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Abstract

Replacing plastics with renewable and environmentally friendly substitutes is becoming ever more critical as we begin to realize the consequences of their negative impacts on the environment. Plant polysaccharides are the most abundant biopolymers on Earth, and hemicelluloses like xylan that are enriched in many agro-industrial waste streams have vast potential as eco-friendly building blocks for polymer science and engineering. However, xylan is one of the less studied natural polymers for applications that are relevant to the synthetic plastics and polymeric materials markets. Hemicellulose isolated from viscose and Lyocell fiber mills is largely seen as a waste product due to difficulties arising from the potential for structural heterogeneity and its lack of solubility after enrichment. In this work, we developed a strategy to valorize hemicellulose by functionalization with octyl isocyanate to achieve solubility and thermoplastic/hydrophobic properties. Xylan isolated from dissolving pulp waste streams was successfully functionalized with octyl isocyanate in DMSO at an estimated 79% hydroxyl conversion. Reaction parameters, including temperature, time, and stoichiometry were optimized for each reaction. The resultant carbamates of xylan oligo- and monosaccharides have good solubility in chloroform and impressive hydrophobic film forming properties yet retain the composability properties desired for renewable materials that are envisioned to enter the circular bioeconomy. Functionalization of xylan with an aliphatic chain through formation of an aliphatic carbamate is not expected to harbor the same toxicity or carcinogenic characteristics as the reactive isocyanate it is derived from, and thus should not inherently restrict these materials for use in diverse packaging applications. These modified physical properties show that xylan from agro-industrial waste streams has considerable potential to replace petroleum-based feedstocks in the existing packaging industry. In the future, we will continue to further develop strategies for valorization of these materials.

Keywords Viscose waste, Hemicellulose, Xylan, Bioplastics, Biomaterial, Alkyl Isocyanate, Coating

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Introduction

Global production of wood-based cellulosic fibers from dissolving pulp processes has increased by 6.3% per year during 2000–2018, [1] and is expected to continue growth at a rate of 4–6% annually until 2030 due to strong market demand [2]. The industrial processing of viscose fiber generates large amounts of toxic liquor known as viscose waste (VW) at the lye removal stage from the alkaline steeping of the dissolving pulp [3]. Currently, the alkali is being partially recycled using industrial membrane treatments, but the remaining alkaline VW is either incinerated or discharged into the environment.

Xylan is the second most abundant polysaccharide in nature, comprising 20 - 35% of total lignocellulosic dry mass in hardwoods [4]. The xylan content of different lignocellulosic sources (e.g., poplar, eucalyptus, pine, oak, grasses, etc.), and recent efforts on its extraction and derivatization to generate xylan-based bioproducts, are reviewed elsewhere [5-9]. Briefly, xylans are extracted from biomass and agricultural wastes through chemical, enzymatic, and hybrid hydrolysis routes to develop xylo-oligosaccharides (XOS). Derivates of XOS are used for biobased products in the packaging industry, [10] removal of heavy metal ions, [11] and the generation of pre- and pro-biotic foods in health and veterinary applications. In recent decades, there has been an increased interest in developing bio-renewable saccharides from plants as alternatives to petroleum-based industrial feedstocks for the production of new materials and plastic alternatives [5]. Recent studies have reported that VW is enriched with hemicellulose, and the work presented in this manuscript shows that unsubstituted xylan oligoand polysaccharides are particularly abundant in VW when hardwood is used as a biomass source.

For a long time, cellulose has dominated the field and has a proven track record as an eco-friendly feedstock with desired mechanical properties for flexible packaging applications, including food packaging. It has been adopted for a variety of industrial processes, such as solution casting, layer-by-layer assembly, extrusion, coatings, and spray drying [12]. In contrast, xylan has been largely neglected due to its heterogeneity, including its variable degrees of polymerization after processing, side chain substitutions, and insolubility in water and most organic solvents. However, due to its natural abundance and chemical modification potential, continued improvements in the processing and modification strategies of these waste streams are making hemicellulose modification a desirable industrial alternative to both starch and cellulose, with the potential to be mechanically desirable, cost-effective, eco-friendly, and biodegradable.

Several chemo-modification strategies have been attempted in the past two decades targeting the hydroxyl groups of xylans. Methods for chemical derivatization of preactivated xylans with ionic functions (e.g., sulfuric acid half ester groups, carboxymethyl, hydroxypropyltrimethylammonium) and non-ionic functions (e.g., methyl chloride, activated carboxylic acids) were developed by Petzold et al. for applications such as drug delivery, paper strength additives, flocculation aids, and antimicrobial agents [13]. Hansen et al. functionalized birch wood xylan in ionic liquid using multiple long-chain succinic anhydrides and demonstrated an increase in hydrophobicity of the casted films [9, 14]. Other green and renewable reactions involving citric acid and sodium monochloracetate were developed by Salam et al. to functionalize xylan with carboxylic acids for water-soluble applications [15]. Xylan has also been functionalized

through a UV-initiated thiol-ene reaction where allylated xylan was reacted with thiols containing varying functional groups achieving reactive xylan-oligomers [16]. In parallel work, Pahimanolis et al. synthesized thioether xylans in an aqueous solvent by reacting the allylated xylan with thioacetic acid, cysteamine hydrochloride or cysteine, producing novel thiol-, amine- or amino acid functionalized xylans for controlled 3D hydrogel shape printing and foam applications [17]. Ünlü et al. modified xylan in an aqueous basic medium and showed the antimicrobial effect of functionalized xylan [18]. In another interesting work, xylan-tyramine was generated by reacting tyramine with carboxylated xylan to use it as a biomimetic ink with cellulose nanofibril blends for 3D printing applications [19]. Well defined nanoparticles were also prepared by functionalizing xylans with phenylcarbonates by Gerike et al. [20]. Utilizing click chemistry, welldefined micelles and vesicles where hydrophobic fatty acid methyl esters are attached to the aldehyde reacting end groups of xylan-oligomers containing azide reactive groups can be generated [21]. Most recently, Ceoromila et al. chemically functionalized xylan with alkyl ketene dimers (AKD) and acetylation to create a hydrophobically modified xylan, which was then mixed with chitosan biopolymer in a colloidal dispersion. With their best performing sample, the authors achieved WVTR values of $30 \text{ g m}^2 \text{ day}^{-1}$ [22]. Similarly, Brienzo et al. chemically acetylated xylan and combined it with starch biopolymers to create a bioplastic which resulted in WVTR values of $25-40 \text{ g m}^2 \text{ day}^{-1}$ [23].

Overall, the above described techniques demonstrated that the functionalization of xylans has the potential to improve thermal stability, [24] thermal responsivity, [25] hydrophobicity, [14] water solubility [15] and generate reactive xylan-oligomers [16, 17] for further cross-linking applications. Despite the significant effort to valorize xylans in the past decade, industrial adaptation of xylan as a feedstock for packaging applications remains very limited due to poor scaled production and processibility of the functionalized xylans with other packaging materials.

Functionalization of cellulose and nanocellulose has been carried out extensively using aliphatic and aromatic mono- and di-isocyanates [26]. Isocyanates react with -OH groups to form a very stable urethane (carbamate) bond, modulating the material properties depending on the aliphatic or aromatic isocyanate used. In contrast to cellulose, functionalization of xylan has been limited and only attempted with aromatic tolylene-2,4-diisocyanate (TDI) [27, 28]. We functionalized xylose and mannose monosaccharides and viscose xylan polymers with octyl isocyanate (Scheme 1) and observed that monosaccharide-derived carbamates (Mannose-C8, MC8; Xylose-C8, XC8) were found to have very impressive physical and thermal properties, exhibiting thermoplastic behavior and great moisture barrier performance when applied to cellulose sheet as a coating. Viscose xylan from industrial waste streams was also successfully functionalized at an estimated 79% conversion of –OH groups to carbamate bonds. The resulting carbamate of viscose xylan (Viscose-C8, VC8) is soluble in chloroform and can be coated on various materials to provide a hydrophobic film.

