salts such as sodium acetate and sodium chloride in hemicellulose based films impairs their mechanical properties.[28,29] The salt removal stage, however, adds an extra step and eventually extra cost to the overall film production process and thus hinders its simplicity and cost effective realization. The present work challenges the conventional way of thinking that salt impurities should be removed from the xylan based polymers prior to film casting by investigating the effect of the salt potassium acetate (KAcO) on corn cob xylan based films. The isolated xylans were first characterized in terms of their film forming capability. The mechanical properties of the films with and without KAcO were determined both in the presence and absence of the plasticizer sorbitol. The effect of KAcO on the films was compared with that of NaCl in order to consider the utilization of a different base and a different acid during the isolation process (NaOH instead of KOH during hemicellulose extraction and HCl instead of acetic acid during the hemicellulose precipitation step) and to compare the effects of the two salts on the films.

Table 2 Yield, molecular weight and compositional data for the salted and desalted xylans isolated from corn cobs

	Xylan Type Salted (S-)	Desalted (DeS-)
Yield (%)[a]	20.4 ± 1.4	15.3 ± 1.3
Average molar mass (g/mol)	25000	40000
Potassium acetate (%)	14.0	1.8
Lignin (%)	12.8 ± 0.5	10.6 ± 0.6
Protein (%)	< 1	< 1
Monosaccharide composition (%)[b]		
Xylose	50.6 ± 4.2	56.4 ± 5.8
Arabinose	31.7 ± 4.6	27.9 ± 3.3
Galactose	13.2 ± 2.6	11.5 ± 2.2
Glucose	4.5 ± 1.2	4.2 ± 1.6

[a] With respect to the initial weight of corn cobs prior to extraction. [b] Ratio of each sugar to total sugars.

Results and discussion

Film forming capability of isolated xylans

Following the extraction of xylans from corn cobs into the alkaline solution, the polymers dissolved in the potassium hydroxide solution were precipitated by the addition of acetic acid and ethanol. In order to remove the KAcO formed during this stage as a result of the reaction between potassium hydroxide and acetic acid, the recovered polymers were partially dissolved in water and re-precipitated by the addition of ethanol. This process was repeated three times in order to remove the salts present together with the precipitated xylans. The polymers obtained this way are referred to as "desalted xylans" throughout the text and denoted with the sample code "DeS". Alternatively, KAcO was retained together with the xylans simply by avoiding the solubilization and re-precipitation steps and the polymers obtained this way are referred to as "salted xylans" and their corresponding sample codes start with "S". Different types of films were cast from these polymers by the addition of KAcO, NaCl and sorbitol. The composition of each type of film and its corresponding sample code is given in Table 1.

As shown in Table 2, the yield was lower for the desalted xylans compared to salted ones. The reduction in the KAcO content of the xylans from 14% to 1.8% contributes to the decrease in the yield while the loss of other small molecules, which did not precipitate in ethanol during the desalting step, should have also contributed to the decrease in the yield. The desalting operation resulted in an increase in the average molar mass while slightly decreasing the lignin content of the xylans. The increase in the molar mass of the polymers at the end of the desalting step is likely due to the loss of smaller xylan molecules during the solubilization and precipitation cycles. The monosaccharide composition of the desalted xylans was

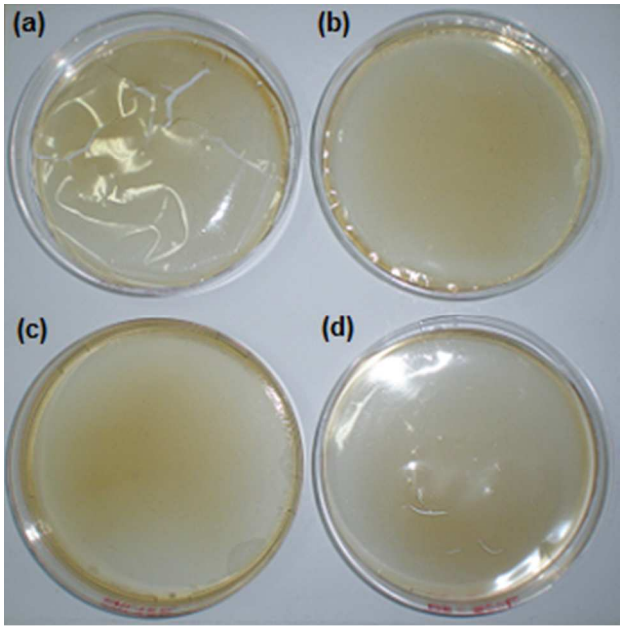

Fig. 1 Appearance of xylan based films with different compositions. (a) Film fragments obtained from desalted xylan (DeS-0), (b) Desalted xylan based film containing 10% KAcO as an additive (DeS-10K). (c) Film obtained from xylan retaining the KAcO formed during the xylan isolation process (S-0). (d) Desalted xylan based film containing 10% sorbitol as an additive (DeS-10S).

similar to that of the salted ones. For both type of polymers, xylose was the dominant monosaccharide followed by arabinose indicating that the hemicellulose isolated from corn cobs was xylan. The effect of the desalting process on the yield, molecular weight, lignin content and monosaccharide composition of the polymers are in agreement with the results recently reported by Egües et al.[29] who observed similar trends when the crude and purified (washed) corn cob xylans were compared.

