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Preparation and characterization of arabinoxylan esters and arabinoxylan ester/cellulose ester polymer blends

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Abstract

A water-soluble, high molecular weight arabinoxylan was isolated from corn fiber. This arabinoxylan was a highly branched and complex polysaccharide composed of xylose, arabinose, galactose, glucuronic acid and glucose. Treatment of this arabinoxylan with a C2–C4 aliphatic anhydride using methanesulfonic acid as a catalyst or trifluoroacetic anhydride as a promoter rapidly and conveniently provided the corresponding arabinoxylan esters. The arabinoxylan esters were isolated as high molecular weight, amorphous solids with glass transition temperatures ranging from 61 to 138 °C. The arabinoxylan esters are soluble in a range of solvents and can tolerate significant amounts of water as a co-solvent. The arabinoxylan esters are thermally stable to near 200 °C but undergo significant and rapid thermal degradation when heated above the onset of thermal degradation. Optically clear films of arabinoxylan acetate and cellulose acetate were prepared by casting films from common solvents. Thermal analysis of these blends indicated that the blends were comprised of a single phase or two phases depending upon the composition of the solvent, solvent concentration, and rate of evaporation of the solvent.
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1. Introduction

In many respects, most plants can be viewed as being a natural composite material comprised of cellulose, hemi-cellulose, and lignin. However, these composites have no solubility in common solvents and cannot be processed as a thermoplastic. Hence, these composites are typically separated into individual components of differing degrees of purity depending upon the application. Both cellulose and lignin have been studied extensively and they have found utility in a wide variety of industrial applications. The vast majority of cellulose and lignin used in industrial applications originates from wood. Plant hemicellulose, which comprises roughly 25–35% of plant materials depending upon the source (Prade, 1996), has found relatively little industrial utility. The reported industrial applications for plant hemicellulose include their use as viscosity modifiers, gelling agents, tablet binders, or wet strength additives (Whistler, 1993). Recently, there has been interest in the use of hemicellulose as a nutraceutical (Sugawara, Suzuki, Totsuka, Takeuchi, & Ueki, 1994), in chiral separations (Okamoto, Kawashima, & Hatada, 1984), and as an HIV inhibitor (Magerstaedt et al., 1991). More often, the hemicellulose is hydrolyzed to a mixture of monosaccharides which can be converted to chemicals such as furfural, erythritol, or xylitol or used as fermentation feedstock for making chemicals such as ethanol or lactic acid (Heikkila et al., 2001).

Hemicellulose is generally defined as being polysaccharides that can be extracted by water or aqueous alkali from plant tissue (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Whistler, 1993). Hemicellulose can be comprised of a wide variety of monosaccharides including xylose, arabinose, glucose, galactose, mannose, fucose, glucuronic acid, and galacturonic acid depending upon the source. The most common hemicelluloses, largely found in hardwood or annual plants, are comprised of a 1,4-β-D-xylopyranosyl main chain with a varying number of side chains based on L-arabinofuranosyl, 4-O-methyl-D-glucuronopyranosyl,

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D,L-galactopyranosyl, or D-glucuronopyranosyl units. Hemicellulose isolated from hardwood and annual plants differ from one another. The main hemicelluloses found in hardwood are partially acetylated (4-O-methyl-D-glucuronopyranosyl)-D-xylans and these are often simply called xylans. The hemicelluloses found in annual plants such as maize, rice, oats, sunflower, rye, barley, and wheat, are generally more structurally diverse and complex. These plant hemicelluloses have a 1, 4-β-D-xylopyranosyl main chain that can be heavily branched with Xylp- Araf-, Galp- mono-, di, and trisaccharide side chains. These plant hemicelluloses can be neutral or acidic depending on if they contain 4-O-methyl-D-glucuronopyranosyl or D-glucuronopyranosyl substituents. Generally, the two predominant monosaccharides in these annual plant hemicelluloses are xylose and arabinose and they are thus termed arabinoxylans.

Isolation of hemicellulose from wood and annual plants has been investigated for many years (Ebringerova & Heinze, 2000). The pulping industry would seem to be a most viable source of hemicellulose. In reality, along with the lignin matrix, the hemicellulose is partially or completely degraded during the pulping process (Ebringerova & Heinze, 2000). Alternative methods exist for extraction of wood hemicellulose, but they are not likely to be reduced to commercial practice in the near future (Glasser, Kaar, Jain, & Sealey, 2000). Because wood hemicellulose cannot be easily isolated in polymeric form by conventional pulping methods, the material properties of these polysaccharides have not been fully defined and exploited. Annual plants have proven to be a rich source of hemicellulose (Ebringerova & Heinze, 2000). However, many of the early methods developed for extraction of hemicellulose from annual plants were not efficient and did not cleanly provide the targeted polysaccharides. Despite intensive early investigations, a simple commercial process for extraction and isolation of annual plant hemicellulose has never been completely realized.

Worldwide, there has been recent and extensive dialogue in the governmental, business, and scientific communities concerning the development of a sustainable economy based on sustainable resources, which has prompted different organizations to once again examine annual plants or grains as sources of hemicelluloses (Amon et al., 1998). Wood as a source of hemicellulose continues to be a raw material of interest, but other materials, such as wheat bran, corn fiber, and rice bran, have attracted significant attention. Significant effort has been expended in developing more efficient methods that would enable efficient isolation of hemicellulose from a variety of plant sources (Doner & Hicks, 1997; Ebringerova & Heinze, 2000; Gabrielii et al., 2000).

While preparation of ether derivatives of arabinoxylans is relatively straight forward (Buchanan et al., 2002; Fang, Fowler, Tomkinson, & Hill, 2002; Jain, Sjostede, &Glasser, 2001), synthesis of fully substituted, high molecular weight

ester derivatives is not. The classical method for preparing ester derivatives of this type entails the use of base catalysis and polar solvents such as formamide (Carson & Maclay, 1946; Carson & Maclay, 1948; Renard & Jarvis, 1999). The reported reaction times were typically very long and it was very difficult to obtain complete esterification of the various types of hemicelluloses. Recently, Sun has reported on the esterification of wheat straw hemicellulose dissolved in LiCl/DMF using DMAP as a base catalyst (Fang et al., 2000). Presumably, these methods were developed out of concern that acid catalyzed esterification of these hemicelluloses would lead to cleavage of acid sensitive glycosidic linkages and loss in molecular weight.

With this background, we recently disclosed a method for the isolation of a highly purified, high molecular weight arabinoxylan from corn fiber (Buchanan et al., 2002). Our interest in this polysaccharide was three-fold. The properties of the parent arabinoxylan were naturally of interest. We were also very interested in preparing ester and ether derivatives of this polysaccharide and examining their physical properties. Our third interest was in composites of arabinoxylan esters with cellulose esters. In this account, we describe the methods we have developed for esterification of arabinoxylan from corn fiber, characterization of these new polysaccharide derivatives, and our surprising finding that cellulose esters and these arabinoxylan esters can form compatible blends.

2. Materials and methods

2.1. Materials

The arabinoxylan was obtained by our previously described method (Buchanan et al., 2002). Carbohydrate analysis indicated that the arabinoxylan was composed of 47.2 mol% xylose, 33.4 mol% arabinose, 11.6 mol% galactose, 6.6 mol% glucuronic acid, and 1.2 mol% glucose. Cellulose acetate (degree of substitution (DS) = 2.47), cellulose acetate butyrate ($DS_B = 1.72$, $DS_A = 1.03$), acetic, propionic, and butyric anhydrides were obtained from Eastman Chemical Company. The purity of each anhydride was greater than 99.9%. Methanesulfonic acid (MSA) and trifluoroacetic anhydride (TFAA) were obtained from Aldrich and were used as received.

2.2. Methods

Modulated differential scanning calorimetry (MDSC) curves were obtained using a Universal V2.4F TA spectrometer. First scan MDSC heating curves were obtained by heating at $5°\,min^{-1}$ to the desired temperature. Second scan MDSC heating curves were obtained by first cooling the sample after the first heating in the instrument over ca. 17 min. The sample was then heated at $5°\,min^{-1}$ to the desired temperature.

