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Abstract

Hemicellulose is a polysaccharide that is widely found in nature but is currently under-utilized and under-valued as a commercial raw material. It would be worthwhile to seek new uses for this material in order to enhance its value. A common type of hemicellulose is xylan, which is found in a number of wood species and in cotton. In this work, we reviewed several modification reactions that have been done with xylan. These include xylan ethers (e.g., cationic and anionic xylan derivatives) and their blends that can be added to paper to improve its strength. Xylan esters have also been made, particularly to render hydrophobic character to xylan, thereby imparting some surfactant properties to the polymer. The strength of hydrophobicity has been found to increase with the length of the alkyl chain. The reaction of xylan with a diisocyanate has produced a polyurethane, which may be used as a bioplastic. These various xylan derivatives increase the structural diversity of xylan and provide additional options for use in sustainable and eco-friendly product development efforts.

Introduction

In recent years, there has been a lot of interest in sustainability and green polymer chemistry (Moshood et al., 2021; Cheng and Gross, 2020). In our laboratories, we have been using agricultural raw materials to produce sustainable, biodegradable, and more eco-friendly products (Cheng et al., 2020; Cheng, 2021). A particular focus is to utilize agricultural byproducts or waste in order to produce more value-added materials. One opportunity is xylan, which is a common type of hemicellulose and one of the most abundant carbohydrates on earth. It can be obtained from plant materials such as wood and cotton. However, it is currently underutilized and undervalued. Our interest is to derivatize, polymerize, or blend them to produce value-added materials. Our preference is to use simple processes and commercially available reagents so that we can minimize the cost of the resulting products.

In the past few years, we have worked with several collaborators to develop a number of new products or reaction methodologies involving xylan. For example, we have made ethers from xylan, such as anionic and cationic ethers (Cheng et al., 2018). We have made esters from xylan, such as xylan acetate and succinate (Biswas et al., 2020). We have produced three hydrophobically modified xylans, using alkenyl succinic anhydride and alkyl ketene dimer (Cheng et al., 2021). We have generated blends of hemicelluloses (Mendes et al., 2017) and xylan derivatives (Cheng et al., 2018), and finally we have made polymers, such as polyurethanes from xylan (Cheng et al., 2017). These various efforts are summarized in Figure 1.



Figure 1. Scheme for the preparation of xylan-derived products

Materials and Methods

Toluene-2,4-diisocyanate (TDI), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), hydrochloric acid, sodium monochloroacetate (MCA) and 1,2-dimethoxyethane (DME) were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide, isopropanol, and dialysis tubings were acquired from Fisher Scientific (Pittsburgh, PA). Ethanol was purchased from Fisher or Decon Laboratories (King of Prussia, PA). Glycidyltrimethylammonium chloride (GTMAC) was obtained from SKW QUAB Chemical, Inc. (Saddle Brook, NJ). Alkyl ketene dimer (AKD, AquapelTM 364) was a gift, courtesy of Solenis, LLC (Wilmington, DE). Both octyl succinic anhydride (OSA) and tetrapropenyl succinic anhydride (TPSA) were bought from Milliken Chemical Co. (Spartanburg, SC). Deuterated dimethylsulfoxide (d₆-DMSO) was purchased from Cambridge Isotope Laboratories (Andover, MA). The starch samples (Cato® 255 and Opti-Pro® 650) were obtained from Ingredion Inc. (Westchester, IL). Beechwood xylan was obtained from either Sigma Aldrich or Lenzing AG (Lenzing, Austria). Cottonseed hull was acquired from a producer of cottonseed oil in Mississippi. The extraction of xylan from cottonseed hull followed the procedure by Goksu et al. (2007) and was described in detail earlier (Cheng et al., 2017).

The xylan samples were subjected to different reactions as shown in Table 1. We deliberately chose reactions that involved 1 or 2 steps. In the case of anionic and cationic xylan, although the reaction contained two steps, they were done in one pot. Experimental details can be found in the original references.