Once the recovered polymers were dried, film forming solutions were prepared by the dissolution of the xylans in water and the solutions were cast into petri plates. Following the evaporation of water, films or film fragments with an approximate thickness of 0.45 mm were formed as shown in Figure 1. In the case of DeS-0, which was made from desalted xylan, an intact film could not be obtained where large cracks were observed between the film fragments (Figure 1a). Addition of sorbitol (10% w/w on dry basis) facilitated a better film formation but cracks with around 0.5-2 cm length could still be observed in DeS-10S (Figure 1d). Unlike DeS-0, retaining KAcO together with the xylans at the end of the extraction resulted in the formation of intact films without any cracks for S-0 (Figure 1c). Addition of 10% KAcO (w/w on dry basis) into the film forming solution composed of desalted xylan also enabled the formation of the crack-free film DeS-10K (Figure 1b). These observations indicate that KAcO is more effective than sorbitol in terms of facilitating the formation of intact xylan based films and retaining KAcO at the end of the extraction process is useful in terms of film formation.

Mechanical properties of xylan based films

The mechanical properties of polymeric films are of prime importance for various applications including packaging. Ultimate tensile strength (UTS), elongation at break (e_b), elastic modulus (E) and tensile energy to break (TEB) values were determined for each type of film. TEB (also known as toughness) is equal to the area under the stress-strain curve and since this area depends both on the UTS and the e_b of the material, TEB was considered as an overall measure of the films' mechanical properties. As mentioned in the previous section, the desalted xylans did not form intact films and only film fragments could be obtained from this polymer resulting in DeS-0. Despite this issue, the mechanical properties of the fragments from DeS-0 were determined so that the effect of the additives KAcO and sorbitol on the films could be better evaluated.

The mechanical property data for different types of xylan based films are given in Figure 2. Retaining the salt together with xylan during the isolation procedure decreased the UTS of the S-0 films by 2 fold compared to the fragments from DeS-0. As opposed to the lower UTS, the e_b value of the film S-0 was almost 3 times higher compared to the film fragments from DeS-0. These UTS and e_b values are reflected to the TEB values, which were 0.7 MJ/m^3 and 1.7 MJ/m^3 for DeS-0 and S-0, respectively, indicating the beneficial effect of retaining the KAcO together with xylans during the isolation process. The film DeS-10K, which was obtained by the addition of 10% (w/w) KAcO on a dry basis to the film forming solution of desalted xylan, had even a higher TEB value of 3.3 MJ/m^3. On the other hand, addition of 10% sorbitol to obtain the film DeS-10S instead of 10% KAcO resulted in a more than 2 fold decrease in the e_b values while resulting in similar UTS values with that of DeS-10K. These UTS and e_b values eventually resulted in a lower TEB value of 1.2 MJ/m^3 for DeS-10S compared to DeS-10K. This is a quite surprising result since it indicates that KAcO results to an increased plasticization compared to sorbitol, which is one of the most frequently used plasticizers in the hemicellulose based film literature. Furthermore sorbitol appears to work more efficiently as a plasticizer when it is present together with KAcO in the films as it can be realized from the mechanical properties of the film S-10S. S-10S has an e_b value of 20.6%, which is the highest value for e_b among all the films. Presence of 5% (w/w) sorbitol together with 5% (w/w) KAcO in DeS-5S5K also resulted in a higher e_b value (8.1%) than that of DeS-10S (3.3%), which contains 10% sorbitol alone.

The presence of 5% or 10% sodium chloride (NaCl) or sodium acetate (NaAcO) in the xylan based films containing 40% sorbitol was shown to decrease the UTS by approximately 1.5 to 2 fold while e_b values remained almost the same compared to salt-free films.[28] Presence of NaAcO in corn cob xylan based films was also shown to be detrimental for the mechanical properties.[29] As opposed to these results, the present study shows that KAcO not only improves film formation but also the presence of 10% KAcO in the films