Results and discussion

We initially used mannose and xylose monosaccharides as models to design optimized functionalization strategies for hemicelluloses, and then expanded these methods for use with xylan feedstocks. Carbamate reactions were performed with octyl isocyanate in the presence of dibutyltin dilaurate (DBTDL) catalyst at 80 °C as shown in Scheme 1 using the reaction setup presented in Scheme 2. We determined that monosaccharides represent good models to compare with the reactions of xylan oligo- and polysaccharides (i.e. viscose xylan) and alkyl isocyanate. The tin-catalyzed reaction between polyols and isocyanate was described in detail elsewhere [29]. Briefly, the proposed reaction mechanism begins with alcoholysis of DBTDL to its tin alkoxide, which then undergoes N-coordination with the isocyanate. The alkoxide anion is transferred to the coordinated isocyanate to give an N-stannylurethane, which again undergoes alcoholysis to regenerate the original DBTDL and yield carbamate esters. Recently, this reaction mechanism was shown experimentally to vary depending on reaction stoichiometry [30].

While urethane (syn. Ethyl carbamate, CAS# 51–79-6) is considered a carcinogen, our functionalized saccharides contain a urethane (or carbamate) bond between the aliphatic group and the polysaccharide, which would not be expected to harbor the same toxicity or carcinogenic characteristics as bare urethane molecules. Cellulose carbamate is a long-proven material with the same carbamate bond to the polysaccharide, and it has been proposed for absorbent products for hygiene, medical applications, and films for food packaging applications [29]. Generally, a carbamate ester has the same chemical structure as a urethane. The functionalized materials in the current work only share the urethane/carbamate bond and are not polyurethanes. Thus, we classified our xylan-based functionalized materials as carbamates. Functionalized monosaccharides of mannose and xylose are termed Mannose-C8 (MC8) and Xylose-C8 (XC8), respectively. Similarly, the functionalized viscose xylan obtained from the viscose waste is named Viscose-C8 (VC8). Reaction temperature, time, and stoichiometry were optimized for each reaction, and a 2:1



Scheme 1 Schematic of carbamate reactions with (a) monosaccharide and (b) viscose xylan oligosaccharides with octyl isocyanate. The nucleophilic DBTDL catalyst prompts an -OH group of the target saccharide to attack the isocyanate's carbonyl, forming a highly stable carbamate bond, and multiple levels of substitution can be targeted by controlling reaction stoichiometry



Scheme 2 Hemicellulose and octyl isocyanate reaction setup. A Simplified reaction scheme B) Laboratory setup

stoichiometric excess of isocyanate to hydroxyl groups was chosen to maximize functionalization.

The estimated level of functionalization (LOF) for XC8 and MC8 are 17.5% and 25.7%, respectively. The LOF was calculated by taking the experimentally observed aliphatic side chain weight added to the 200 mg of starting saccharide as a percentage of the theoretical maximum product weight from complete functionalization of all available –OH groups (presence of urea and product losses from reaction materials processing are also considered in the calculations).

Octane was selected as a solvent for monosaccharide-based reactions as it is most suitable for efficient end-product separation after testing various polar and non-polar solvent systems. The viscose xylan was poorly functionalized due to incompatibility with the solvent. Thus, reaction conditions for xylan were optimized by eliminating the moisture from the reaction setup and using anhydrous DMSO as a solvent, which resulted in an average LOF of 79.4% for xylan (Table 1). The final VC8, MC8, and XC8 products obtained through DMSO and octane solvents, respectively, are fully soluble in CHCl₃.

Chemical analysis of raw and functionalized materials

Overall, the VC8 sample had the highest level of functionalization, and this work shows that in a compatible solvent system, viscose xylan has the potential to be functionalized with standard isocyanate chemistries at high yield in industrial applications. Monosaccharide model systems exhibited markedly less functionalization, most likely due to the octane solvent. However, octane is employed for monosaccharide reactions due to the ease of product separation compared to DMSO-based reactions.

The products generated from the tin-catalyzed reaction of hemicelluloses and octyl isocyanate were analyzed by Fourier-transform infrared (FTIR) spectroscopy, where we observed the disappearance of the isocyanate $v_{\rm NCO}$ band at 2273 cm⁻¹ in comparison with the octyl isocyanate control spectra (Fig. 1a) and a

 Table 1
 Reaction yields of saccharides functionalized with octylisocyanate

Sample	Reaction feed weight (mg)	-CNO/-OH ratio	Yield (mg)	LOF %	%RelStDev*
MC8	200	0.87	351	17.5	4.13
XC8	200	1.04	413	25.7	12.5
VC8	200	1.56	540	79.4	11.3

MC8 Mannose-C8, XC8 Xylose-C8, VC8 Viscose-C8, *n = 3

concomitant increase in the intensity of the carbamate $v_{\rm CO}$ band at 1720 cm⁻¹ in contrast with the control spectra of raw materials (Fig. 1(b-d)). Supporting information figure S2 serves as an additional control experiment to determine the peak behavior of carbamate versus urea formation in standard isocyanate reactions. Urea is an undesired by-product that occurs during the reaction between moisture and isocyanate. The main differences between the FTIR spectra of the saccharide reactants and carbamate products appear in the region around 1700 cm⁻¹. The $\nu_{\rm CO}$ band of carbamate exists between 1750-1700 cm⁻¹ while the ν_{CO} band of urea exists between 1700 cm⁻¹ to 1650 cm⁻¹. The characteristic peak of isocyanate at 2273 cm⁻¹, which corresponds to the $\nu_{\rm NCO}$ band, and several CH vibrational modes at 2957 cm⁻¹, 2982 cm⁻¹, and 2857 cm⁻¹ are due to the octyl side chain appended to xylan. Raw saccharides and their carbamate derivates were compared with the IR spectrum (Fig. 1). D-Mannose and D-Xylose have a large, broad OH vibrational band due to the presence of multiple OH groups, which are converted to an NH band centered at 3335 cm⁻¹, post modification, indicating the formation of the carbamate linkage. The functionalized materials, MC8, XC8, and VC8, also gained strong CH vibrational peaks from the C₈ sidechain of octyl isocyanate, which is distinct from the CH peaks observed in raw materials. The most notable band present in the modified material is the sharp peak at 1720 cm⁻¹ due to the newly formed COO bond in the carbamate linkage, clearly demonstrating successful carbamate reactions of D-Mannose, D-Xylose, and viscose xylan with alkyl isocyanates (Fig. 1).

Characterization of XC8 by ¹H NMR showed clear proton signals from xylose at $\sim 4-6$ ppm (Fig. 2a, d). 2D COSY, HSBC, and HMBC NMR experiments were used to analyze the reaction products as presented in the supporting information Figures S3(a-c), confirming the correct product by a 3-bond correlation between the carbamate bond's carbonyl at 158 ppm and xylose's proton signals. We evaluated different industrially available viscose xylan from the viscose waste streams for their potential use as feedstocks for scaled up functionalization. ¹H NMR analysis of xylans from different viscose waste sources (i.e., Futamura and Lenzing) showed no significant structural differences, and a representative spectrum is shown in Fig. 2c. VC8 showed broad xylan proton signals from $\sim 3-5$ ppm (Table 2 and Fig. 2c, f), but we were unable to confirm the presence of the carbamate linkage with HMBC NMR experiments despite using > 8 h collection times. The reason for this remains unclear, but we believe the functionalization was successful due to marked changes in VC8 physical properties and solubility in organic solvents.



