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Research Article

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**Biodegradable and Transparent Films with Tunable UV-Blocking Property
from Xylose Residue by a Top-Down Approach**

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Abstract

As over exposure of the earth to ultraviolet (UV) light and increased amount of petroleum-based plastic waste, biodegradable UV-blocking materials are desired for diverse sustainable applications. Xylose residue, as the byproduct of xylitol production from corn cobs, is mainly composed of cellulose and lignin. Here, we develop a series of xylose residue films through a top-down approach (i.e., tunable delignification and regeneration) without any additional additives. The treated xylose residues with lignin content of 4.4-29.7% are used to prepare regenerated films, which exhibit excellent UV-blocking capability: 68.6-99.2% for UVB (290-320 nm) and 47.1-98.2% for UVA (320-400 nm). Moreover, these films remain a great optical transparency (50.6-86.6%) and show enhanced water vapor permeability ($2.17\text{-}2.76 \times 10^{-11} \text{ g}\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{mmHg}^{-1}$), surface hydrophobicity (water contact angle=72.3-86.4°), and thermal stability. Overall, our sustainable UV-blocking films have potential applications in the fields of electronics, food packaging, and windshields, etc. This study provides new insights into converting xylose residue directly to high value-added functional bioproducts.

Keywords: Xylose residue, UV-blocking films, Top-down fabrication, Delignification, Regeneration

Introduction

As the depletion of stratospheric ozone in recent decades, excessive ultraviolet (UV) radiation, including UVA (320–400 nm) and UVB (280–320 nm), results in greater damage to plants, animals, and even outdoor devices on the earth's surface (Calvo et al. 2012; Sasani Ghamsari et al. 2017; Williamson et al. 2014; Yang et al. 2019). Therefore, UV-blocking films have attracted increased attention from researchers for applications in diverse fields, such as electronics, food packaging, and windshields (Babaei-Ghazvini et al. 2018; Gause and Chauhan 2016; Shen et al. 2020; Yun et al. 2010). Nowadays, a variety of UV-blocking films have been developed with great properties (Bahramian 2020; Cohen et al. 2017b; Guo et al. 2017; Hu et al. 2020; Wang et al. 2012; Zhou et al. 2020). However, conventional UV-blocking films are mainly based on petroleum-based polymers, such as polyethylene (PE) (Zhou et al. 2020), polyethylene terephthalate (PET) (Bahramian 2020; Guo et al. 2017), polypropylene (PP) (Cohen et al. 2017b), and polyurethane (PUR) (Wang et al. 2012). These materials are non-sustainable and non-biodegradable, which may have a shortage of feedstock resources and lead to serious secondary pollution in the nature. Furthermore, introducing functional materials, i.e. UV blockers, is the most common method to endow films with UV blocking property. To date, many organic agents (such as benzotriazole and benzophenone derivatives) and inorganic agents (such as TiO_2 and ZnO) have been widely used to fabricate UV-blocking films (Cohen et al. 2017a; Neamjan et al. 2012; Parejo et al. 2006). Wang et al. fabricated a transparent cellulose film containing 2.95 wt% CeO_2 nanoparticles, which exhibited desired UV shielding properties (Wang et al. 2019). Similarly, Cohen et al. developed a PP film embedded with polymeric benzotriazole nanoparticle; it decreased UV transmission from 95% to 0% (Cohen et al. 2017a). Nevertheless, most of organic UV protection agents are unstable and toxic (Koetke et al. 2010); inorganic nanoparticles are easily agglomerated, which have a negative effect on the anti-ultraviolet performance of films (Althues et al. 2007). All these problems limited the large-scale industrial production and wide practical applications of UV-blocking films.

Recently, various biomass-derived materials have been recognized as a potential candidate compared to petroleum-based materials due to their environmental friendliness and biodegradability (Chen et al. 2016; Dutta et al. 2009; Fu et al. 2015; Galindez et al. 2019). As an agriculture residue in xylitol-production industry, xylose residue is the abundant, easily available, and renewable bioresource. In the whole world, a large number of xylose residue are obtained as by-products of xylitol annually. For example, approximately 23 million ton of xylose residue are produced each year in China (Guo et al. 2018). However, most of them were discarded as wastes and could not be utilized in high value-added fields (Zhang et al. 2012). It remains a challenge to convert xylose residue into high-valuable materials through facile approaches.

Xylose residue is mainly composed of cellulose and lignin. Cellulose, the most abundant natural polymer in nature, has been widely used in various fields due to its many merits, such as renewability, biocompatibility, and biodegradability(Sadeghifar et al. 2016; Zhu et al. 2018). Lignin, as the natural aromatic material, possesses conjugated structures and unsaturated systems, which endows lignin with many excellent properties, such as UV blocking property, thermal stability, oxidation resistance, and hydrophobicity. Therefore, the combination of cellulose and lignin is a promising and feasible approach to prepare sustainable UV-blocking materials. The bottom-up approach by mixing cellulose and lignin have been reported to fabricate UV-blocking materials; however, the poor dispersion of lignin in the composite and the complex process hindered their large-scale production. Since xylose residue consists of both cellulose and lignin, the direct fabrication of UV-blocking films from xylose residues through a top-down method would be dramatically promising.