Differential scanning calorimetry (DSC) curves were obtained using a Universal V3.1E TA spectrometer. The DSC heating curves were obtained by first heating at 20° min^{-1} to the desired temperature followed by cooling the sample in the instrument over ca. 17 min. The 2nd scan DSC heating curves were then obtained by heating the sample at 20 ° min^{-1} to the desired temperature.

The thermal stability of the arabinoxylan and arabinoxylan esters were determined by thermogravimetric analysis (TGA) using a Universal V3.1E TA spectrometer. Typically, the sample was heated under nitrogen from 20 to 400 °C at 20 ° min^{-1}.

Molecular weights were determined using a Waters Model 150C high temperature gel permeation chromatograph equipped with an RI detector. For arabinoxylan, the operating temperature was 25 °C and the mobile phase was 0.001 M NaOH on a PL-gel aqueous column. The molecular weights are reported relative to pullulan standards. For the arabinoxylan esters, the operating temperature was 40 °C and the mobile phase was NMP with 1 wt% acetic acid on a PL-gel mixed bed column. The molecular weights are reported relative to polystyrene equivalents.

NMR spectra were collected using a JEOL Model Eclipse + 600 NMR spectrometer. The sample (10 mg) was dissolved in 0.5 ml of DMSO-d_6 containing TFA-d and added to a 5-mm OD NMR tube. The spectra were collected at 80 °C. Chemical shifts for the proton NMR spectra were referenced to DMSO-d_6 at 2.49 ppm.

2.2.1. Isolation of hemicellulose B

Corn fiber (466.7 g, dry wt.) and distilled water (4000 ml) were added to a 5000 ml 3-necked round-bottomed flask equipped with an overhead stirrer, a condenser, and a thermometer attached to a Therm-O-Watch temperature controller. The pH of the mixture was adjusted to a pH of 8.5 with NaOH. The mixture was heated with stirring to 80 °C and was held at this temperature with stirring for approximately 15 min. Amylase (GC 521, 16.7 ml, Genencor, Palo Alto, CA) and protease (Protex 6L, 10.0 ml, Genencor, Palo Alto, CA) were added to the mixture simultaneously. The mixture was stirred for 2.5 h at 80 °C with no attempt to control pH. The mixture was filtered through a 1 mm pore size Buchner funnel. The retained fiber was washed with eight 2000 ml portions of hot water (45–55 °C) followed by a single 2000 ml wash with distilled water. After drying at 60 °C in a vacuum oven, 229.1 g of destarched, proteolyzed corn fiber was obtained.

Destarched, proteolyzed corn fiber (168 g dry weight) and 2.4 l of 0.83 M NaOH were added to a 5 l 3-necked round-bottomed flask equipped with an overhead stirrer, a condenser, and a thermometer attached to a Therm-O-Watch temperature controller. The mixture was stirred for 2 h while maintaining the reaction temperature between 94–99 °C. The heterogeneous reaction mixture was filtered through a 70–100 μm glass frit funnel that was kept in an oven at 63 °C. The solids were washed with 1 l of H$_2$O

followed by a second wash of 1.5 l H$_2$O. The combined filtrate was concentrated to 600 ml before adding 2.9 l of acetic acid, which gave a white precipitate. The solids were allowed to settle for 3 h before all but ca. 300 ml of the solution was decanted from the solids. The hemicellulose was then isolated by filtration and washed with EtOH. After drying, 67.4 g of arabinoxylan was obtained as a mixture of hemicellulose A and B.

A solution of corn fiber arabinoxylan containing both insoluble hemicellulose A (2.1 wt% by GPC) and soluble hemicellulose B (97.9 wt%) was prepared by dissolving 30 g of arabinoxylan in 1385 g of H$_2$O at pH 7. The solution was centrifuged at 3100×g for 1 h. The solution was decanted from the solids and the solids were washed extensively with H$_2$O. The liquids were filtered through a 3.5–5.0 μm glass frit funnel before concentrating to a 7.2 wt% solids solution. A portion (56.6 g) of the solution was poured slowly into 350 ml of glacial acetic acid. The resulting slurry was stirred for 30 min then transferred to a 40–50 μm glass frit funnel. The liquids were allowed to drain before adding fresh (350 ml) glacial acetic acid. After removing the liquids, the solids were washed with three 200 ml portions of EtOH before drying at 80 °C under vacuum, which gave 3.4 g (83% recovery) of hemicellulose B as a white solid.

The hemicellulose A separated above by centrifugation was extracted in a soxlet extractor with pH 7 H$_2$O for 7 days. The remaining solids were then dried at 80 °C under vacuum for 48 h. This provided 0.62 g (2.1 wt % based on the weight of starting arabinoxylan) of a tan solid.

2.2.2. General procedure for preparation of arabinoxylan acetate

To 55.4 g of aqueous arabinoxylan (Hemi B, 7.2 wt% arabinoxylan) was slowly added 350 ml of glacial acetic acid while stirring. The white precipitate that formed was allowed to stand for ca. 45 min before the liquids were decanted. Fresh glacial acetic acid was added (3×100 ml), and the solids were allowed to stand in the acetic acid for 5–10 min before decanting the liquids. After the 3rd exchange, the acetic acid wet white solids (51 ml of acetic acid) were transferred to a 100 ml 3-neck round bottom flask equipped for mechanical stirring. To the acetic acid wet arabinoxylan was added 20 ml of acetic anhydride. The flask was immersed in a preheated 50 °C oil bath and the slurry was stirred for 10 min before adding 45 mg of MSA in 1 ml of glacial acetic acid. Within 10 min, all of the solids were dissolved in the reaction media except for a few small particles. One hour after adding the MSA, the homogeneous reaction mixture was filtered through a 10–15 μm glass fritted funnel. The filtrate was then poured into 250 ml of 8 wt% aqueous acetic acid while stirring vigorously followed by 200 ml of deionized water. The solids were isolated by filtration and washed with deionized water until the filtrate reached a pH of 7. The solids were then dried at 60 °C and 50 mm Hg. This provided 4.71 g of a white solid.

Proton NMR revealed that the solid was an arabinoxylan acetate having a degree of substitution of 2.11.

2.2.3. General procedure for preparation of arabinoxylan propionate or butyrate

To 57.1 g of aqueous arabinoxylan (Hemi B, 7.2 wt% arabinoxylan) was slowly added 350 ml of glacial acetic acid while stirring. The white precipitate that formed was allowed to stand for ca. 30 min before the liquids were decanted. Fresh glacial acetic acid was added (100 ml), and the solids were allowed to stand in the acetic acid until the solids hardened before decanting the liquids. Butyric acid was then added to the solids (3×100 ml) and the solids were allowed to stand in the butyric acid for 5–10 min before decanting. After the 3rd exchange, solids were transferred to a 40–60 μm glass fritted funnel and the solids were washed with butyric acid (10×100 ml). Each time the liquids were allowed to slowly drain before applying a vacuum to remove the remaining excess liquids. The butyric acid wet white solids (31 ml of butyric acid) were transferred to a 100 ml 3-neck round bottom flask equipped for mechanical stirring. To the butyric acid wet arabinoxylan was added 31.7 ml of butyric anhydride. The flask was immersed in a preheated 50 °C oil bath and the slurry was stirred for 10 min before adding 47.5 mg of MSA in 5 ml of butyric acid. After 1.5 h, no reaction was evident so the reaction temperature was increased to 60 °C. After 2.7 h total reaction time, an additional 45.9 mg of MSA in 1 ml of butyric acid was added to the reaction. Four hours after beginning the reaction, the solution viscosity was observed to increase significantly. The reaction was allowed to proceed for 14.5 h before the reaction mixture was filtered through a 10–15 μm glass fritted funnel. The filtrate was then added to an equal volume of MeOH. Water (100 ml) was then added slowly to the MeOH containing filtrate, which gave a white sticky solid. The liquids were decanted and the sticky solid was taken up in 80 ml of MeOH and 120 ml of acetone. Water (100 ml) was then added slowly which gave a slightly tacky white solid. This solid was taken up in 125 ml of acetone and poured into 80/20 water/MeOH giving a hard white solid. The solids were washed with 1.5 l of 80/20 water/MeOH before drying at 60 °C and 50 mm Hg. This provided 4.69 g of a white solid. Proton NMR revealed that the solid was an arabinoxylan butyrate having a degree of substitution of 2.01.