Fig. 1 FTIR analysis of raw saccharide starting materials and corresponding carbamate reaction products. **a** octyl isocyanate, **b** D-Mannose, **c** Mannose-C8 (MC8), **d** D-Xylose, **e** Xylose-C8 (XC8), **f** Viscose Xylan, **g** Viscose-C8 (VC8). The carbonyl peak corresponding to the carbamate bond appeared at 1725 cm⁻¹, indicating a successful modification of mono- and oligosaccharides with the aliphatic side chains of octyl-isocyanate. The spectra of octyl isocyanate and raw materials are used as control samples to evaluate the functionalized materials

MC8 displayed the weakest saccharide signals (Fig. 2b, e), showing only what was tentatively assigned as the proton signals from the CH_2 of the secondary alcohol at 4.1 ppm. ¹H and ¹³C ppm shifts for this signal match very closely with ChemNMR theoretical values (data not presented). A possible explanation for the lack of other signals is that functionalization is believed to be random on all but the secondary alcohol, and the chemical shift difference between functionalized and non-functionalized mannose signals causes only the secondary alcohol and its corresponding CH ends to show up. Calculated functionalization for MC8 was also lower than expected, as mannose was predicted to have a higher functionalization potential than xylose due to its primary alcohol.

Instead, our data showed the opposite trend, which could be due to mannose having less compatibility with octane than xylose.

Monosaccharide-based XC8 and MC8 were further analyzed by MALDI-TOF MS (Fig. 3). Dithranol matrix prepared in chloroform (30 mg/mL) was used to crystallize the reaction products (10 mg/mL) in a 10:1 ratio. Mannose-C8 products had distinct masses of 628 and 783 Da, representing mannose with three and four substitutions (Fig. 3a). Analysis of XC8 products showed masses (m/z, z=1) of 304, 459, 615 Da that represent xylose with one, two, and three isocyanate substitutions, respectively (Fig. 3b). The products at 284, 440 and 594 Da represent isocyanate–water interactions (Fig. 3c).



Fig. 2⁻¹H NMR analysis of raw saccharides and modified products. **a-c**.¹H 600 mHz NMR spectra of un-modified saccharides in DMSO-d₆. **d-f** Spectra of carbamate products in CDCl₃

 Table 2
 D-(+)-Mannose, D-(+)-Xylose, and Viscose Xylan

 DMSO-d₆
 Chemical shifts assignments – (ppm)

Signal	Mannose Shift (ppm)	Xylose Shift (ppm)	Viscose Shift (ppm)
H ¹	4.87	4.85	4.27
OH^1	6.21	6.14	5.00
H^2	3.52	3.11	3.04
OH^2	4.48	4.46	5.10
H ³	3.51	3.33	3.25
OH ³	4.40	4.68	-
H^4	3.35	3.23	3.51
OH^4	4.59	4.82	-
H^5	3.50	3.47	3.17
H ^{5'}	-	3.34	3.87
H ⁶	3.62	-	-
H ^{6'}	3.44	-	-
OH ⁶	4.31	-	-

Based on MALDI-TOF MS analysis of functionalized monosaccharides, two main product types were generated: isocyanate-monosaccharide conjugates and those representing the polymerization of isocyanate in the presence of trace amounts of moisture (i.e. urea). We also performed control experiments by selectively skipping reactants in the monosaccharide and isocyanate reactions (i.e. xylose, octyl isocyanate, DBTDL) to evaluate the formation of carbamates and urea. Mass analysis of the corresponding products of control experiments, where individual reactants are absent in reactions, are presented in supporting information Figure S4.

Thermal properties of Xylose-C8 (XC8), Mannose-C8 (MC8), and Viscose-C8 (VC8)

Thermal properties of XC8, MC8, and VC8 were evaluated by thermogravimetry (TGA) and differential scanning calorimetry (DSC) to observe the phase transitions of the materials and their thermal stability as a function of temperature (Figs. 4 and 5). Octyl isocyanate (OI) and DBTDL are in the liquid phase at ambient temperature. All products were cleaned thoroughly post-functionalization to remove any unreacted molecules, such as OI, DBTDL, saccharides, and urea. Products were characterized by FTIR, NMR, and MALDI-TOF then further evaluated for their thermal properties. TGA data analyses, along with 1st derivate plots for XC8, MC8, VC8, VC8/ MC8 (30/70 wt%), and n-octyl urea as a control material are presented in Fig. 4. The xylose and mannose TGA plot show that monosaccharides start degrading at above 150 °C, and as per the corresponding weight derivative curves (Fig. 4). Significant loss of mass is observed at 225 °C and 285 °C which confirms the TG thermal degradation behavior of xylose and mannose provided in detail by Räisänen et al. and Huang et al. [31, 32]. According to Räisänen et al., xylose and mannose degradation begin before melting, indicating water loss and fusion as polymerization markers through glycosidic linkages at~145 °C (caramelization), followed by continuous stages of pyrolysis as temperature increases. The weight derivative profiles also indicate that the thermal stability of xylose and mannose is below 225 °C. The thermal behavior of Xylose-C8 and Mannose-C8 relative to xylose and mannose show that the functionalized monosaccharides share the thermal stability of monosaccharides below



Fig. 3 Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS). a Carbamates of D–Mannose, b Carbamates of D–Xylose, (c) dithranol matrix (control)

225 °C (Fig. 4a and b), while rapidly degrading as volatile compounds like n-octyl urea (Fig. 4d) with degradation maximum at ~ 270 °C, potentially due to lack of glycosidic linkages at caramelization temperature of 145 °C. Mass loss is ~ 60% and ~ 90% in the case of XC8 and MC8 at 270 °C and 325 °C, respectively. In contrast, xylose and mannose lost ~ 35% and ~ 55% of initial mass at 325 °C, signifying the marked differences in the caramelization process associated polymerization of materials. Further, at the pyrolysis temperatures (above 500 °C), both xylose and mannose have a residual mass of 20%, while XC8 and MC8 completely evaporated. The monosaccharides are solids at ambient conditions, while linking aliphatic C8 side chains converted them to wax-like substances (Figure S1b) under ambient conditions. In contrast, the control n-octyl urea (Fig. 4d, red profile) appeared as a fine powder at room temperature, yet evaporated completely above 200 °C as a volatile compound. Thus, the wax-like nature of the functionalized monosaccharides appears to be the result of an equilibrium between the monosaccharide backbone and the saturated hydrocarbon side group (C8).

Figure 4c presents the TGA of the viscose xylan (degree of polymerization 8 - 40 units) obtained from industrial sources along with the functionalized Viscose-C8 and their corresponding 1st derivate plots. Despite the

structural difference between the viscose xylan (without substitutions) and naturally occurring xylan (e.g. beechwood) [33], the TGA thermal degradation profile is consistent with prior reports [34]. The loss of weight that occurs up to 100 °C (xylan, black profile) indicates loss of moisture, and unlike monosaccharides, the xylan TGA derivative shows a single peak for the significant loss of mass at 295 °C (Fig. 4c). The degradation of viscose xylan is similar to that of the monosaccharides at their pyrolysis temperatures, leaving ~ 20% residue. Comparatively, functionalized Viscose-C8 followed the trend of XC8 and MC8, losing mass rapidly at 265 °C.