Herein, for the first time, we prepared flexible and sustainable UV-blocking films based on xylose residue without any additional additives via a facile top-down approach: tunable delignification and direct regeneration. The obtained films exhibited highly effective UV-shielding capability but remained a great optical transparency. Their morphological and chemical structures were analyzed. In addition, the xylose residue films showed great water vapor barrier property, thermal stability, mechanical behavior, and surface hydrophobicity, mainly due to the original nature of lignin. This work sought to demonstrate the effect of delignification on the properties of UV-blocking films, and further provide new insights into the development of sustainable functional materials based on biological macromolecules.

Materials and methods

Materials

Xylose residue was obtained from Longlive Biotechnology Co. Ltd. (Shandong, China). It was washed with water by sonication for 30 min and dried in an oven at 60 °C for 12 h. Then, the clean xylose residue was crushed by a grinder and picked out through a sieve with 80 meshes per square inch. The ionic liquid, 1-ethyl-3-methylimidazolium acetate ([Emim]Ac), was purchased from Chengjie Chemistry Co., Ltd. (Shanghai, China). Sodium hydroxide was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China).

Fabrication of sustainable ultraviolet-blocking films

The fabrication process of the UV-blocking films was illustrated in Fig. 1. In industry, corn cobs were used to produce xylitol, remaining a large amount of xylose residue (Residue 1). After partial delignification by 2% NaOH at 80 °C with the solid to liquid ratio of 1:10, the residue 2 that was mainly composed of cellulose and lignin was

converted into the mixture with different lignin content (4.4%, 9.6%, 19.5%, and 29.7%). Subsequently, approximately 5 wt% residue was directly dissolved in [Emim]Ac under magnetic stirring at 90 °C for about 2 hours. The obtained uniform xylose residue/ILs solutions were degassed in vacuum oven and casted on a smooth and flat glass plate. After regeneration though immersing in deionized water to remove ionic liquid and drying in oven at 60 °C for 12 h, the xylose residue films were finally obtained.

Fig. 1 The schemes showing the fabrication process of xylose residue films

Characterization

The as-prepared films were coated with gold-palladium in a sputter coater (Hitachi E-1010, Japan) and then observed with a scanning electron microscope (SEM, JMS-7401, Japan) at acceleration voltages of 3 kV. Fourier transform infrared (FTIR) spectrometer (Nicolet iN10-MX, Thermo Scientific) equipped with an attenuated total reflectance (ATR) was utilized to study the chemical structure of films. A total of 32 cumulative scans were taken in the transmittance mode, with a resolution of 4 cm⁻¹ in the region of 4000-600 cm⁻¹. The crystalline structure of native xylose residue, cellulose film and xylose residue films was studied by X-ray diffraction analyzer (XRD, D8 Advance, Bruker) equipped with Ni-filtered Cu K α_1 radiation ($\lambda=0.154$ nm). The scattering range was 5-40° at an increment of 0.05° with a scanning rate of 8° min⁻¹.

The optical transmittance of obtained films was measured with a UV-Vis spectrometer (UV-2550, Shimadzu)

in the wavelength range 200-600 nm, which revealed the transparency and UV-blocking feature of films. The blocking percentage for UVB (280-320 nm) and UVA (320-400 nm) was calculated by eqn. (1) and (2), respectively:

$$\text{UVB blocking (\%)} = 100 - \frac{\int_{280}^{320} T(\lambda) d(\lambda)}{\int_{280}^{320} d(\lambda)} (\%) \quad (1)$$

$$\text{UVA blocking (\%)} = 100 - \frac{\int_{320}^{400} T(\lambda) d(\lambda)}{\int_{320}^{400} d(\lambda)} (\%) \quad (2)$$

Where $T(\lambda)$ is the average spectral transmittance of the films, $d(\lambda)$ is the bandwidth, and λ is the wavelength.

The water vapor permeability (WVP) of films was determined following the standard ASTM E 96/E 96M. The test film was sealed to a 10 ml beaker containing 12 g anhydrous calcium chloride. The device was dried at 105 °C for 24 h at beginning of the experiment. To maintain an 85% relatively humidity (RH) gradient, saturated KCl solution was placed in desiccator at 25 °C. The WVP was calculated following the eqn. (3):

$$\text{WVP} = \frac{qd}{ts\Delta P} \quad (3)$$

Where q/t is the slope of the weight increase versus time (g/s), d is the thickness (cm) of the film, s is the area of the film which is exposed to humidity condition (4.91 cm²), ΔP is the difference of the vapor pressure between the two sides of films (23.76 mmHg). Three replicates were measured for each sample.