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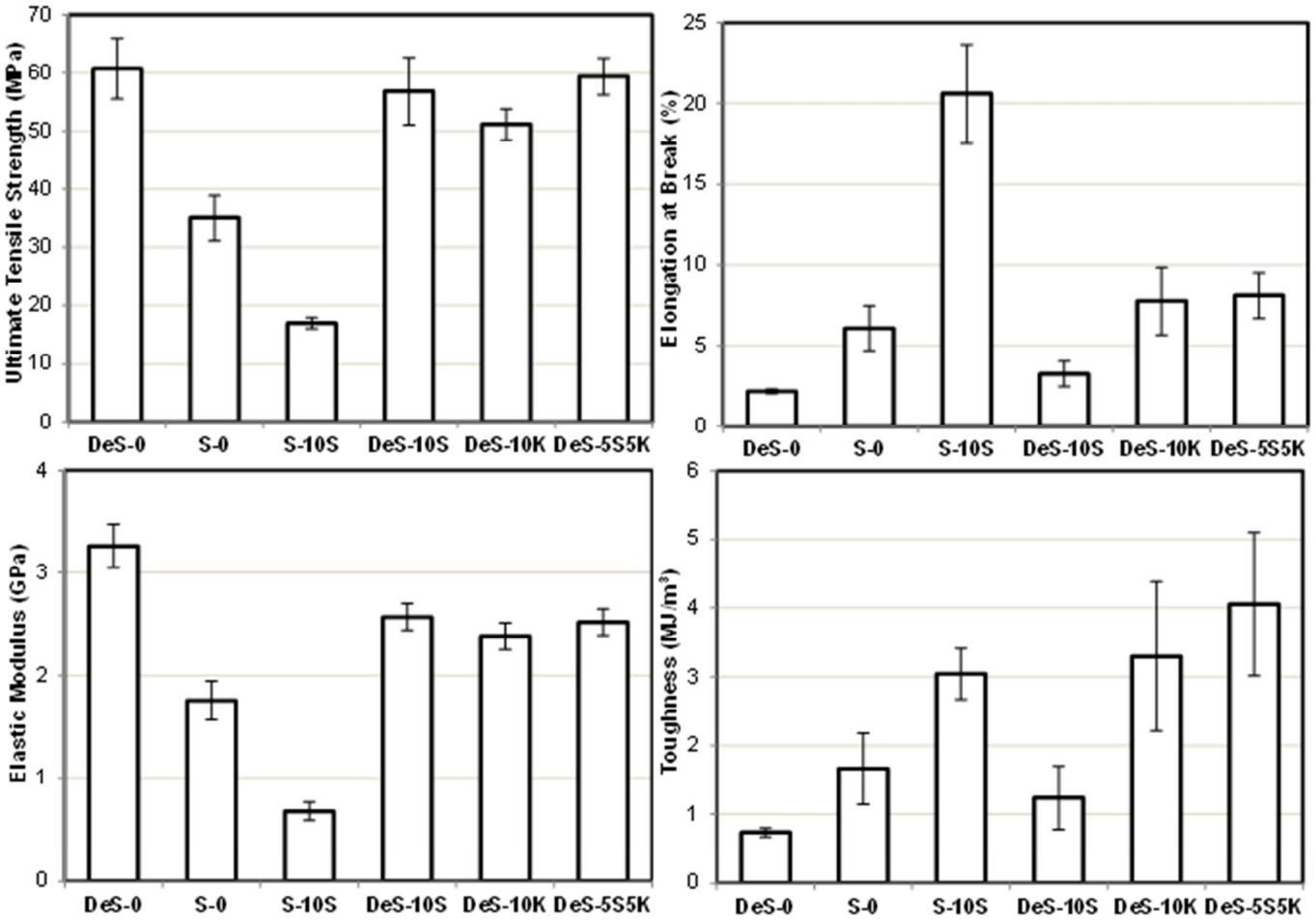

Fig. 2 Mechanical properties of xylan based films in the presence and absence of potassium acetate and sorbitol. Explanations for the sample codes are given in Table 1.

increases the e_b from 2.2% to 7.8% while UTS decreases only slightly compared to DeS-0. Furthermore the presence of 5% KAcO together with 5% sorbitol in the film DeS-5S5K also increased the e_b up to 8.1% while resulting in similar UTS values with DeS-0. Based on their observations regarding the undesired effect of NaCl and NaAcO on the mechanical properties, Mikkonen et al.[28] was right to suggest that xylans should be free of residual salts in order to obtain films with good mechanical properties. However it appears that not all the salts are the same in terms of their effect on the mechanical properties of xylan based films. Although product purity is an important issue, more purity almost always means more cost as this will raise the need for additional purification steps, which is obviously undesirable for the large scale production of the intended commodity. Regarding the hemicellulose based coatings and films, this issue was also emphasized from a different perspective in two recent studies where it was shown that instead of pure xylans, using rather crude hemicellulose fractions obtained from the wood hydrolysate could be advantageous when it comes to achieving lower oxygen permeabilities.[18,19] Based on the mechanical properties of the KAcO containing films in the present study, it appears that it is not always necessary to remove the salts formed during the isolation of xylans from lignocellulosic feedstocks in order to obtain xylan based films with good mechanical properties.