Derivative	# Steps	Solvent	Reagent	Catalyst	Temp (°C)	Refs.
Xylan acetate	1	None	Acetic anhydride	Metal chloride	60-110	Biswas et al., 2020
Xylan succinate	1	DMSO	Succinic anhydride	Metal chloride	60-110	Biswas et al., 2020
Anionic Xylan (CMX)	2	NaOH/IPA	NaOH; NaMCA	None	65	Cheng et al., 2018
Cationic Xylan (QAX)	2	NaOH/DME	NaOH; GTMAc	None	ambient	Cheng et al., 2018
Xylan-ASA	1	DMSO	OSA, TPSA	None	120	Cheng et al., 2021
Xylan-AKD	1	DMSO	AKD	None	90	Cheng et al., 2021
Xylan polyurethane	1	DMSO-LiCl	TDI	None	145	Cheng et al., 2017

Table 1. Summary of the reactions used on xylan

Results and Discussion

Xylan Polyurethanes

Polyurethanes are well known commercial polymers, typically produced by reacting a diisocyanate with a polyol and used as foams, elastomers, bushings, adhesives, surface coatings, and synthetic fibers. The replacement of a petroleumbased polyol with a carbohydrate can potentially reduce cost and make the product more biodegradable. Earlier, we made polyurethanes from sucrose, cyclodextrin, maltodextrin, and sorbitol (Biswas et al., 2015a, 2015b, 2018, 2019). Consistent with our interest in xylan, we also made polyurethanes from xylan, using TDI (Figure 2) (Cheng et al., 2017).



Figure 2. Reaction of xylan with TDI to form a polyurethane

Some representative reactions are shown in Table 2 (Cheng et al., 2017), involving xylan from both beechwood and cottonseed hull. As the amount of TDI was increased, the product was initially soluble and then became partly insoluble because of crosslinking. The first five reactions were done using conventional heat at 145°C for 30 minutes in DMSO. The other five reactions were done using microwave. For microwave, only 3 minutes at 145°C were needed. Thus, the use of microwave saved time and energy.

Table 2. Polyurethane formation	involving xylan and	different levels of	TDI via conver	tional or microwav	e heating
at 145°C in DMSO solvent					

Sample	Xylan	TDI/xylan	Heat mode	Time	obsd tol/xyl	Solubility
_	-	mol ratio		(min)	ratio (NMR)	in DMSO
C1	beechwood	0.11	Conventional	30	0.04	soluble
C3	beechwood	0.23	Conventional	30	0.14	soluble
C5	beechwood	0.36	Conventional	30	0.16	slightly insoluble
C6	beechwood	0.46	Conventional	30	0.22	partly insoluble
C8	cottonseed hull	0.34	Conventional	30	0.30	soluble
M1	beechwood	0.11	Microwave	3	0.06	soluble
M2	beechwood	0.23	Microwave	3	0.10	soluble
M3	beechwood	0.36	Microwave	3	0.14	partly insoluble
M4	beechwood	0.46	Microwave	3	0.25	partly insoluble
M5	cottonseed hull	0.34	Microwave	3	0.24	soluble

Synthesis of Xylan Ethers

The synthesis of ethers from polysaccharides is a two-step reaction but can be done in one pot (Heinze and Koschella. 2005; Biswas et al., 2014). This was the case for the synthesis of carboxymethyl xylan (CMX) and quaternary ammonium derived xylan (QAX) (Figure 3). The first step was the formation of alkali xylan at high pH, using NaOH/water, and an alcohol (isopropanol) or an ether (1,2-dimethoxyethane, DME). In the second step, a suitable derivatizing agent was needed: monochloroacetic acid (MCA) for CMX, and glycidyl trimethylammonium chloride (GTMAC) for QAX. The products were then neutralized with an acid and then precipitated with an alcohol.

Carboxymethyl xylan (CMX), anionic



Quaternary ammonium derived xylan (QAX), cationic



Figure 3. Reaction of xylan to form the anionic derivative (CMX) and the cationic derivative (QAX)

Some CMX reactions are shown in Table 3 (Cheng et al., 2018). As we increased the amount of MCA, the degree of substitution (DS) of the carboxymethyl group increased. The effect of NaOH was more nuanced. It was needed to form the alkali xylan, but once it exceeded a certain level, the exact amount became less important. However, if too much NaOH was used, then more acid would be needed for neutralization during the workup process.

The reaction to form QAX could be done in the same way. A few reactions are shown in Table 4 (Cheng et al., 2018). In this case, we kept the amount of NaOH the same. As the level of GTMAC was increased, the DS for the quaternary group increased, as expected.