DSC was performed to further evaluate the temperature-dependent transitions (Tg, Tm, Tc) of the functionalized materials relative to raw materials and n-octyl urea. A forward heating and reverse cooling cycle (-20 °C to 200 °C to -20 °C) was performed with raw materials (Fig. 5a). These DSC data show that Tg and cold crystallization are absent during the heating cycle as expected. An endothermic peak (downward) was observed corresponding to the Tm for all raw materials. A melting temperature of 156 °C for xylose and 138 °C for mannose was extrapolated by analyzing the onset, extrapolated peak, and the endset of the endothermic peaks. As suggested by Räisänen et al., raw materials undergo chemical changes (i.e. caramelization) prior to their melting





Fig. 4 Thermogravimetry analysis of raw and modified materials. AD-Xylose vs Xylose-C8. bD-Mannose vs Mannose-C8. c Viscose-xylan vs Viscose-C8. d n-Octyl urea and the blend of xylan and mannose reactions (VC8/MC8). TGA of n-octyl urea and raw materials are used as control samples to evaluate the functionalized materials. 1st derivative of weight is also provided to identify the maximum degradation temperatures of each material

temperature. As per the DSC data, the observed caramelization temperatures of xylose and mannose are ~145 °C and ~115 °C, respectively, which is in agreement with previously published works (Fig. 5a). In contrast, DSC data of viscose xylan (without substitutions) has a broad endothermic peak in the range of 75 °C to 200 °C, while a



Fig. 5 Differential Scanning Calorimetry (DSC) of raw materials and functionalized materials. **a** Comparison of D-Mannose vs. D-Xylose vs. viscose xylan. **b** Comparison of Mannose-C8 (MC8), Xylose-C8 (XC8), and Viscose-C8. **c** Comparison of VC8/MC8 blends. DSC of octyl urea and raw materials are used as control samples to evaluate the functionalized materials. 'exo up' indicates the peak orientation of the exothermal peak (i.e. upward)

melting peak (Tm) is absent in naturally occurring xylan polysaccharides [34]. To rule out the potential effects of moisture and hysteresis in viscose xylan material, DSC was performed on dried viscose xylan samples, and the endothermic peak was sustained at the same position during repeated heating-cooling cycles (data not presented). It is currently not clear why viscose xylan has an endothermic peak (Tm ~ 120 °C) lower than mannose (Tm~138 °C). TGA thermal degradation data shows functionalized Viscose-C8 evaporates rapidly at 265 °C as a volatile compound similar to XC8, MC8, and octyl urea (Fig. 4c). Thus, the endothermic peak corresponding to the viscose xylan in Fig. 5a is probably the melting temperature (Tm),~120 °C. Further evaluation of viscose xylan structure-function relationships is outside the scope of the current work.

DSC analysis was carried out on functionalized materials, including Xylose-C8, Mannose-C8, and Viscose-C8, with the n-octyl urea as a control material, to evaluate the Tg, Tm, Tc, cold crystallization, and material hysteresis (Fig. 5b). Tg was absent from all functionalized materials similar to their unfunctionalized counterparts. During the heating cycle, an endothermic peak corresponding to the Tm values 90 °C, 84 oC, and 80 oC was determined for n-octyl urea, XC8, and MC8, respectively. Similarly, on the reversing cooling cycle, an exothermic peak (upward) corresponding to the recrystallization temperature (Tc) values 85 oC, 60 oC, 34 oC were determined for n-octyl urea, XC8, and MC8, respectively (Fig. 5b). The Tm and Tc data of XC8 and MC8 indicate that these materials display potentially plastic properties. Thus, to further explore the thermal stability and plastic properties of XC8 and MC8, DSC analysis was performed with gradual changes in temperature over multiple heating and cooling cycles in the range of 25 °C to 250 °C (Figure S5). The material crystallization peak in indicates that the samples are relatively pure compounds and no further chemical modifications occur during heat cycles up to 200 °C (Figures S5b and S5c). However, at temperatures over 200 °C, both XC8 and MC8 displayed significant chemical changes, as confirmed by the corresponding Tm and Tc values (Figures S5b and S5c) and corroborating the thermal stability values observed with the TGA analysis of 225 °C. Further, the gradual shift in the Tc values (Figure S5b, S5c) of XC8 and MC8 during multiple heat cycles indicated that XC8 and MC8 are heterogenous in nature, functionalized with different levels of aliphatic side chain substitutions, and undergo further relaxation and molecular realignment. Clearly, the DSC data presented in Fig. 5b and Figure S5 shows that the XC8 and MC8 have a thermoplastic nature and are thermally stable at up to 200 °C. The thermal flow properties were further evaluated using rheological analyses. The rheology of MC8 and XC8 was established relative

to temperature cycle (25 °C- 125 °C - 25 oC) with an Anton-paar rheometer (supporting information Figure S6). Material phase transitions from solid-melt-solid (optical images provided in Figure S6) were recorded in repeated cycles along with the storage and loss modulus at a defined oscillation frequency of the rotating disc, which confirmed the plastic-like flow properties of XC8 and MC8.

The DSC data presented in Fig. 5b, supporting information Figure S5, and the rheology data in supporting information Figure S6 demonstrates that XC8 and MC8 behave as thermoplastics suitable for melt processing for coatings and blending with other bioplastics for packaging applications. Solvent-free melt processing of materials is more appealing for industrial applications due to their waste-free processing compatibilities. The TGA, DSC, and rheological data indicated that the XC8 and MC8 are suitable for applications in both solvent-based and solvent-free industrial processes.

Thermoplastics are commonly solid and brittle at room temperature and become soft and pliable with increased temperature. Amorphous thermoplastics undergo a gradual transition from soft to hard material phase, are translucent, and are easy to thermoform. In contrast, semi-crystalline thermoplastics transition to a solid from the melt state at a specific temperature. Semi-crystalline thermoplastics are opaque when cooled to solids [35]. Thus, the DSC crystallization peak (Tc) of XC8 and MC8 is interesting for understanding the nature of functionalized materials as they represent a semicrystalline thermoplastic behavior and both materials are wax-like opaque materials at the room temperature (Fig. 5b and Figure S5). To confirm the semi-crystalline nature of functionalized monosaccharides, relatively pure MC8 material was dissolved in chloroform at 50 mg/mL, dip-coated on a silicon wafer, and allowed to dry under ambient conditions. The dried surfaces were imaged with scanning electron microscopy (Fig. 6). SEM micrographs show the presence of semicrystalline and amorphous regions in the film surface topography, confirming the semicrystalline thermoplastic nature observed in both DSC (Fig. 5b) and rheological studies (supporting information Figure S6). The semicrystalline structures presented in Fig. 6(b, d, f) appear to show a snapshot of microstructure formation at different stages (primary, secondary, and tertiary) and may depend on the number of aliphatic C8 chain substitutions on the monosaccharide. Further analysis of the MC8 semicrystalline structures presented in Fig. 6(b, d, f) requires molecular dynamic simulations and is outside the scope of the current manuscript.

In contrast to the XC8 and MC8 material properties, DSC analysis of VC8 indicates that xylan functionalization with C8 alkyl side chains was insufficient as the solubility of VC8 in CHCl₃ is improved while thermoplastic properties are absent (Fig. 5b). DSC analysis of VC8 in shows two endothermic peaks and an exothermic peak (Fig. 5b). However, peak intensity is negligible, and the materials remain solid and do not flow in rheology experiments (data not presented). To improve the melt processibility of VC8 for industrial barrier coating applications, we attempted to blend monosaccharides with viscose xylan prior to reaction with octyl isocyanate. In the Mannose-C8 and Viscose-C8 compositions, the mannose weight fraction varied from 85% - 65%, complementary to the viscose weight fraction of 15% - 35%. The functionalized blends (VC8/MC8) with up to 35% viscose weight fraction, upon thorough cleaning and drying, yielded wax-like materials similar to the Mannose-C8. When the viscose fraction is increased to 50% in the reaction blend, the resulting products turn into powders similar to the viscose xylan and become less suitable for melt processing. However, mannose/viscose blends with higher viscose fractions over 50% were completely soluble in chloroform, similar to the Viscose-C8, and likely highly suitable for solvent-based coating applications. Here, DSC data is presented only for the VC8/ MC8 blends suitable for melt processing. The thermal characterization of these products is presented in the supporting information Figure S7 (TGA) and Fig. 5c (DSC). While the TGA thermal degradation profile of the VC8/MC8 blends remains identical to those of XC8 and MC8, the temperature-dependent material transitions presented tunable thermal properties of the VC8/ MC8 blends. The melting temperatures of the blends gradually increased from 71 °C – 77 °C, corresponding to the increase in viscose xylan weight fraction. Similarly, the recrystallization temperature increased from 33 oC - 42 °C, corresponding to the increase in viscose xylan weight fraction. Overall, we observed that blending a mannose with the viscose xylan yielded VC8/MC8 blend materials that are thermoplastic (melt flow) in nature with thermal properties that are tunable based on the blend ratio of VC8 and MC8 (Fig. 5c), which can be leveraged to improve coating processes and corresponding barrier performance.