2.2.4. Preparation of arabinoxylan ester/cellulose ester blends

Blends were prepared by weighing the components into a jar. In the case where acetone was the solvent, acetone was added to give a 10 wt% solids solution. The jar was capped and placed on a roller until all solids were dissolved. Water was then added to acetone solution to the desired concentration. In the case involving 85/15 acetone/MeOH and 90/10 THF/MeOH, the solvent mixture was prepared

and added to the weighed solids to give a 10 wt% solids solution. Films were prepared either by pouring the solution into a dish, which was capped to allow slow evaporation of the solvent, or by using a 15 mil draw-down blade to prepare thin films (0.03 mm).

3. Results and discussion

Recently, we described in detail the process we developed for isolation of the arabinoxylan, cellulose, and lipid fractions from corn fiber (Buchanan et al., 2002). Briefly, the process (Fig. 1) for isolation of the arabinoxylan involves first treating the corn fiber with a combination of amylase and protease to remove the starch and protein. Treatment of the destarched, proteolyzed corn fiber with 1–1.5 M NaOH at 70–90 °C results in the solubilization of the arabinoxylan, which can be separated, from the cellulose component by filtration. The aqueous arabinoxylan solution is concentrated, preferably by ultrafiltration as this also lowers the salt concentration, before precipitating with acetic acid. The arabinoxylan is isolated by filtration and washed with an alcohol to remove residual water and acetic acid. The arabinoxylan isolated by this process is comprised of two components, hemicellulose A and B. Hemicellulose
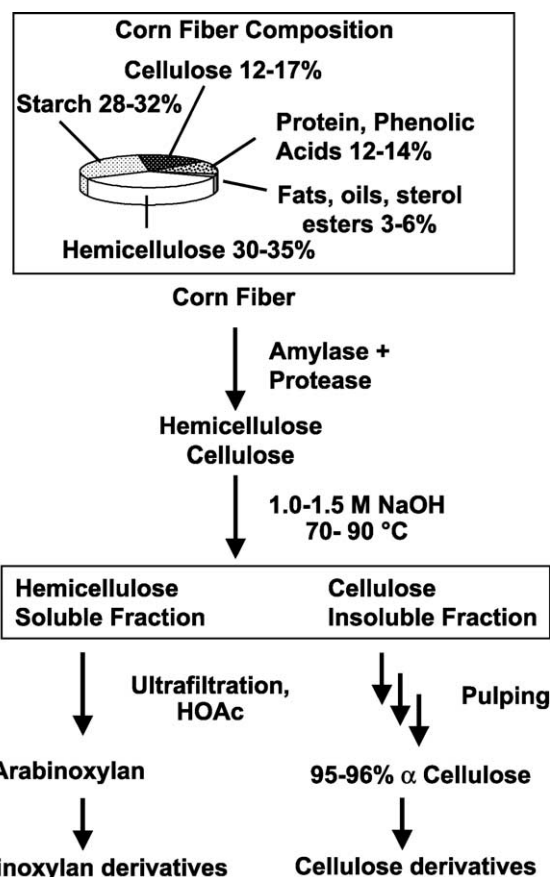

Fig. 1. Composition of corn fiber and the basic scheme for the separation of arabinoxylan from corn fiber.

B, the desirable component, is a high molecular weight polysaccharide ($>500,000$) soluble in water over the entire pH range. Hemicellulose A is a lower molecular weight polysaccharide ($<25,000$) that is soluble in water only at a pH greater than ca. 10. From our process, the arabinoxylan we isolate typically contains about 2–5 wt% hemicellulose A. However, hemicellulose A can be readily separated from hemicellulose B by taking advantage of the differences in solubility at pH 5–7 (vide supra).

3.1. Esterification of corn fiber arabinoxylan

Acid catalyzed esterification of corn fiber arabinoxylan potentially offers the most efficient and cost effective means for preparing arabinoxylan esters. Consequentially, we examined the esterification of corn fiber arabinoxylan using H_2SO_4 and MSA as acid catalysts in the esterification of polysaccharides. We also examined TFAA as a 'promoter or impeller' in the esterification of corn fiber arabinoxylan (Buchanan & Parker, 1991; Morooka, Norimoto, Yamada, & Shiraishi, 1984). From our prior experiences, we know MSA can be a very effective catalyst in esterification of polysaccharides and, at moderate temperatures, MSA promotes little molecular weight loss. Although widely used in the esterification of polysaccharides, H_2SO_4 can cause rapid loss of polysaccharide molecular weight. It has been shown that TFAA promoted esterification of cellulose provides very high molecular weight cellulose esters (Buchanan & Parker, 1991). Additionally we have also examined the impact of activation on the esterification of corn fiber arabinoxylan. As noted above, after extraction into a basic aqueous medium, we isolate corn fiber arabinoxylan by precipitation with acetic acid. Relative to dried corn fiber arabinoxylan, our anticipation was that this acetic acid wet arabinoxylan would be more easily esterified.

Figs. 2 and 3 provide representative examples of the changes in molecular weight and carbohydrate composition during prolonged MSA and H_2SO_4 catalyzed acetylation of corn fiber arabinoxylan. In both experiments, the first data point was taken at the point at which the arabinoxylan was fully soluble in the reaction medium. The observed changes in molecular weight and carbohydrate composition are due to prolonged exposure to the reaction conditions. In the case of MSA, there was essentially no change in carbohydrate composition after 53.5 h of exposure to the reaction conditions. The molecular weight of the arabinoxylan acetate (AXA) at 3 h was 415,000 and this dropped to 323,000 after 10.5 h. From 10.5 to 53.5 h, the molecular weight only decreased from 323,000 to 265,000. In contrast, with H_2SO_4, the molecular weight initially determined at 2 h for the AXA was 172,000. The molecular weight of the AXA in the H_2SO_4 catalyzed reaction declined very rapidly reaching 48,900 after 10 h. Interestingly, even with prolonged exposure to the reaction medium over the range of reaction temperatures and concentrations of H_2SO_4 examined, the molecular weight of the AXA plateaued near 35,000 (Fig. 4). With regard to the carbohydrate composition of the AXA prepared by H_2SO_4 catalysis, the mol % arabinose was observed to decrease while the percentage of xylose and galactose remained essentially constant. The initial ratio of xylose/arabinose increased from 1.7 to 2.9. This would suggest preferential cleavage of the arabinose from the arabinoxylan. Although the data is not provided in this account, characterization of the crude filtrate after isolation of the AXA by precipitation revealed that the isolated material was almost exclusively a mixture of α- and β-arabinofuranoside tetraacetate.