No	xylan, g	NaOH, g	MCA ^a , g	molar ratio, MCA ^a /xylan ^b	molar ratio, NaOH/xylan ^b	product, g	DS
C-1	5	5	0.25	0.06	3.3	3.0	0.1
C-2	5	5	1	0.23	3.3	4.75	0.2
C-3	5	0.25	2	0.45	0.165	3.9	0.4
C-4	5	6.25	4.39	0.99	4.125	5.0	0.7
C-5	5	6.25	9	2.04	4.125	> 5	0.9

Table 3. Reaction of xylan with NaOH and monochloroacetic acid (MCA) to form CMX

^a MCA was added as the sodium salt; molecular weight was 116.5.

^b Xylan molecular weight (on the anhydroxylose basis) was assumed to be 132

 Table 4. Reaction of xylan with NaOH and glycidyl trimethylammonium chloride (GTMAC) to form QAX

No	xylan,	NaOH,	GTMAC	molar ratio,	molar ratio,	product,	DS
	g	g	solution ^a , g	GTMAC ^b /xylan ^c	NaOH/xylan ^c	g	
Q-1	5	0.9	7	0.85	0.594	2.3	0.7
Q-2	5	0.9	15	1.83	0.594	2.9	1.4
Q-3	5	0.9	24.6	3.00	0.594	3.4	1.9

^a GTMAC was supplied as 70% solution in water; the above weight was corrected for 0.7.

^b Molecular weight of GTMAC = 151.64.

^c Xylan molecular weight (on the anhydroxylose basis) was assumed to be 132.

One of the applications of polysaccharide derivatives is the paper additive area, particularly to improve paper's dry strength. Some data on the use of CMX and QAX are summarized in Table 5 (Cheng et al., 2018). In Table 5, paper by itself showed a dry strength of about 0.065 MPa. When we added CMX or QAX, the strength was increased to about 0.084 MPa, about a 30% increase. However, when we added the two materials together onto paper (approximately 1:1 in the molar ratio of anionic charges in CMX and the cationic charges in QAX), they formed a polyelectrolyte complex, which increased the strength to about 0.116 MPa (80% increase). Now, commercially starch

is used as a dry strength agent for papermaking. Two starches (Cato 255 and Opti-Pro 650, both from Ingredion Inc.) were included in our testing as shown in Table 5, and their performance was roughly the same as that of CMX and QAX – about 0.080 MPa. Thus, the blend of CMC and QAX gave much better performance and is a superior strength additive.

sample	additive	additive	tensile modulus ³	tensile strength ³
	conc. (%)	weight %	(MPa)	(MPa)
paper control	0	0	4.12±1.42 ^a	0.065±0.004 °
paper + CMX	5	8.2	4.31±2.04 ^a	0.083±0.004 ^b
paper + QAX	5	6.6	4.12±1.92 ^a	0.084±0.006 ^b
paper + CMX + QAX	5 + 5	7.7	6.68±2.64 ^a	0.114±0.003 ^a
$(\text{process } 1)^1$				
paper+CMX + QAX	5 + 5	12.2	4.96±1.23 ^a	0.117±0.005 ^a
$(\text{process } 2)^2$				
Paper + Cato 255	5	7.65	4.12±1.83 ^a	0.079±0.008 ^b
Paper + Opti-Pro 650	5	7.0	5.27±1.88 a	0.081±0.005 ^b

Table 5. Mechanical testing of paper loaded with CMX, QAX, CMX/QAX blend, and starch additives

¹ In process 1, the paper strips were coated consecutively with CMX solution and QAX solution, and then air dried. ² In process 2, the paper strips were coated with CMX solution and dried; they were then coated with the QAX solution and then dried in air.

³ Average \pm SD (n= 7) for each treatment. Data in each column with the same superscript letter indicate that the treatments are not significantly different at \pm =0.05 in the analysis of variance.

Synthesis of Xylan Esters

Cellulose esters (like cellulose acetate) are important commercial products (Koschella et al., 2006). Like cellulose acetate, xylan acetate can be made with acetic anhydride and strong mineral acid. It has been noted (Fundador et al., 2012, Stepan, 2013) that xylan acetate has thermoplastic properties, and it can potentially serve as an eco-friendly and sustainable replacement for petroleum-based plastics in film, fiber, and laminate applications. As alternative synthesis of xylan esters, we looked at the acylation of xylan through the use of selected Lewis acids. Five metal halides were studied (AlCl₃, FeCl₃, SbCl₃, SnCl₂, ZnCl₂) and compared to iodine as acylation catalysts (Biswas et al., 2020). The products made included acetylated and succinylated xylan. All the metal chlorides were active as catalysts for esterification, but their activities differed, particularly with respect to temperature. Through the choice of a suitable catalyst, xylan esters with different degrees of substitution were made. A possible mechanism is shown in Fig. 4, where the metal cation complexes with the anhydride and facilitates the acylation of xylan.