The solubility of raw materials and MC8, XC8, and VC8 in different organic solvents are provided in Table 3. While limited solubility of raw materials is observed in organic solvents except in DMSO, XC8, MC8 and VC8 are completely soluble in chloroform and DMSO up to 100 mg/mL. However, all materials remain highly insoluble in most organic solvents owing to their amphiphilic nature.



Fig. 6 Scanning electron microscopy of Mannose-C8. a, c, e MC8 topography images of the coated film. b, d, f Enlarged micrographs from images a, c, e. Both the amorphous and semi-crystalline regions are observed in the film surface topography

Table 3 Solubility data of raw sugars and their functionalized materials in mg/mL

Sample	Chloroform	Acetone	DMF	EtOH 100%	MeOH	DMSO	DMF
Mannose	none	none	10	none	none	30	10
MC8	100	none	none	none	none	100	none
Xylose	none	none	none	none	none	30	none
XC8	100	none	none	none	none	100	none
Viscose waste	none	none	none	none	none	100	none
VC8	100	none	none	none	none	100	none

MC8 Mannose-C8, XC8 Xylose-C8, VC8 Viscose-C8

Surface characterization and barrier performance studies The development and testing of barrier performance for bio-based coatings plays a critical role in enhancing the protective properties of various surfaces. To evaluate this, bio-based coatings derived from MC8, XC8, and VC8 were dissolved in chloroform to create uniform coatings on silicon wafers, cellulose sheets, and cardstock substrates using our home-made automated hybrid dip-coater with film applicator (see supporting information Figure S1(e, f)). Following the coating process, the films were subjected to drying under ambient conditions and evaluated for coating thickness using atomic force microscopy—AFM (Fig. 7) and surface properties using contact angle analysis with DI water droplets (Fig. 8). AFM topography imaging of uncoated cellulose sheets revealed a well-oriented fiber as a result of the industrial extrusion process (Figs. 7a, b). AFM topography of cellulose sheets coated with MC8 (Fig. 7c) revealed a heterogeneous material topography with amorphous and semi-crystalline regions similar to the SEM micrographs (Fig. 6), as expected from the heterogenous reaction of mannose and octyl isocyanate in octane solvent. To study the film thickness, a gentle scratch is made on the coating using a blunt tip to expose the cellulose substrate next to the coating. The AFM topography cross sectional analysis revealed a consistent ~ 2 μ m coating thickness (Fig. 7d).

Figure 8a shows a representative image of typical XC8, MC8, and VC8 coatings on cellulose sheets prepared using our automated film applicator and chloroform as a solvent. Cellulose sheets with different functionalized material coatings were further subjected to static contact angle (CA) analysis by sessile drop method to evaluate



Fig. 7 AFM analysis of cellulose sheets with and without MC8 coating. **a** and **b** Topography image of uncoated cellulose sheet. **c** Topography image of MC8-coated cellulose substrate. **d** cross-sectional analysis of MC8 coated cellulose sheet height image



Fig. 8 Contact angle analysis of XC8, MC8, VC8 coated cellulose substrates using a DI water droplet. **a** Solvent-based MC8 coating on cellulose substrate using doctor blade. **b** contact angle analysis of cellulose film without coating. **c** Contact angle on commercially available PVDC coated cellulose substrate. **d** Contact angle on MC8 coated cellulose substrate. **e** Contact angle on XC8 coated cellulose substrate. **f** Contact angle on VC8 coated cellulose substrate. The measured contact angle for each material condition is provided at top right corner

the coating surface's hydrophilic and hydrophobic properties. Commercial cellulose sheets with and without PVDC coating were used as controls to compare the CA performance of XC8, MC8, and VC8 (Fig. 8b-f). A DI water droplet was used to determine the angle between the coating surface on cellulose sheets and the tangent of the droplet's semi-spherical shape at the edge of the droplet. The contact angle is further determined using droplet image analysis software based on the young's Eq. (1) [36].

$$\gamma_{SV} = \gamma_{LV} \cdot \cos\theta + \gamma_{SL} \tag{1}$$

Where γ_{SV} is the surface tension of the solid, γ_{LV} is the surface tension of the liquid, and γ_{SL} is the liquid–solid interfacial tension.

Notably, distinct characteristics were observed among the coatings. The contact angle of an uncoated cellulose (27°) sheet shows immediate wetting by a DI water droplet (Fig. 8b), while PVDC coated cellulose sheets show a significantly better contact angle of 62° (Fig. 8c). The XC8 coated bare cellulose sheet, upon initial contact with the droplet showed a high contact angle of ~ 101° (Fig. 8d). However, the coating started wetting when exposed to DI water for over an hour. In contrast, MC8 (~98°, Fig. 8e) and VC8 (104°, Fig. 8f) coatings maintained their surface resistance to water, displaying an exceptional barrier to wetting over extended periods. The theoretical surface tension value for DI water is 72.8 dynes/cm [37]. A high surface tension liquid resulting in CA over 90° indicates that the MC8, XC8, and VC8 coatings may potentially have a low surface free energy. However, measuring the surface free energy of solid films requires a method provided by the ASTM D3575 standard and not in the scope of the current manuscript. Overall, comparisons with commercially available cellulose sheet samples (Fig. 8b, c) underscored the superior performance of MC8, XC8, and VC8 coatings as effective water/moisture barriers.

Moisture barrier performance

To explore moisture barrier performance for potential coating applications, water vapor transmission rate (WVTR) analysis was conducted on cellulose sheets coated with both thin films (see Fig. 8a) as well as hot press coatings under standard conditions of 50% RH and 38 °C. Initially, a solvent-based dip coating method (refer to supporting information Figure S1e, S1f) was employed to apply a 10 µm thick coating of MC8, XC8, and VC8 in chloroform on water-permeable cellulose sheets. However, WVTR analysis of these films was hindered by microcracks that developed post-solvent evaporation, leading to swift failure. To address this, $50 \pm 5 \,\mu m$ melt coatings of MC8 were prepared on 20 µm cellulose sheets using a Carver ${}^{{}^{\mathrm{TM}}}$ hot press to achieve a uniform and completed sealed coating (see supporting information Figure S1a). While VC8 proved unsuitable for melt coatings due to previously mentioned challenges, a blend of MC8/VC8 was formulated that achieved stable melt coatings as discussed above with the TGA and DSC analysis. XC8 was excluded from use in VC8 blends due to its poor water stability, as indicated by contact angle analysis (Fig. 8d). Thus, $50 \pm 5 \ \mu m$ melt coatings of MC8 and VC8/MC8 blends were prepared on 20 µm thick cellulose sheets using the Carver[™] hot press (supporting information Figure S1a-S1d) and were determined to be stable for WVTR tests. Uniform test conditions of 38 °C and 50% RH was used for all measurements.