The data contained in Table 1 demonstrate the importance of activation and other aspects of the esterification of corn fiber arabinoxylan. Entry 1 illustrates the MSA catalyzed esterification of non-activated, dried corn fiber
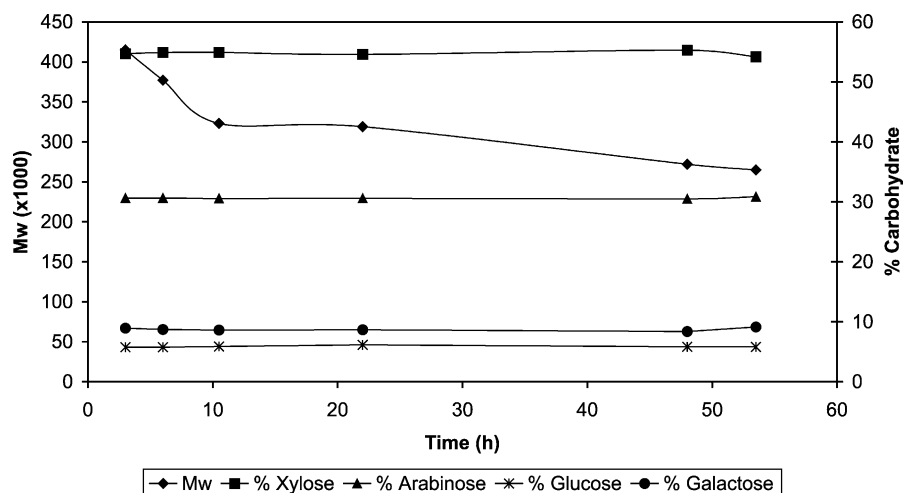

Fig. 2. The change in weight-average molecular weight and the carbohydrate composition over an extended time period during acetylation of corn fiber arabinoxylan using 0.65 wt% MSA at 25 °C.
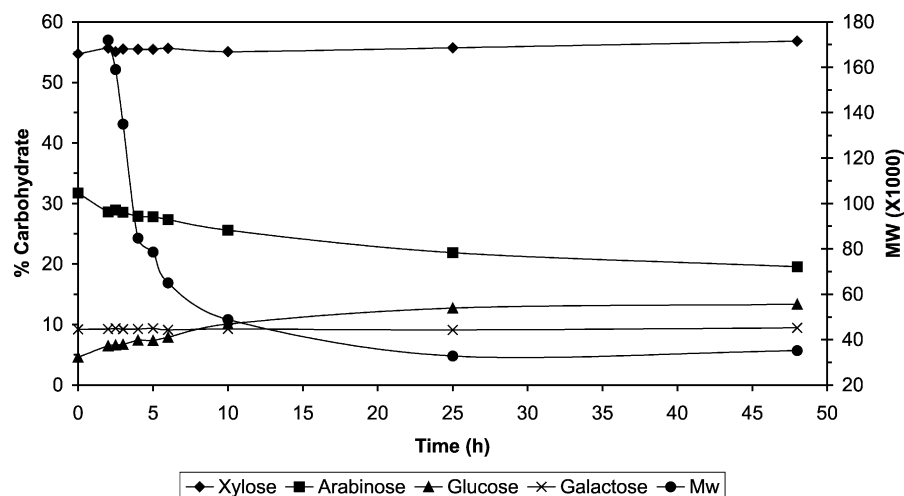
Fig. 3. The change in weight-average molecular weight and the carbohydrate composition over an extended time period during acetylation of corn fiber arabinoxylan using 0.65 wt% H_2SO_4 at 35 °C.

arabinoxylan. Relative to the reaction of acetic acid activated arabinoxylan with acetic anhydride, which requires only 1 h for complete esterification (entry 6), significant solids (48 wt% of starting material) were present after a reaction time of 4.5 h. After removing the unreacted solids, the AXA was isolated by precipitation. Characterization of the AXA revealed that the molecular weight and the DS were comparable to that obtained from acetic acid activated arabinoxylan (cf. entries 1 and 6). Hence, while the DS and MW were essentially the same, relative to acetic acid activated arabinoxylan, esterification of non-activated arabinoxylan leads to a lower product yield and longer reaction times. In the case of entries 2–5, the arabinoxylan was precipitated with acetic acid, the acetic acid was removed by washing with EtOH, and the arabinoxylan was stored wet in EtOH. Prior to esterification, the EtOH was exchanged for acetic acid. At low concentration of MSA (entries 2, 3), all of the arabinoxylan was not

solubilized and the solids had to be removed by filtration prior to precipitation. Furthermore, the DS indicated that the arabinoxylan was not fully esterified and the molecular weight was observed to decrease. At higher concentrations of catalyst (entries 4, 5), the DS indicated that the arabinoxylan was fully esterified but the MW was significantly diminished. With the exception of entry 12, the remaining entries in Table 1 are for arabinoxylan that was precipitated with acetic acid and used directly in the esterification reaction. Using 1.1 wt% MSA as the catalyst, an AXA was prepared having a DS of 1.99 and a molecular weight of 485,000 (entry 6). After exchanging the acetic acid for propionic acid, an arabinoxylan propionate (AXP) was prepared at the same catalyst loading but a longer reaction time was required (entry 7). In the case of arabinoxylan butyrate (AXB, entry 8), relative to AXA (cf. entry 6), a higher concentration of catalyst, a higher temperature, and longer reaction time was required to
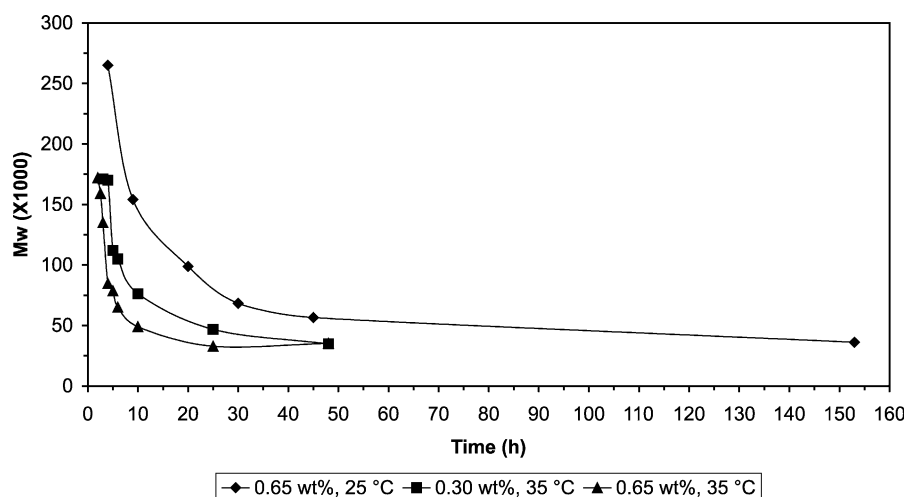

Fig. 4. The change in weight-average molecular weight over an extended time period during acetylation of corn fiber arabinoxylan using H_2SO_4.

Table 1 (Summary of reaction conditions and characterization of arabinoxylan esters

Entry	Arabinoxylan starting material (g)[a]	Ester	Catalyst, promoter	Reaction temperature (°C)	Reaction time (h)	Yield (g)	% Metals[b] SM/product	DS (^{1}H)	Mw (10^4)	Mw/Mn
1[c]	B, 1.7	C2	23 mg MSA	50	4.5	1.24	0.05/ND	2.09	58.6	7.0
2[d]	B, 0.7	C2	4 mg MSA	35(1 h), 50(2 h)	3	0.68	1.6/ND	1.58	43.6	6.2
3[d]	B, 0.7	C2	9 mg MSA	35(0.5 h), 50(3 h)	3.5	0.87	1.6/ND	1.76	24.3	4.4
4[d]	B, 0.7	C2	246 mg MSA	35	3	0.86	1.6/ND	2.24	10.4	4.8
5[d]	B, 0.7	C2	511 mg MSA	35	2.5	0.88	1.6/ND	2.33	12.7	7.3
6[e]	B, 4.0	C2	45 mg MSA	50	1.0	4.71	0.05/ND	1.99	48.5	7.8
7[e]	B, 4.0	C3	46 mg MSA	50	3.3	5.58	0.05/ND	2.06	58.8	11.9
8[e]	B, 4.1	C4	93 mg MSA	60	14.5	4.69	0.05/ND	2.15	42.5	10.0
9[e]	B, 4.0	C2	12 ml TFAA[f]	50	1	5.7	0.1/0.1	2.10	48.6	17.7
10[e]	B, 4.0	C2	10 ml TFAA[f]	50	3.5	5.11	0.05/ND	2.09	29.5	7.5
11[e]	B, 9.1	C2	12 ml TFAA[f]	49	1	4.8	56.6/0.3[g]	2.10	28.1	15.2
12[e]	A, 4.0	C2	12 ml TFAA[f]	50	1	0.3	ND	–	–	–
13[e]	A + B, 4.0	C2	12 ml TFAA[f]	54	1	2.2	57.8/11.7	2.19	17.3	5.54
14[e]	A + B, 4.0	C2	12 ml TFAA[f]	64	1	2.2	57.8/15.8	2.22	6.76	4.46

[a] A: Hemicellulose A, B: Hemicellulose B, A + B: hemicellulose A (ca. 3 wt%) and B. Based on dry weigh of arabinoxylan.