Figure 4. Possible mechanism for the metal chloride-catalyzed acetylation of xylan; R = xylan, M = metal ion

Thus, in our work (Biswas et al., 2020), we showed that the Lewis acids used were capable of catalyzing the esterification reaction, but the effect varied with different metal ions. The six Lewis acids showed the following approximate reactivity trend (at 1 mL Ac₂O, and 0.05 g catalyst):

$$AlCl_3 > FeCl_3 > iodine > ZnCl_2 > SbCl_3 > SnCl_2$$

For AlCl₃ and FeCl₃, an acetyl DS of 2 could be accomplished at a reaction temperature of 100°C. For the other Lewis acids, a higher temperature (110°C) was needed to achieve higher DS levels. We also showed that xylan acetate with lower DS values could be made by dialing back on the temperature or amount of catalyst used.

For xylan acetate, the reaction was carried out with xylan, acetic anhydride, and the Lewis acid; no solvent was needed. However, for xylan succinate, DMSO was needed as a solvent because the melting point of succinic anhydride was 120°C. As in the case of xylan acetate, different succinate DS values could be obtained for xylan succinates by using different catalysts or different reaction conditions. An advantage of this approach is the avoidance of strong mineral acids for xylan esterification. Since the handling of strong mineral acids can be hazardous, alternative and safer catalysts (like Lewis acids) are preferable.

Hydrophobically Modified Xylan

A hydrophobically modified polymer typically contains polymeric chains that are water-soluble with hydrophobic side chains or end groups. In aqueous solutions, the hydrophobes can impart an interfacial or surfactant-like property to the water-soluble chains and can also aggregate with one another, giving rise to pseudo-plastic rheological behavior. Many hydrophobically modified polymers are used for rheology modification, enzyme immobilization and drug encapsulation (Glass, 2000; Cunha and Gandini, 2010a, 2010b).

Because xylan is water-soluble, we have derivatized xylan with three hydrophobic reagents (AKD, OSA, and TPSA) (Fig. 5). Structurally, OSA and TPSA belong to the general class of alkenyl succinic anhydrides (ASAs). AKD and ASA are known as sizing agents for paper (Reynolds, 1989). In our work, AKD, OSA, and TPSA all reacted with xylan in DMSO at high temperatures (Cheng et al., 2021). The xylan-AKD derivatives could be made at 90°C, using dimethyl sulfoxide as solvent and 4-dimethylaminopyridine as promoter. Samples with degrees of substitution (DS) up to 0.006 were produced. The xylan-ASA derivatives were synthesized at 120°C in dimethyl sulfoxide with DS up to 0.105–0.135. The xylan-AKD and xylan-TPSA adducts had not previously been reported, and these products were new. For each derivative, several samples with different DS values were made. From the turbidity observations, the strength of hydrophobicity follows this trend: AKD > TPSA > OSA. In other words, the more alkyl carbons the xylan derivative contained, the more hydrophobic it became.

In the development of formulations involving hydrophobic polymers, it is known that the chain length has a significant impact on the desired end-use functions. For example, hydrophobically modified hydroxyethyl celluloses with different hydrophobe lengths and types exhibit different adsorption to acrylic latex, resulting in different paint behavior. Thus, it is helpful to have different types of hydrophobically modified polymer available, and the best material can then be selected for a given application. The two new hydrophobically modified xylans developed by us may be useful additions to the family of hydrophobically modified polymers in this context.



Figure 5. Reactions of xylan with AKD, OSA, and TPSA, and the reaction products

Polymer Blends involving Hemicelluloses

Polymer blending is a useful methodology to formulate new products from two or more materials. The blending of a cationic xylan and an anionic xylan for paper applications has been described above (Table 5). Moreover, we have previously reported the blending of two uncharged (electrically neutral) hemicelluloses (Mendes et al., 2017); these blends permit a wider range of properties to be accessible than each hemicellulose alone.

Summary

Our research goal with respect to xylan was to develop new xylan-based products that could enhance the scope of its applications while keeping the reactions relatively easy to implement and using commercially available reagents. We designed several types of xylan-related materials, such as anionic and cationic ethers, xylan esters, hydrophobically modified xylans, xylan polyurethanes, and blends. These various xylan derivatives increase the structural diversity of xylan and provide additional opportunities for use in sustainable and eco-friendly product development efforts.

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