The moisture barrier performance of the melt-coated cellulose sheets was evaluated, revealing that a $50 \pm 5 \ \mu m$ thick MC8 coating on 20 µm water-permeable cellulose sheet exhibited a moisture barrier performance of 36.57 g m⁻² day⁻¹ (Table 4). Moreover, MC8/VC8 blend ratios of 15/85 (wt%) and 35/65 (wt%) coated on water permeable cellulose sheet yielded WVTR values of 33.41 g $m^{-2} day^{-1}$ and 31.5 g $m^{-2} day^{-1}$, respectively (Table 4). In comparison, the commercially available uncoated cellulose sheet WVTR test failed, and the PVDC-coated cellulose sheet measured a WVTR value of 5.6 g m^{-2} day⁻¹. These commercial uncoated cellulose sheets were originally designed for food contact applications such as chocolate, confectionery, and dairy products, and the PVDC coated cellulose sheets are intended for single-use packaging in dried foods, home and personal care item, crisps/chips, tea, coffee, and confectionary markets. As

Table 4WVTR analysis of different fractions of viscose waste blended with mannose to prepare VC8/MC8 blends in comparison withNatureFlex cellulose sheet with and without PVDC coating

Material	Temperature (°C)	RH (%)	WVTR (g m ⁻² day ⁻¹)
Unocated cellulose sheet	38	50	Test failed
PVdC coated cellulose sheet	38	50	5.65
MC8coated cellulose sheet	38	50	36.57
VC8/MC8 (15/85 wt %) cellulose sheet	38	50	33.41
VC8/MC8 (35/65 wt%) coated cellulose sheet	38	50	31.58

presented in the Table 4, the incorporation of Viscose-C8 in the blend coatings resulted in a gradual enhancement of moisture barrier performance.

To allow our products' performance to be compared with common flexible packaging materials in Table S8, one can assume the WVTR of a coating is halved when the thickness of the barrier coating is doubled [38]. From this, we can extrapolate our value of ~ 30 g m⁻² day⁻¹ at 38 oC and 50% RH (Table 4) at 50um thickness to~60 g $m^{-2}\ day^{-1}$ at 25um thickness, and per [39], our value of ~ g m⁻² day⁻¹ at 38 oC and 50% RH can be approximated at ~110 g m⁻² day⁻¹ at 38 oC and 90% RH. As seen in Table S2, this falls in between LDPE (12.5 g m^{-2} day⁻¹) and PA6 (~200 g m⁻² day⁻¹) materials, [40] both of which are very widely used in food packaging applications, and matches closely with EVOH (80 g m⁻² day⁻¹), which is also extensively used in food packaging applications such as agriculture produce or shelf stable food packaging [41]. Although the hot press method used to make the coatings in-lab resulted in a fixed film thickness of 50 um, the WVTR of our coatings could be tuned in the future by employing other coating methods to allow various thicknesses to be achieved, or by employing alternate modified atmosphere packaging (MAP) techniques like micro-perforations to allow them it to meet an even wider range of applications. The WVTR data obtained from the MC8 and VC8/MC8 melt-coated cellulose sheet present promising opportunities for exploring the valorization of hemicelluloses sourced from industrial viscose wastes. Given the diverse nature of hemicelluloses, dependent on the origin of hardwood or softwood and the availability of xylan oligo- and polysaccharides in viscose wastes, the tunable material properties showcased in this study underscore the potential for bio-based functionalized material coatings for moisture barrier protection and durability in diverse applications.

Composting studies

Xylose-C8, Mannose-C8, and Viscose-C8 were further tested for their hydrophobic coating performance and compostability. Thin coatings (~2 μ m) were applied using the automated film applicator (Figure S1e) technique on commercially available cellulose sheets. A 2-inch×1-inch sections of water-permeable cellulose sheets coated with XC8 and MC8, together with controls consisting of commercially available cellulose sheets with and without PVDC coatings as a barrier substrate, were inserted into a specially designed composting frames shown in (Figure S1g, h). The frames were placed in a porous bag (Figure S1i) and placed in a container with composting soils following the ASTM D5338 standard test. Weekly assessments were made to qualitatively evaluate the degradation of these substrates, as depicted in Fig. 9. Results indicated that the uncoated water-permeable cellulose sheet underwent rapid degradation by soil organisms, fully composting by the third week. XC8-coated bare cellulose sheet exhibited slightly improved performance compared to uncoated cellulose sheets, fully composting by the sixth week. The XC8 compositing data is in agreement with the contact angle analysis which revealed a gradual decline in water barrier performance for XC8

Sample	Control	Week1	Wk2	Wk3	Wk4	Wk5
Uncoated cellulose film (UC)		-				
Xylose-C8 1 side coating on UC						
Mannose-C8 1 side coating on UC	Ph					
PVdC coated cellulose film	1	1. 01	1 0 11			

Fig. 9 Composting study of coated cellophane sheets in comparison with commercially available semipermeable cellulose sheets and PVDC coated cellulose sheets

films compared to MC8 and VC8 films. MC8-coated bare cellulose sheets demonstrated remarkable stability beyond the fifth week, akin to commercially available PVDC-coated cellulose sheets, although complete composting occurred by the tenth week. Taken together, the compostability of VC8-coated substrates are comparable to those with MC8 coatings. We have also tested the coating performance and compostability on aluminum foil, glass, and paper stock substrates as shown in supporting information Figure S8, with better compostability performance. These findings underscore the robust, eco-friendly coating applications of these materials.

Functionalized Xylan (VC8) barrier performance

All reported saccharide products (XC8, MC8, and VC8) exhibit impressive chloroform solubility post modification, which perhaps speaks to the true level of functionalization more than the calculations derived from yield, which can be skewed by the presence of urea. Urea removal proved to be challenging, as the solubility profiles of octyl-urea and saccharide-derived carbamates are very similar, and optimal methods will vary depending on the saccharide used. Improvements to the purification methods of saccharide-carbamates are still on-going.

VC8 is soluble in chloroform at concentrations above 100 mg/mL with gentle heating (~40 oC), although it is presumed from NMR analysis that it does not form a molecular solution. A 50 mg/mL chloroform solution was coated onto water permeable cellulose sheet at 2 – 5 μ m thickness, and hydrophobicity was investigated. Raw cellulose sheets instantly wet and begins absorbing dye water, as shown in Fig. 10a, while VC8 coated bare cellulose sheet was extremely hydrophobic, aggressively repelling and beading water (Fig. 10b), even after

Page 16 of 21

multiple hours of water contact (see supporting information video).

Conclusions

The study has highlighted the substantial potential of hemicelluloses, particularly viscose xylans sourced from viscose wastes, in replacing petroleum-based, nonrenewable industrial feedstocks for the generation of new barrier coatings. The saccharide-carbamates developed in this research exhibit impressive thermal processing capabilities, moisture barrier performance, and postmodification compostability. Additionally, these functionalized saccharides demonstrate strong suitability for both solvent and melt processing methods, enabling the formulation of diverse blends for bioplastic applications. Further, the functionalized saccharides are highly suitable for industrially relevant solvent and melt processibility to prepare various blends for bioplastic applications. Although the aggressive reactivity of isocyanates with water, especially in combination with the hygroscopic nature of sugars, might pose some challenges for producing these materials on an industrial scale, isocyanate reactions form highly stable carbamate bonds and are used in the current work as a model system to valorize viscose xylans with useful material properties for barrier coating applications. In follow-up works, green chemistry could replace isocyanate chemistry while producing the same carbamates of viscose xylans with proposed material properties to be relevant for eco-friendly industrial-scale applications, Overall, this study highlights the successful utilization of natural agricultural waste products as renewable alternatives within current industrial production practices, with isocyanate chemistry playing a pivotal role. A key limitation in current processes associated with saccharification and fermentation of lignocellulose is the incapacity of typical bioprocessing yeast and bacterial strains to metabolize pentose sugars like



Fig. 10 Cellulose sheet uncoated (Left) and cellulose sheet coated with Viscose-C8 (Right)

xylose [42]. This is unfortunate, as pentose sugars are the building blocks of the hemicelluloses that make up one of the most abundant components of plant biomass [43]. Saccharomyces cerevisiae and Clostridium thermocellum are promising microbial chassis for lignocellulosic bioethanol production, but many problems are associated with their abilities to ferment and utilize xylose and xylans limits efficacy of the process [44–46]. Looking ahead, our future research endeavors will explore diverse hemicellulose-enriched feedstock streams, including undigested residual carbohydrates enriched in xylo-oligosaccharides for use production of these bio-sourced value-added products [47]. For example, C. thermocellum growth is inhibited by hemicellulose hydrolysis products [47, 48]. Additionally, we will also study alternative functionalization routes in an effort to create a fully renewable and eco-friendly material that retains desirable physical properties, in hopes that one day all environmentally damaging materials can be replaced with ecofriendly substitutes.