[b] The metals for enties 2–5, 10–13 were determined by ash analysis. The metals for entries 6–9 were determined by ICP. ND: not determined.

[c] No activation.

[d] The arabinoxylan was precipitated and stored wet in EtOH. The EtOH was exchanged for acetic acid prior to esterification.

[e] The arabinoxylan was water activated.

[f] Due to the relative costs of MSA and TFAA and the observed efficiency of MSA, no attempt was made to optimize the amount of TFAA needed for successful esterification.

[g] The product was initially precipitated with water. The precipitate was taken up in acetone and reprecipitated in 10% aqueous acetic acid.

achieve a high DS. Most interestingly, the molecular weight of the AXB remained comparable to AXA and AXP (entries 6, 7) despite the more harsh conditions.

When TFAA was used as a promoter for the esterification of corn fiber arabinoxylan instead of catalytic amounts of MSA, acetic acid activated arabinoxylan was successfully acetylated. The AXA was essentially identical to that obtained from MSA catalyzed esterification (cf. entries 6 and 9). With TFAA, when the reaction time was extended from 1 to 3.5 h, the molecular weight was observed to drop from 486,000 to 295,000 (entry 10). Entry 11 illustrates TFAA promoted acetylation of a corn fiber arabinoxylan having a high salt content. The high salt content of the arabinoxylan is due to the method of isolation (Buchanan et al., 2002). Entry 11 demonstrates that it is not necessary to highly purify the arabinoxylan prior to esterification as the salts can be removed from the product during precipitation of the arabinoxylan ester.

As noted earlier, the hemicellulose A component of corn fiber arabinoxylan has very limited solubility in water at a pH less than ca. 10. Entry 12 illustrates that hemicellulose is also quite difficult to esterify. The hemicellulose was allowed to swell in pH 7 water before exchanging the water for acetic acid. Using the same reaction conditions used for esterification of the hemicellulose B component (cf. entries 9 and 12), essentially no esterification was observed. This difficulty in esterifying the hemicellulose A component extends to esterification of mixtures of hemicellulose A and B (entries 13 and 14). Treatment of a mixture of hemicellulose A and B with acetic anhydride in the presence

of TFAA resulted in a decreased product yield and an AXA with a much lower molecular weight. Clearly, it is advantageous to separate hemicellulose A and B prior to esterification of corn fiber arabinoxylan.

3.2. Characterization of arabinoxylan esters

Fig. 5 provides a typical ^{1}H NMR spectrum for an AXA. Due to the severe overlap and broad resonances in the proton and carbon-13 NMR spectra of these arabinoxylan esters, no structural details for the arabinoxylan esters could be obtained by NMR spectroscopy. However, the DS for the arabinoxylan esters could be easily determined from the
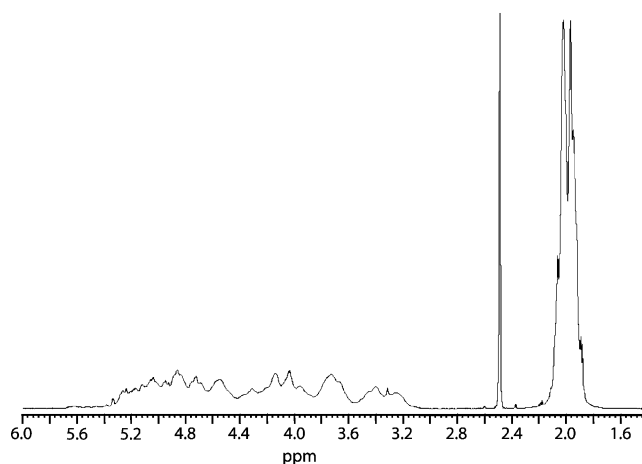

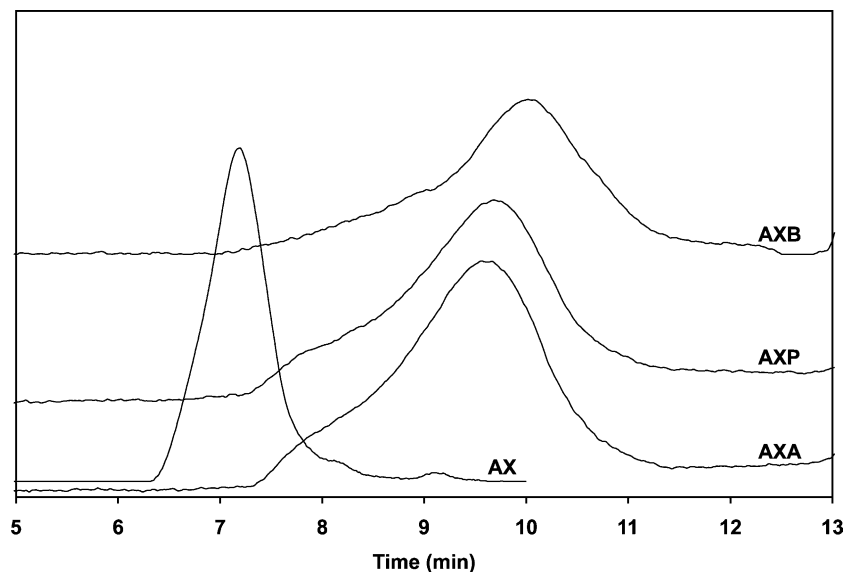Fig. 5. ^{1}H NMR spectrum (DMSO-d$_6$, 80 °C) of an arabinoxylan acetate.

Fig. 6. GPC curves for unmodified corn fiber arabinoxylan (AX) and for the acetate (AXA), propionate (AXP), and butyrate (AXB) esters of the arabinoxylan.

^{1}H NMR spectra according to the equation:

DS = (ester methyl proton integral/3)/(carbohydrate ring proton integral/6.2).

The value of 6.2 for the number of carbohydrate ring protons is based on the carbohydrate and linkage analysis of the parent arabinoxylan. Fully substituted arabinoxylan esters with a high molecular weight typically had a DS in the range of 2.0–2.1. In the case of arabinoxylan esters, where the molecular weight was significantly lowered during the esterification, the observed DS tended to be higher.

As the data contained in Table 1 show, it was possible to obtain arabinoxylan esters with weight-average molecular weights near 500,000. Poor activation and, to a lesser degree, higher reaction temperatures and longer reaction times lead to lower molecular weights. Fig. 6 shows typical

GPC traces for AXA, AXP, and AXB. Also included is a typical GPC trace for the parent arabinoxylan. As can be seen, the parent arabinoxylan has a relatively uniform molecular weight dispersion (Mw/Mn = 4–5) while the polydispersity of the arabinoxylan esters are typically larger (Mw/Mn = 7–17. Table 1). Particularly prominent is a tail toward a higher MW in each GPC trace for the arabinoxylan esters. The abrupt drop in MW, relative to the parent arabinoxylan, for arabinoxylan esters isolated immediately after all of the arabinoxylan has been solubilized in the reaction mixture (Fig. 2), the consistency of a molecular weight during prolonged reactions, and the relative insensitivity of molecular weight to substitutent type suggest that the observed change in MW in moving from the parent arabinoxylan to arabinoxylan ester is likely due to a change in polymer aggregation rather than being the result of chain cleavage.
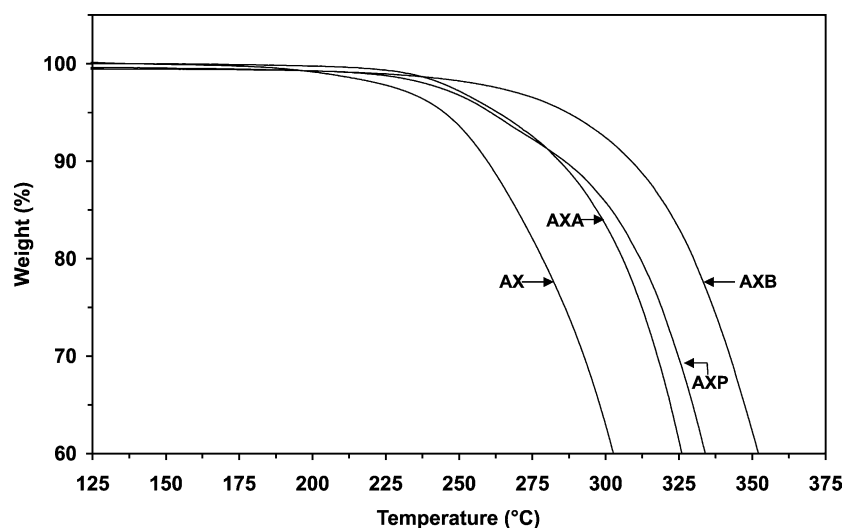