A comparison of the mechanical properties of the film DeS-10K with other xylan based films reported in the literature is provided in Table 3. In a similar manner to Mikkonen et al.[28], Egües et al.[29] have also attributed the poor mechanical properties of films cast from crude corn cob xylan to the presence of NaAcO. As shown in Table 3 (reference no 29), washing the polymers for increased purity was reported to

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Table 3 Mechanical properties including ultimate tensile strength (UTS), elongation at break (eb) and elastic modulus (E) of various xylan based films together with other biodegradable or synthetic polymer films

Reference	Main Polymer Matrix	UTS (MPa)	e_b (%)	E (GPa)	Notes
Present study	Corn cob xylan (DeS-10K)	51.2	7.8	2.4	Contains 10% KAcO as additive.
29	Corn cob xylan	9.0	8.1	0.3	Contains sodium acetate.
29	Corn cob xylan	53.5	7.1	1.7	Polymers used in the above entry were washed (purified) prior to film casting.
28	Oat spelt xylan	~7	~16	-	Contains 10% NaAc or NaCl in addition to 40% sorbitol.
15	Rye xylan	42.5	11.9	2.3	
10	Aspen wood xylan	~40	~2	-	
14	Corn hull xylan	53.8	6.2	1.3	
35	Barley husk xylan	~50	~2.5	2.9	
12	Cotton stalk xylan	51.7	3.1	3.1	
19	Mixed aspen and birch wood xylan	48.6	2.2	2.5	Xylan obtained from wood hydrolysate. Contains 40% carboxymethylcellulose.
30	Birch wood xylan	53.0	1.3	0.6	Xylan obtained from birch wood hydrolysate. Contains 40% carboxymethylcellulose.
31	Polyhydroxybutyrate (PHB)	31	7.3	2.0	
31	Polylactic acid (PLA)	42	7.2	1.4	
32	Corn starch	37	3	1.2	
33	Ethylene vinyl alcohol (EVOH)	~90-200	~90-200	~2.0-3.5	Tested both in the machine and transverse direction.
34	Polypropylene (PP)	151-270	32-150	2.8-5.0	Biaxially oriented polypropylene (BOPP) film. Tested both in machine and transverse direction.

increase the UTS of the films more than 5 fold compared to the films made from unwashed xylans that contained NaAcO.[29] It is also worth noting that both the UTS and e_b values of DeS-10K and the purified film reported by Egües et al. are almost identical where DeS-10K had a higher modulus despite it contained 10% KAcO as an additive. Comparison of DeS-10K with other xylan based films reported in the literature shows that the mechanical properties of these films having different biomass origins are similar to DeS-10K, with the e_b value of DeS-10K being higher up to more than 2 fold in most cases. An interesting point here is that despite containing 40% carboxymethylcellulose (CMC), films made from wood hydrolysate xylans[19,30] had similar UTS and more than 3 times lower e_b values compared to DeS-10K.

The data presented in Table 3 also enable a comparison to be made between DeS-10K and the films obtained from conventional biodegradable polymers in terms of their mechanical properties. DeS-10K appears to have slightly better mechanical properties compared to the films made from polylactic acid (PLA)[31], polyhydroxybutyrate (PHB)[31] or starch[32], particularly in terms of tensile strength. However, the mechanical properties of DeS-10K are lower than those of the popular food packaging films ethylene vinyl alcohol (EVOH)[33] or biaxially oriented polypropylene (BOPP)[34] films particularly in terms of e_b values.

Effect of KAcO and NaCl concentration on the indentation hardness and modulus of the films

In order to understand the effect of KAcO on the film properties more thoroughly, KAcO was added to desalted xylan based films at two different concentrations (10% and 25%) and the indentation hardness and modulus of these films (DeS-10K and DeS-25K) were determined via indentation testing. This procedure was also repeated for the films containing NaCl at the same concentrations with that of KAcO (DeS-10N and DeS-25N), with the thought that the comparative data obtained in this manner could provide more insight about the positive effect of KAcO on the film properties.