Materials and methods

All materials were used as received from the manufacturer. Dibutyltin Dilaurate (DBTDL), D-(+)-Mannose and D-(+)-Xylose were purchased from Millipore Sigma (USA). Octyl isocyanate (OI) was purchased from ACROS Organics. Octane and anhydrous DMSO were purchased from Fisher Scientific. Clean samples of enriched xylan were kind gifts provided by Lenzing and Futamura UK from their viscose waste stockpile for our valorization efforts. 20 μm thick NatureFlexTM branded cellulose sheets (A4 size) with and without polyvinylidene chloride (PVDC) coatings are also provided by Futamura UK as a kind gift. The uncoated cellulose films are highly permeable to moisture while the PVDC-coated films are made to provide an excellent moisture barrier. However, both cellulose sheets are designed with excellent barrier to gases and aromas.

A home-made apparatus for reactions utilizing the mono-, oligo-, and polysaccharides and octyl isocyanate mixture is presented in Scheme 2. Briefly, 200 mg of saccharide was ground using a mortar and pestle and added to a 100 mL round bottom flask. This reaction vessel with the saccharide powder was dried for approximately 2 h in a Thermo Fisher vacuum oven at ~ 10 torr and 100 °C. A stir bar was added to the flask, and it was affixed in an oil bath on a hot/stir plate as shown in Scheme 2. A small condenser with a vacuum nipple was attached in between the flask and the 24/40 septum stopper (Chemglass 3022–99), and the sealed reaction vessel was then re-dried on the hot plate at 100 °C and ~ 10 torr for 1 h, before allowing the hotplate to cool to 80 °C for the reaction. The vessel was brought to atmospheric pressure with argon (Airgas, Ultra High Purity) and attached to an oil bubbler acting as a one-way valve to vent solvent vapors as they accumulate during the reaction, with an intermediate trap to prevent drawing oil into the reaction if negative pressure is induced by temperature changes or accidental application of vacuum (see scheme 1). 10 mL of octane (OR) DMSO was added to the reaction vessel, and then 1.5 mL of octyl isocyanate and 15 µL of DBTDL catalyst were gently heated at 50 °C, mixed in a beaker and injected through the septum seal. Different reactants (i.e., mannose, xylose, and viscose xylan) were made to react to obtain their corresponding functionalized hemicelluloses. The desired products are expected to be either amphiphilic or hydrophobic in nature depending on the saccharide and the level of alkyl functionalization. Thus, different post-reaction product cleaning strategies are tested and optimized as described below.

The appropriate solvent for each reaction involving mono- and/or oligosaccharide was chosen for low moisture absorption, better reactant miscibility, and ease of post-reaction production extraction. Octane was used as a solvent for reactions with monosaccharides (mannose and xylose), and DMSO was utilized as solvent for reactions with viscose xylan oligomers.

When octane is used as a solvent in reactions involving monosaccharides, urea/excess isocyanate is best removed by pipetting off the octane from the reaction flask while still hot. It was observed through various analyses that once cooled, any urea formed during the reaction due to stray moisture will precipitate from the octane and blend with the insoluble product and was more difficult to separate. The product was further cleaned from excess isocyanate, catalyst, and any remaining urea by washing twice with 10 mL of 50 °C octane and centrifuging. The product was collected from the centrifuge tubes and dried overnight at 50 °C and ~ 10 torr to remove residual solvent.

When DMSO was used as a solvent in reactions involving viscose xylan oligomer, the end products are cleaned by adding an equivalent volume of octane. The product will precipitate from the DMSO in an interface between the two solvents after a few minutes of centrifugation, and then can be cleaned of residual urea by washing twice with 10 mL of 50 °C octane and centrifuging. Further optimization of urea removal is needed, and the best method may vary with the physical properties of hemicellulose materials (mono-, oligo-, polysaccharides), the humidity of the lab environment, and desired reaction scale and purity.

Materials characterization

Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet 6700 FTIR Spectrometer (Thermo Scientific) combined with OMNIC software was used following the ASTM E1252 method for the FTIR analysis of all materials. Qualitative analysis of the controls (i.e., mannose, xylose, and viscose xylan) and their functionalized products (i.e., Mannose-C8 (MC8), Xylose-C8 (XC8), and Viscose-C8 (VC8)) was performed via solid-state potassium bromide (KBr) pellets in the CO_2 atmosphere. A manual pelletizer hydraulic press was used to create the KBr pellets. Three to 8 mg of material was mixed with approximately 80 mg of KBr powder. The mixture was ground with a mortar and pestle, and a pellet was produced using a hydraulic press. The pellet was then used to analyze the materials presented in Fig. 1.

NMR analysis

Data for the raw materials and their functionalized derivatives was recorded at 298 K with a Varian-NMR spectrometer operating at 600 MHz equipped with a 5-mm NMR cold probe. Mono- and polysaccharides were dissolved in DMSO- d_6 at a 5 mg/mL concentration in 5 mm NMR tubes. Mannose-C8 (MC8), Xylose-C8 (XC8), and the Viscose-C8 (VC8) samples were dissolved in CDCl₃ at a concentration of 5 mg/mL in 5 mm NMR tubes. 1D H¹ NMR spectra were collected for each sample, and 2D COSY (COrrelated SpectroscopY), HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation) NMR spectra were collected on XC8, which was found to give the best spectra out of all modified products. COSY gives a correlation signal between adjacent hydrogen molecules and is often the first step towards structural assignment after a H¹. HSQC gives a correlation signal between each carbon and its corresponding proton, while HMBC shows correlations between carbons and multiple bond distance protons, allowing assignment of quaternary carbons and further confirmation of previous assignments, as well as confirmation of the carbamate bond molecular linkages, which were visible for XC8.

Matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectrometry

Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF MS). Matrix-assisted laser desorption/ionization mass spectrometry was carried out using a Microflex spectrometer (Bruker, USA). A dithranol matrix appropriate for organic solvents and 2,5-dihydroxybenzoic acid (DHB) suitable for aqueous solutions are used to prepare the samples accordingly for MALDI-TOF mass analysis as per the method by Belu et al. [49]. All functionalized materials were dissolved in appropriate solvent at a concentration of 10 mg/mL and mixed with the matrix dithranol or DHB (30 mg/mL) at a ratio of 1:1.