Fig. 7. TGA spectra for unmodified corn fiber arabinoxylan (AX) and for the acetate (AXA), propionate (AXP), and butyrate (AXB) esters of the arabinoxylan. To remove the effects of residual moisture, the TGA spectra for AX and AXA were normalized to 100 wt% at 140 °C.
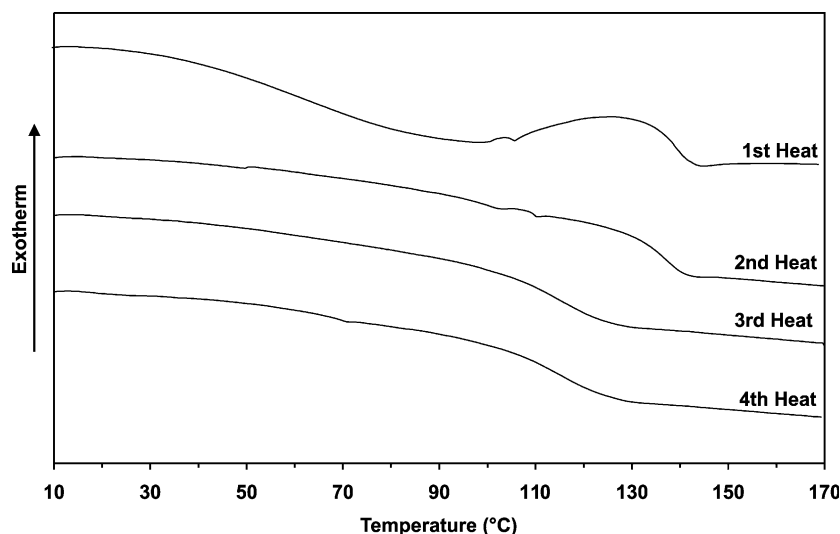
Fig. 8. DSC spectra of AXA (1st scan, 0 to 170 °C; 2nd scan, 0 to 220 °C; 3rd scan, 0 to 170 °C; 4th scan, 0 to 170 °C).

Fig. 7 provides typical TGA spectra for the parent arabinoxylan, AXA, AXP, and AXB. The onset of degradation for all three of the ester derivatives lies near 225 °C. However, the rate of degradation after onset decreases as the chain length of the substituent increases. For AXA, AXP, and AXB, 10 wt% weight loss was reached at 277, 286, and 309 °C, respectively. Relative to the parent arabinoxylan, the thermal stability of the arabinoxylan esters was increased.

The DSC spectra provided in Fig. 8 illustrates the sensitivity of the T_g of AXA to the thermal history of the sample. When a sample of AXA was heated from 0 to 170 °C at 20 ° min^{-1}, a T_g of 138 °C was observed in the 1st heating curve. After cooling in the instrument to 0 °C, the sample was heated to 220 °C and a T_g of 136 °C was obtained in this 2nd heating curve. The sample was once again cooled, heated to 170 °C, cooled, and heated to 170 °C. A T_g of 115 °C was obtained in both the 3rd and 4th heating scan. It was mildly surprising that even though we remained below the decomposition onset (Fig. 7), the T_g of the AXA dropped quite significantly. This data indicates that a reproducible T_g of AXA can only be obtained if the sample is kept under the onset of thermal degradation. It should also be noted that a T_m is not observed for AXA in any of these DSC experiments and there is no change in ΔC_p between the 1st and 2nd heating curves for samples where the 1st scan is stopped at 170 °C. This suggests that AXA is amorphous or that the Tm lies above the decomposition temperature. Characterization of AXP and AXB revealed that they were also sensitive to thermal degradation.

Figs. 9 and 10 illustrate the effect of type of substituent and DS on the T_g of these arabinoxylan esters. In the series
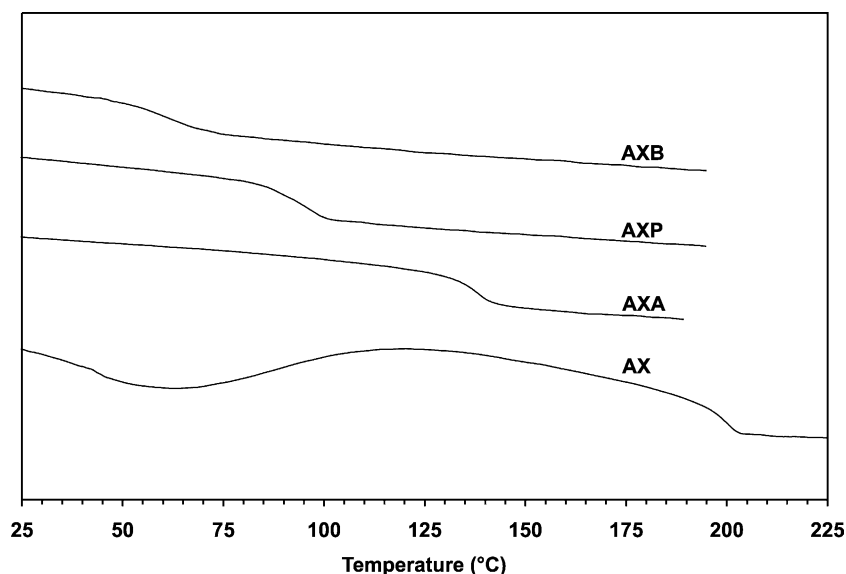

Fig. 9. Modulated DSC spectra (1st scan, reversing component) for unmodified corn fiber arabinoxylan (AX) and for the acetate (AXA), propionate (AXP), and butyrate (AXB) esters of the arabinoxylan.

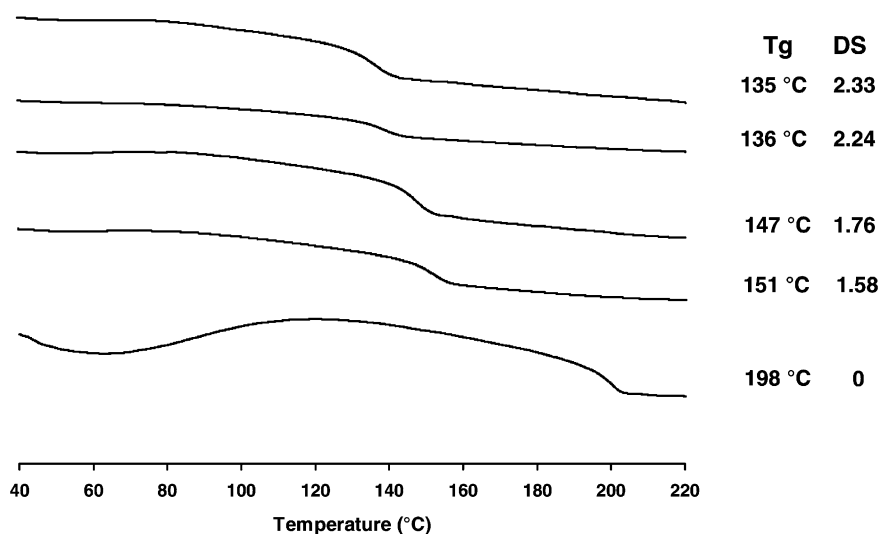|	Tg	DS
	135 °C	2.33
	136 °C	2.24
	147 °C	1.76
	151 °C	1.58
	198 °C	0

Fig. 10. Modulated DSC spectra (1st scan, reversing component) for a series of AXA with different degrees of substitution.

of parent arabinoxylan, AXA, AXP, and AXB, the respective T_g's are 198, 138, 97, and 61 °C. In the case of arabinoxylan acetates, as the DS decreased, the observed T_g increased. That is, the T_g of these arabinoxylan esters decreases as the length of the side chain and the total DS increases. The decrease in T_g with increasing DS is likely the result of a decrease in polymer–polymer interactions arising from hydrogen bonding. The decrease in T_g as the length of the side chain increases is likely due to both a decrease in polymer–polymer interactions and to an increase in free volume.