The indentation hardness test results show that compared to the additive free DeS-0, increased KAcO concentration in the films resulted in increased penetration depth while opposite was true in the case of NaCl addition to the films (Figure 3). This indicates that the presence of KAcO made the films softer while NaCl resulted in harder films compared to DeS-0, which is also supported by the indentation hardness data given in Table 4. DeS-10N is around 1.6 times harder than DeS-10K, while the gap is increased to 4 fold when the concentration of the salts is

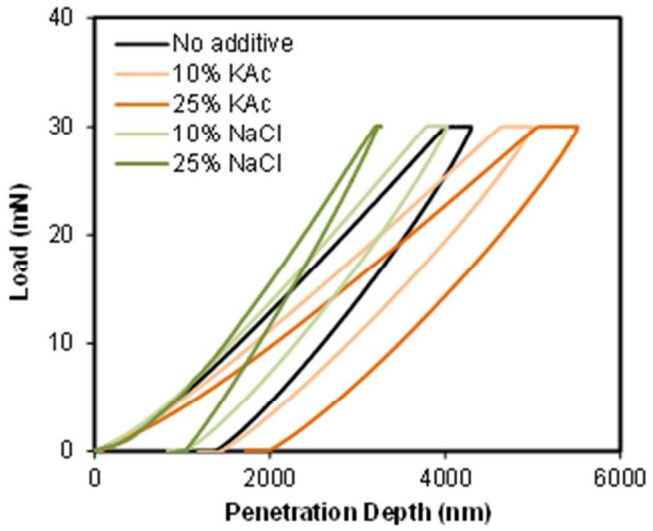

Fig. 3 Load-Displacement curves obtained from the indentation testing of the xylan based films containing different salts as additives at two different concentrations.

increased from 10% to 25%, indicating that the presence of NaCl results to harder films compared to KAcO. Similar to their effect on the film hardness, the presence of KAcO reduced the elastic modulus of the films while increasing the concentration NaCl in the films resulted in increased modulus values. Based on these findings, it is apparent that the xylan based films can give totally different responses to the inclusion of different salts into their structure.

The softening of the films with increasing KAcO concentration implies that the presence of KAcO results to the plasticization of the films. Taking into account that KAcO is a highly hygroscopic salt, which is capable of absorbing significant amounts of moisture from the surroundings, the typical explanation for the plasticization of the films would be related to their water contents. Since water acts as a plasticizer for hemicellulose based films,[10,29,36,37] higher KAcO content in a film could have resulted in a higher water content, which would decrease the hardness of the films by acting as a plasticizer. However as shown in Table 4 the water contents of the films containing KAcO (DeS-10K and DeS-25K) are similar to DeS-0 under the conditions in which the indentation tests took place. Therefore it appears that it is not water that is responsible for the plasticization of the films. It was recently shown that the salt choline chloride itself acts as a plasticizer when it is included into the hydrophilic polymer starch, thereby increasing the flexibility of the starch based films.[38] Considering this finding together with the similar water contents of the films DeS-0, DeS-10K and DeS-25K, a possible explanation for the softening of the films in the presence of KAcO would be that KAcO acts as a plasticizer in the xylan based films, which was not the case for NaCl.

Cross-sectional and surface morphologies of the films containing different salts

Table 4 Hardness, elastic modulus and water content data for xylan based films containing different additives

Film Type	Hardness (MPa)	Elastic Modulus (GPa)	Water Content (%)
DeS-0	172.6 ± 15.0	0.755 ± 0.016	8.9 ± 0.2
DeS-10K	139.5 ± 12.6	0.543 ± 0.009	9.0 ± 0.1
DeS-25K	93.4 ± 5.7	0.469 ± 0.006	9.2 ± 0.1
DeS-10N	222.3 ± 26.4	0.841 ± 0.026	8.4 ± 0.3
DeS-25N	366.6 ± 12.4	1.285 ± 0.011	7.7 ± 0.4

In order to understand the reason behind the different responses of xylan based films to the presence of KAcO and NaCl, the cross-sectional and surface morphologies of the films were characterized by means of scanning electron microscopy (SEM) and optical transmission light microscopy, respectively.

It can be observed from the SEM images shown in Figure 4 that the films DeS-0, DeS-10K and DeS-10N displayed totally different cross-sectional morphologies. Compared to the film DeS-0 (Figure 4a), addition of 10% KAcO resulted in a much more continuous and homogenous appearance for DeS-10K (Figure 4c). Compared to the coarse and irregular appearance of DeS-0, the smoother cross-section of DeS-10K might be a result of the plasticization induced by the presence of KAcO in the film. A quite similar transition from an irregular structure to a smoother one was also observed by Abbott et al., when the salt choline chloride was used in addition to urea in order to plasticize starch.[38] Unlike the smooth and homogenous appearance of DeS-10K, dendrite like shapes were observed in the disordered cross-section of the NaCl containing film DeS-10N (Figure 4d). The bottom portion of DeS-10N's cross-section was swarming with cubic structures probably made up of crystallized NaCl particles, which indicates a serious compatibility problem between NaCl and the polymer matrix. The dramatic differences in the cross-sectional morphologies of DeS-10K and DeS-10N make it evident that different salts may behave differently in a xylan based polymer matrix. Another important observation to be made here is that the similarly homogenous cross-sections of the films S-0 (Figure 4b) and DeS-10K (Figure 4c) indicates that KAcO induces a similar effect on the films whether it is included as an additive to the films or it is retained with the xylans at the end of the isolation process.