Thermogravimetry (TGA)

A DiscoveryTM series thermogravimetric analyzer (TGA) (TA Instruments) was used to evaluate the physical changes in the materials, such as thermal stability and degradation, as a response to the current temperature. The sample preparation and the analysis follow the ASTM E1131 standard. A sample size of 8 mg was prepared for mass analysis as a function of temperature in an atmosphere of nitrogen (flow rate 10 mL/min), and this data is presented in Figs. 4. The samples in the TGA Pt pans (crucible) are heated at a rate of 20 °C/min up to 600 °C. In addition, a 1st derivative curve of weight loss data as a function of temperature was plotted to reveal the material phase transition temperature and the temperature peak at which the maximum thermal decomposition (rate of change or inflection point) of the material was observed, which indicated the material thermal stability.

Differential Scanning Calorimetry (DSC)

A Discovery[™] series modulated DSC2500 (DSC) was used to study the thermal properties of xylose, mannose, and viscose xylan and their derivatives following the ASTM E794 standard method for melting and crystallization temperature analysis and ASTM E1356 for glass transition temperature analysis. DSC is a common method to identify the material's temperature-dependent transitions such as glass transition temperature (Tg), melting temperature (Tm), and crystallization temperature (Tc) based on the material's endothermic (Tm) and exothermic response (Tc). A sample size of 8 mg was prepared in Tzero aluminum pans (TA instruments # 901,683.901; temperature range -180 °C to 600 °C) and the experiments were performed in the nitrogen atmosphere at a flow rate of 10 mL/min in the temperature range of -60 °C to 250 °C. Repeated heating and cooling cycles are performed at 10 °C/min rate to plot the heat flow vs temperature curves to study the material's phase transitions, thermal stability, thermal properties, and hysteresis. TRIOS automated software (TA Instruments) in combination with the peak analyzer module in the graphing software OriginPro[®] are utilized to analyze the onset, extrapolated peak, and endset of each peak in DSC plot to determine the Tm (endothermic peak) and Tc (exothermic peak) values.

Atomic force microscopy

A Dimension Icon SCANASYST atomic force microscope (Bruker, USA) was used to analyze the coating thickness on cellulose sheets. Coated samples were gently scratched with a blunt tip to expose the substrate next to the coating, and the corresponding thickness was measured via topography analysis of substrates. The AFM scan speed of 1 Hz was used with each subsequent micrograph recorded with a time shift of 512 s. A SCANASYST-AIR cantilever probe (length ~ 115 μ m, frequency 70kHz) was used to scan the films. Bruker Nanoscope Analysis software was used to prepare the AFM micrographs and cross-sectional analysis of films.

Scanning electron microscopy

Thermo Fisher Scientific (FEI) Teneo, a field emission scanning electron microscope (FESEM) [50], available at the University of Georgia—Georgia Electron Microscopy facility, was used to image the surface topography of MC8-coated substrates. It was equipped with beam deceleration capabilities, which can mitigate charging effects for non-conductive samples such as MC8, XC8, and VC8 on cellulose sheets developed in the current work. Thus, metal film sputtering to analyze the surface topography was not required and the original surface topography can be preserved in the SEM micrograph as shown in Fig. 6.

Film coatings and contact angle (CA) analysis

Coatings of MC8, XC8, and VC8 were prepared on the cellulose sheets using our home-made automated film applicator (supporting information Figure S1e). These films were then dried in ambient conditions and analyzed for DI water droplet static contact angle using the sessile drop method [36, 51] to determine the surface wettability and hydrophobic properties, (Fig. 8(b-f)). ImageJ, in combination with contact angle analysis software developed by the Nanostructured Materials Lab at the University of Georgia, was used for droplet shape analysis and CA estimation. The contact angle method used in the current work follows the ASTM D5946 standard.

In order to obtain a reproducible CA of different coatings, we used a silicon wafer as a standard base to hold the cellulose sheets with different coating surfaces and DI water for the liquid droplets with a droplet size of ~ 5 mm. Film coatings were observed with an optical microscope prior to the measurements for any defects. All measurements are performed at room temperature. Once the drop is collected on the surface, the optical image was captured with a liquid–solid interface in focus for further droplet shape analysis.

Hot-pressed films and WVTR analysis

A CarverTM hot press (Figure S1a) was used to obtain uniformly coated 50 μ m thick substrates with MC8 flakes on cellulose sheets (supporting information Figure S1 (b, d)). The hot press was equipped with a two-plate system

where the bottom flat plate was static while the top flat plate was movable up and down with a hydraulic press. The bottom plate can be heated to the desired temperature. A $6'' \times 6''$ cellulose sheet with MC8 material spread on top was heated to 100 °C on top of the hot base plate of the press. Once the temperature was stabilized, the hydraulic press was activated to press the plates together creating a uniformed coated cellulose with MC8 coating. Cellulose sheets coated with MC8 were tested for moisture barrier performance (WVTR) in nitrogen atmosphere using a LabThink W3/230 WVTR test system with test area of 50 cm², as per the ASTM F1249 standard (supporting information Figure S1c). LabThink automated experimental control, data management, and analytical software were used to automatically determine the WVTR (g m⁻² day⁻¹) values of cellulose sheets with and without coatings.

Dip-coatings and composting studies

A homemade, automated hybrid film applicator embedding a doctor blade for film coating and a reservoir for dip coating, as shown in supporting information Figure S1(e, f) was used to prepare 1-sided or 2-sided thin film coatings of functionalized materials on cellulose substrates. In-house designed and 3D printed composting trays with slots to hold $2'' \times 1''$ size films as shown in supporting information Figures S1(g, h) were used as scaffolds to hold MC8 and XC8 coated cellulose sheets. These trays were packaged in to composting bags as shown in supporting information Figure S1i. The composting studies were performed on these films following the ASTM D5338 standard in The BioseniaticSM Laboratory facilities available at the new materials institute, UGA.

Compost inoculum preparation, pretesting, and heavy metal analysis

Mature compost was sourced from two separate industrial composting facilities at thermophilic sampling locations (40 ± 5 °C). Both compost samples had spent 2 – 4 months at either composting facility. The compost was then particle sieved through a 4.76-mm (0.187-inch) screen. The two samples of separately sourced compost were then blended in a 50/50 mass-ratio to increase the microbiological diversity of the test inoculum. More information on the quantitative analysis of inoculum is provided in supporting information Table S1.

Abbreviations

VW XOS 7 TDI Mannose-C8, MC8 Xylose-C8, XC8 7 DBTDL DETENDED

Viscose waste Xylo-oligosaccharides Tolylene-2,4-diisocyanate Mannose-derived carbamate Xylose-derived carbamate Viscose-C8 Dibutyltin dilaurate

LOF	Level of functionalization
MALDI-TOF MS	Matrix Assisted Laser Desorption/Ionization Time of
	Flight Mass Spectrometry
TGA	Thermogravimetry
DSC	Differential Scanning Calorimetry
OI	Octyl isocyanate
CA	Contact angle
ASTM	American Society for Testing and Materials

Supplementary Information

The online version contains supplementary material available at https://doi. org/10.1186/s44316-024-00009-8.

Supp	lementary	Material	1
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Supplementary Material 2.

Acknowledgements

We thank the University of Georgia Agricultural and Environmental Services Laboratories (AESL) and Austin F. Wright and Evan M. White at the Bioseniatic[SM] Laboratory for assistance with compost inoculum validation experiments (with partial support from the Walmart Foundation Project ID# FP00016798).

Authors' contributions

DCJ, NSY, and JCM performed various experiments presented in this manuscript. MJP and DCJ conducted the NMR analysis. SM and BRU supervised the work presented in this manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This material is based upon work supported by the Center for Bioenergy Innovation (CBI), U.S. Department of Energy, Office of Science, Biological and Environmental Research Program under Award Number ERKP886.

Availability of data and materials

Data is provided within the manuscript or supplementary information files.

Declarations

Competing interests

We filed a provisional patent application to the USPTO on June 6, 2024.

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Received: 3 April 2024 Accepted: 6 July 2024 Published online: 19 August 2024

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