3.3. Cellulose ester–arabinoxylan ester blends

Many different groups have prepared composites of cellulose or natural fibers with different thermoplastic matrices including cellulose esters (Glasser, Taib, Jain, & Kander, 1999). With the two major components in most plant materials now available, we wondered if we could recombine arabinoxylan and cellulose esters to obtain novel composites. Based on our understanding of the structures and conformations of these polymers, our expectation at the beginning of this study was that the two components would not form a single phase mixture, but they might form a two-phase mixture with interesting properties.

Because of the sensitivity of the arabinoxylan esters to elevated temperatures, we chose to mix the components in a common solvent and to cast films. We also elected to match substituent type, matching AXA with cellulose acetate and AXB with cellulose acetate butyrate. In our initial experiments, AXA/cellulose acetate blends were prepared by dissolving the components in acetone/10–20 wt% water and casting films from these solutions. Much to our surprise, after the solvent was completely removed, the films were completely optically clear and the blends exhibited a composition dependent T_g over the entire composition

range. Figs. 11 and 12 shows selected 1st scan MDSC heating curves and a plot of calculated and experimental T_g as a function of weight fraction of AXA. The T_g taken from the 1st scan MDSC were only slightly less than that calculated (Fox, 1956) for these blends at lower concentrations of AXA but were in excellent agreement at the higher concentrations of AXA. The T_g's taken from the 2nd scan DSC scans agreed well with the calculated values at lower concentration of AXA but deviated sharply at the higher concentrations of AXA. In the DSC experiments, because of the high T_g and T_m of the CA, the sample was heated to 240 °C in the 1st heating scan to remove the thermal history of the blend. Apparently, at low concentrations of AXA, the CA matrix stabilized the AXA. At higher concentrations of AXA, thermal degradation occurs much as observed with the parent AXA.

The film samples from this initial experiment with these AXA/CA blends were then stored at ambient conditions for 8 months before they were reexamined. Visually, the film remained clear. The film samples were examined by DSC by first heating the sample from 25 to 170 °C followed by cooling in the instrument. A 2nd scan heating curve was then collected by heating the sample to 240 °C. All of the 2nd scan heating curves showed a low temperature T_g that ranged from 138 °C at low concentration of AXA to 147 °C at the higher concentrations of AXA. A second T_g, expected near 190 °C, could not be clearly determined because of the onset of thermal degradation. However, the observation of a T_g at or slightly above that of the AXA suggests that the blends had phase separated after prolonged storage.

From experience, we have learned that solvent choice can often change the clarity of film prepared from solution of polymers and the compatibility of blend components. This prompted us to prepare films of the AXA/CA blends using different solvents. When the water content in
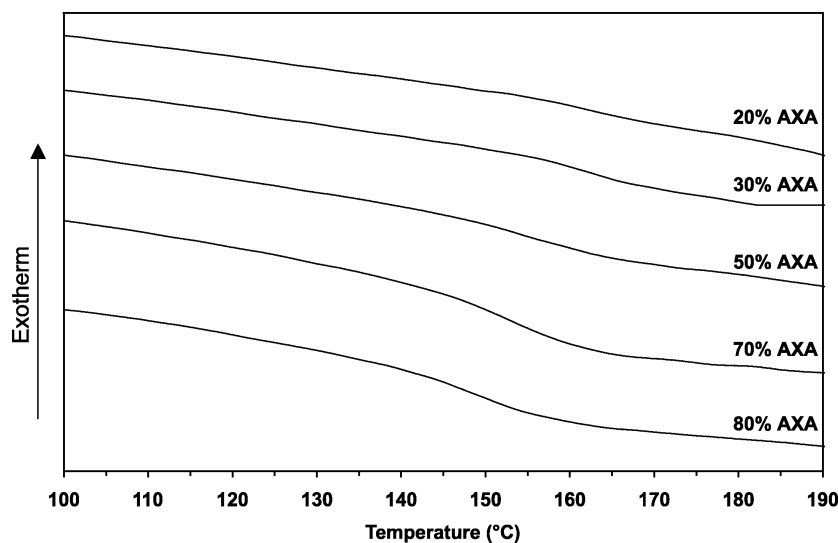
Fig. 11. Modulated DSC spectra (1st scan, reversing component) for selected AXA/cellulose acetate blends prepared by casting film from acetone containing 10–20 wt% H_2O.

the acetone was lowered to 1–2 wt%, the cast film remained optically clear but the blend now exhibited two T_g's corresponding to the parent polysaccharide esters over the entire composition range (Fig. 13). We then selected the 30/70 AXA/CA blend and prepared films from 75/25 acetone/water, 85/15 acetone/MeOH, 90/10 THF/MeOH, and THF polymer solutions. The blends prepared from the acetone solutions exhibited 2 T_g's corresponding to the parent polysaccharide esters. The blends prepared in 90/10 THF/MeOH or THF exhibited a single T_g.

In contrast to the AXA/CA blends, films cast from AXB/CAB solutions were opaque and visually exhibited macroscopic phase separation regardless of the solvent system examined. The solvent systems examined include

acetone/2–5 wt% H_2O (the maximum H_2O that could be added), acetone/MeOH, THF/MeOH, and THF. As Fig. 14 illustrates, the blends exhibited two T_g's over the entire composition range corresponding to the parent polysaccharide esters.

Our tentative hypothesis for rationalizing the experimental results with these blends is based on the ternary phase diagram shown in Fig. 15. In transversing the proposed ternary phase diagram shown in Fig. 15 starting from entry point **A**, one can see that the blends can remain in the miscible region as the solids in solution increase. Conversely, if the entry point is **B**, the immiscible region is transversed before all of the solvent is evaporated leading to the observed phase separation in the recovered film.
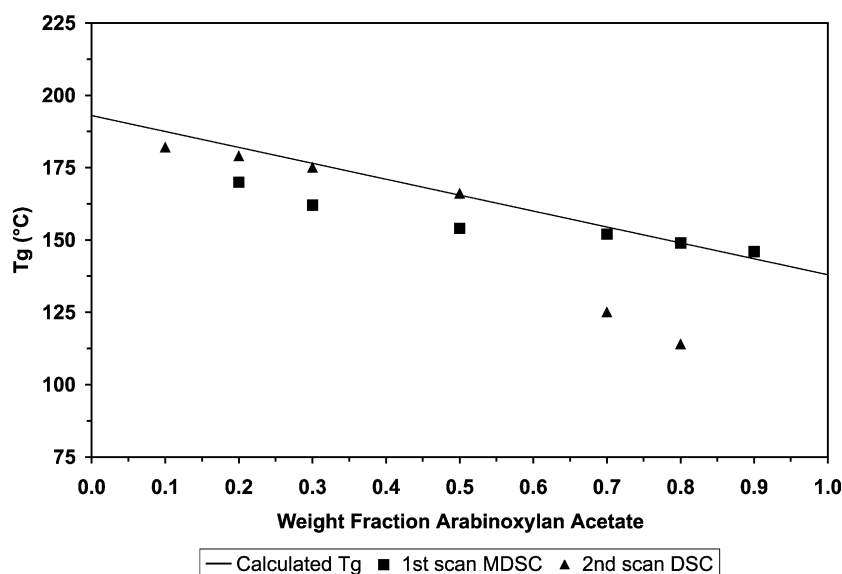