The surface morphologies of the films were characterized by means of optical transmission light microscopy and they were in good agreement with the cross-sectional morphologies of the films. As shown in Figure 5, the films DeS-0, DeS-10K and DeS-25K had smooth and homogenous surface morphologies while DeS-10N and DeS-25N had a rough surface. The surfaces of the NaCl containing films were crowded with tiny particles and pathway like shapes were observed between these. The surface images of the films thus further support the claim that different salts might have different effects on the xylan based films.

Water absorption of the films at different surrounding relative humidity values

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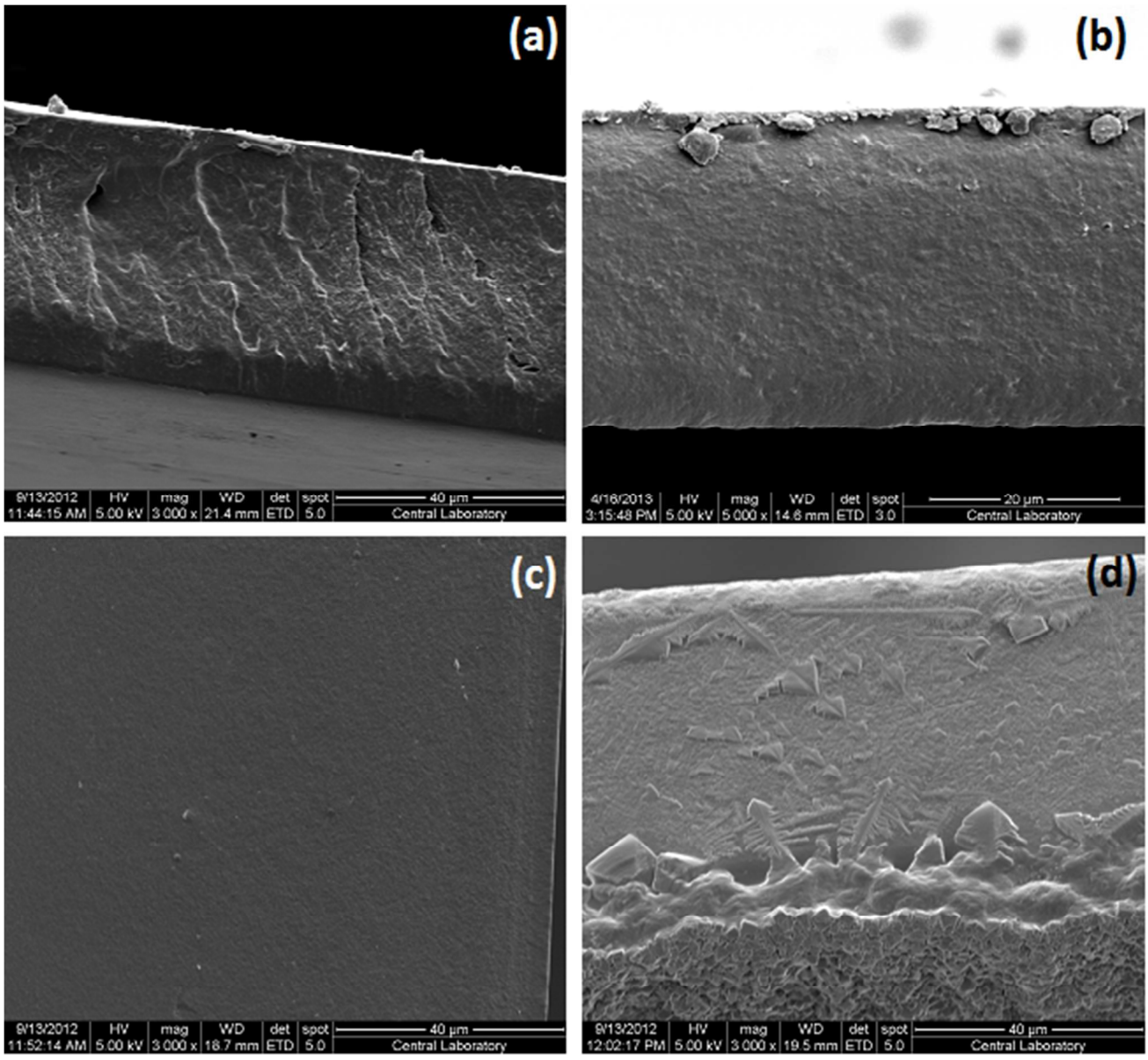

Fig. 4 Cross-sectional appearances of different xylan based films obtained via scanning electron microscopy. (a) DeS-0, (b) S-0, (c) DeS-10K and (d) DeS-10N