Fig. 12. Comparison of the calculated T_g's and experimental T_g's for selected AXA/cellulose acetate blends prepared by casting film from acetone containing 10–20 wt% H_2O.
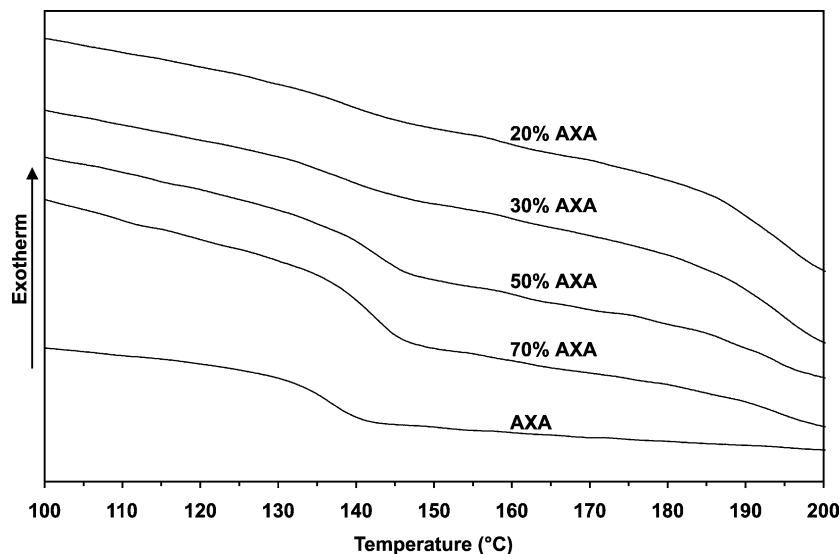
Fig. 13. Modulated DSC spectra (1st scan, reversing component) for selected AXA/cellulose acetate blends prepared by casting film from acetone containing 1−2 wt% H_2O.

It should be noted that the situation is much more complex than that shown. Differences in evaporation rates for binary solvents or rates of evaporation for a single solvent will lead to a constant change in trajectory as the phase diagram is transversed. In the phase diagram of Fig. 15, the solid line of the 2 phase region represents a binodal boundary and the dashed line represents a spinodal boundary. In the case where we observed a single phase for the AXA/CA blends which then phase separated during prolonged storage, we believe that it is likely that the blends passed into the spinodal region and subsequently phase separated.

Regarding the driving force that would allow the blend components to remain in the single phase region, we believe that the glucuronic acid in the arabinoxylan ester must play a significant role in providing a favorable free energy of mixing (ΔG). Given that cellulose esters are extended rods both in solution and in the solid state and that the arabinoxylan esters are highly branched polymers, we think that it is quite likely that intermolecular hydrogen bonding of the glucuronic acid to the cellulose ester is the driving force for blend miscibility through an increase in the enthalpy of mixing (ΔH). In the case of AXA/CA versus AXB/CAB blends, the glucuronic acid found in the arabinoxylan and the relatively small acetyl substituent would allow the addition of larger amounts of solvents such as water and the smaller acetyl substituent should not, relative to the larger butyryl substituent, destabilize any intermolecular hydrogen bonding that may occur. Of course, this in only a tentative hypothesis. Significant additional experimentation will be required to fully define
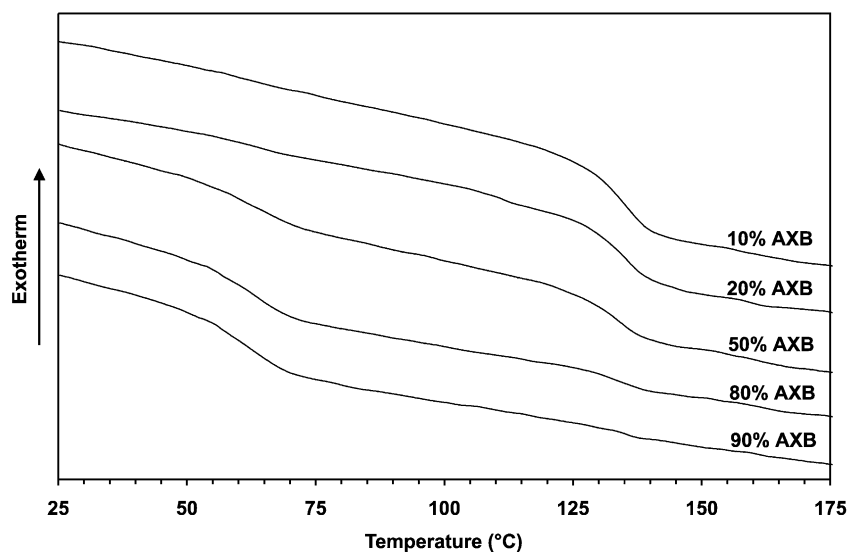

Fig. 14. Modulated DSC spectra (2nd scan, reversing component) for selected AXB/cellulose acetate butyrate blends prepared by casting film from acetone containing 2−5 wt% H_2O.
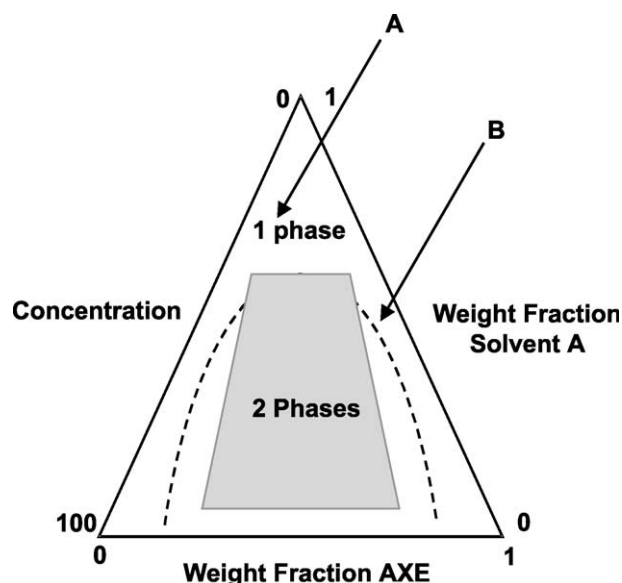
Fig. 15. Schematic phase diagram illustrating the influence of the solvent mixture and concentration on the miscibility of arabinoxylan ester and cellulose ester blends.

the boundaries of the proposed ternary phase diagram and to rationalize the observed experimental results.

4. Conclusions

In this inaugural account, we have shown that aliphatic C2–C4 esters of corn fiber arabinoxylan can be readily and rapidly prepared using MSA as an acid catalyst. These arabinoxylan esters typically have very high molecular weights and they are amorphous solids. Thermal characterization of these arabinoxylan esters revealed that the T_g's of the arabinoxylan esters are rapidly and significantly depressed when the arabinoxylan esters are heated to near the onset of thermal degradation. Additionally, the T_g's of the arabinoxylan esters are highly dependent on the DS and substituent type. The arabinoxylan esters were found to be soluble in a range of organic solvents and in organic solvent/water or MeOH mixtures. Optically clear films of arabinoxylan acetate and cellulose acetate can be prepared by casting film from common solvents. Analysis of these blends indicated that the blends can be comprised of a single phase or two phases depending upon the composition of the solvent, solvent concentration, and rate of removal of the solvent. To our knowledge, this represents the first report of miscible or compatible blends formed by combining the ester derivatives of the two major components of many plant materials, cellulose and hemicellulose. The ability to easily prepare these arabinoxylan derivatives and to incorporate them into mixtures with other polysaccharide esters offers intriguing possibilities of preparing novel composites. Much more work will be required to fully define the utility of arabinoxylan esters and composites. Our additional contributions to this area will be provided in due course.

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