Absorbing excessive moisture from the surroundings can be detrimental for the mechanical and barrier properties of a xylan based film due to the hydrophilicity and water solubility of xylans. The oxygen barrier properties of the hemicellulose based films is considered to be one of their key features for food packaging applications and it was previously shown that increasing the surrounding RH also increased the oxygen permeability and transmission rate of hemicellulose based coatings.[18] Taking into account the hydrophilicity of the salts, monitoring the water absorption of the films with respect to surrounding RH is important in order to determine whether the salts could be harmful to the film properties. Therefore films containing salts were compared with the film made from desalted xylan (DeS-0) in terms of their water contents at four different RH values. As shown in Figure 6, all the films had similar water contents at 30% and 50% RH. At 70% RH, all the films again had similar water contents with the exception of DeS-25K, which had around 1.4 times higher water content

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Fig. 5 Optical transmission light microscopy images of the film surfaces containing (from left to right): No additive (DeS-0), 10% KAcO (DeS-10K), 25% KAcO (DeS-25K), 10% NaCl (DeS-10N) and 25% NaCl (DeS-25N).

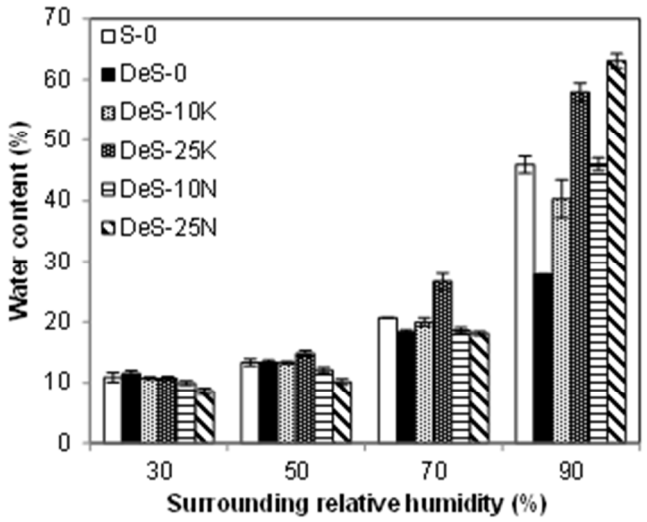

Fig. 6 Water content of the xylan based films with respect to different surrounding relative humidity values.

than DeS-0. When the surrounding RH was increased to 90%, all salt containing films had higher water contents compared to DeS-0 where DeS-25K and DeS-25N had the highest water contents among all the films. At 90% RH, DeS-10K had the closest water content to DeS-0, which was around 1.4 times higher than DeS-0. These results indicate that xylan based films can tolerate the presence of KAcO provided that the RH of the surroundings are not as high as 90%.

Conclusions

As opposed to the current considerations regarding the undesired effects of the salts on the xylan based films, the salt KAcO was shown to be beneficial for the films. KAcO promoted film formation and significantly improved the mechanical properties of the films up to 5 folds in terms of the toughness values when compared to the films obtained from desalted xylans. The enhancement of the mechanical properties was also observed when KAcO was present in the films together with sorbitol. KAcO resulted in the softening of the films, indicating that the plasticization of the films took place in the presence of KAcO as opposed to NaCl. The two salts were found to be different from each other in terms of their compatibility to the xylan matrix. Presence of KAcO in the films led to a smooth and homogenous cross-sectional and surface morphology while dendrites, crystals and a rough surface was observed for the NaCl containing films. These findings show that, depending on the type of the salt, it is not always necessary to get rid of the salts formed during the xylan isolation process in order to obtain xylan based films with adequate properties. Therefore it is possible (and even beneficial) to bypass the purification steps performed in order to avoid the presence of the salts in the films and that would enable the production of xylan based films in a more facile and feasible manner compared to the current state of the art.

Experimental

Isolation of xylans from corn cobs

The procedure of xylan isolation from corn cobs was adapted from previously reported procedures.[39,40] Prior to the alkaline extraction, corn cobs were milled with a Thomas-Wiley mill to a particle size of less than 2 mm. Ground corn cobs (20 g) was swelled in water and filtered with a filtering cloth. The wet corn cob particles were suspended in 10% KOH solution (170 ml) at room temperature with magnetic stirring. At the end of 3 hours the suspension was filtered and centrifuged at 8000 rcf for 10 minutes in order to obtain an alkaline xylan solution devoid of any insoluble particles. The xylans in the solution were precipitated with ethanol-acetic acid solution (500 ml), which had an ethanol:acetic acid volumetric ratio of 10:1. The precipitated polymers were recovered via filtration. In order to remove the salts formed during the precipitation step due to the acid-base reaction between KOH and acetic acid, the recovered polymers were partially dissolved in water (100 ml) followed

by the addition of ethanol (300 ml) into the medium to precipitate the dissolved polymers and this cycle was repeated for three times until the polymers were finally recovered.[40] This last step was not conducted when KAcO was intentionally retained together with the hemicellulose. KAcO content of the isolated polymers was determined via inductively coupled plasma optical emission spectrometry (ICP-OES). The polymers were dissolved in ultra-purified water and the solutions, which were syringe filtered through a 0.22 µm filter, were analyzed with a Perkin Elmer Optima 4300DV ICP-OES instrument to determine the potassium content of the samples.

Characterization of Xylans

The monosaccharide composition of the xylans isolated from corn cobs were determined as described previously[40] where samples were hydrolyzed with sulfuric acid and analyzed via high performance liquid chromatography (HPLC) according to the National Renewable Energy Laboratory (NREL) protocol.[41] A Transgenomics CARBOSep COREGEL-87P column installed to a Shimadzu LC-20A HPLC system was used to analyze the samples at a column temperature of 85 °C by using water as the mobile phase at a flow rate of 0.6 ml min^{-1}. Capillary viscometry was used for the molecular weight determination of xylans[40] by using 4% NaOH solution as the solvent[42] where the corresponding Mark-Houwink equation[43] was used for the calculation of average molar mass. Xylans solubilized in 4% NaOH were also analyzed with a UV/Vis spectrophotometer for the determination of their lignin content according to the absorbance of the solutions at 280 nm where alkali lignin was used as a standard.[40,44] Protein content of the samples was determined via Kjeldahl method.

Preparation of films

A stock solution of the desalted xylans in water was prepared (1 g of xylan / 37.5 ml of water) and the solution was divided equally into separate beakers to have 0.4 g xylan in each beaker on a dry basis. Separate solutions of each additive (KAcO, NaCl and sorbitol) were prepared and mixed with the film forming solutions. On a dry basis, the films contained 10% or 25% of each additive separately. Films also contained 10% KAcO + sorbitol (5% from each) so that a comparison between the films containing the additives together and those containing them separately (films containing 10% of a single additive alone) could be made. For the films obtained from salted xylans, the film forming solutions were obtained by dissolving the xylan (0.4 g) in water (15 ml). The film forming solutions were then poured into plastic petri dishes with a diameter of 9 cm and left to dry at ambient conditions where the temperature and the RH of the surroundings were recorded as 22 ± 1 °C and 47 ± 2% throughout the drying period with a thermo-hygrometer. The films were detached from the petri dishes and used in further characterizations. Each type of film was prepared in duplicates.

Tensile testing

The mechanical properties of the films were determined using a Zwick/Roell Z250 universal testing machine equipped with a 100 N load cell and pneumatic grips. The cross-head speed during tensile testing was 5 mm/min and the initial grip separation distance was 2 cm. Strip shaped tensile testing specimens were obtained from the films using a Zwick ZCP 020 manual cutting press. 5 samples were tested for each type of film except DeS-0 where 3 samples could be obtained due to the limited intact area available. Throughout the tests, the testing room was maintained at a RH of 47% and at 22.5 °C by means of a Tecnair LV climatic room conditioner. Prior to testing, films were conditioned in a climatic chamber (MMM Medcenter Climacell 111) at 50% RH and 23 °C for 24 h.

Indentation testing

The indentation tests were conducted with a CSM Instruments nanoindentation tester. The load was applied to the specimens with a Berkovich tip and the maximum load value was fixed to 30 mN. In order to calculate the hardness and elastic modulus values, the collected data was analyzed by the nanoindentation tester's software using Oliver-Pharr method.[45] The water content of the films was determined from the weight loss that took place upon drying of the films at 105 °C for 24 h. The average temperature and RH of the testing room was recorded as 23 °C and 33%, respectively. The films were conditioned for 2 days under these conditions prior to the test.

Water sorption measurements

Water sorption profiles of different films were determined at four different RH conditions (30%, 50%, 70% and 90% RH). Three samples for each type of film to be tested were placed inside a climatic chamber capable of maintaining the desired RH and temperature. The temperature inside the chamber was maintained at 23 °C throughout the measurements. Samples were stored in the chamber for three days at each RH value and weighted. The water content of the samples at each RH was determined after drying the samples at 105 °C for 24 h.

Characterization of cross-sectional and surface morphology of the films

A Quanta 400F scanning electron microscope (SEM) was used to characterize the cross-sectional morphology of the films. Prior to the SEM analysis, the samples were fractured in liquid nitrogen and samples were coated with gold prior. SEM analysis of the samples was conducted at an accelerating voltage of 5 kV. For the surface characterizations of the films, the samples were placed on glass slides and analyzed with a Leica CM E optical transmission light microscope.

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Notes and references

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