Surface wettability of the obtained films was measured by a water contact angle (WCA) meter (SL200KS, Kino). A drop of deionized water about 10 μL was placed on the surface of films from a micro-syringe. The film samples (1×3 cm²) were fixed on the movable sample plate leveled horizontally before measurement. The measurements were repeated three times for each sample. The mechanical properties of the films were measured using Zwick Z005 with a 100 N load cell at room temperature. The thickness of films should be tested with a micrometer (Lorentzen and Wettre, precision 1 μm) before measurements. The samples were cut in the rectangular specimens of 10 mm long and 40 mm wide, and at least five replicate specimens were tested from each film. Thermal stability of the films was characterized by thermogravimetric analysis (TGA) using a thermogravimetric analyzer (TG/DTA6300, Seiko) under a N₂ atmosphere from 50 to 600 °C with a heating rate of 10 °C/min.

Results and discussion

Componential and morphological analysis

Lignin contents in the delignified xylose residue treated by 2% NaOH were tuned via changing reaction time (0-3 h), which may be attributed to that a suitable concentration of NaOH can break the bond between lignin and

carbohydrate(Chahal 1983). As shown in Supplementary Fig. S1, the lignin content in xylose residue decreased from 29.7% to 1.2% with the reaction time increased from 0 to 3 h. The initial treatment in the first 1 h exhibited apparent effect on the delignification of xylose residue. However, further prolonging the treatment time to 3 h had a limited effect on decreasing lignin content in xylose residue, which may be contributed that the reaction has already reached an equilibrium state in the first 1 h. After treatment for 8, 30, and 60 min, the xylose residues with the lignin of 19.5%, 9.6%, and 4.4% were obtained, respectively. These residues and the untreated one with 29.7% lignin were selected as raw materials for the fabrication of the UV-blocking films. The films were referred as F-29.7, F-19.5, F-9.6, and F-4.4. For comparison, the pure cellulose based regenerated film was also prepared and referred as F-Cell.

The morphology of xylose residue films was critical to their properties, such as transparency, surface wettability and mechanical strength. The photographs of F-Cell, F-9.6, and F-29.7 were presented in Fig. 2a-c. As can be seen, the F-Cell showed a high optical transparency, which was demonstrated by the clearly identified printed text under the film. Although the xylose residue films of F-9.6 and F-29.7 had a yellow-brown color, they also exhibited a great optical transparency; this was essential to their practical applications as UV-blocking films in a wide range.

The surficial and cross-sectional morphology of films were further investigated by SEM. The F-Cell displayed a smooth and neat surface (Fig. 2d). However, F-9.6 and F-29.7 showed a relatively rough surfaces (Fig. 2e, f), which was probably attributed to the existence of lignin. On the other hand, as shown by the cross-sectional images of films (Fig. 2g-i), the F-9.6 and F-29.7 possessed roughly but densely laminated structures than the F-Cell, which may be due to the hydrophobic property of lignin(Petridis et al. 2011).

Fig. 2 (a-c) Photos of F-Cell, F-9.6, and F-29.7 placed close to the printed pattern underneath. (d-f) The surface morphologies of F-Cell, F-9.6, and F-29.7. (g-i) The cross-sectional morphologies of F-Cell, F-9.6, and F-29.7

Chemical and crystalline structure

FT-IR spectra of the regenerated films are shown in Fig. 3a. The F-Cell and all xylose residue films had obvious absorbances associated with cellulose. The bands at 3359 and 2891 cm^{-1} are attributed to O-H stretching and C-H stretching. A small absorbance at 1421 cm^{-1} is assigned to the symmetric bending of CH_2 . The bands at 1370 , 1315 and 1152 cm^{-1} correspond to the O-H bending, C-H bending and C-O anti-symmetric stretching, respectively. The absorbance at 1046 cm^{-1} could be attributed to the C-O-C stretching on the pyran ring. A small sharp band at 893 cm^{-1} is ascribed to the β -glucosidic linkages between glucose in cellulose. In addition, the spectra of xylose residue films exhibited characteristic bands of lignin at 1602 , 1514 , 1453 and 833 cm^{-1} , which are assigned to the aromatic skeletal vibrations and C-O stretching in lignin(Liu et al. 2008). Furthermore, the absorption intensity of these bands was enhanced with the increased lignin content. The crystalline structure of raw xylose residue and as-prepared films was evaluated by XRD patterns and illustrated in Fig. 3b. The raw xylose residue displayed characteristic peaks at 15.5° , 22.2° , and 34.5° —corresponding to (110), (110), (200) and (004) crystal plane, respectively—which belonged to the typical diffraction of cellulose I(Ling et al. 2018). After dissolving by

[Emin]Ac and regenerating in deionized water, the obtained films showed the crystal form of cellulose II according to the diffraction peaks at 12.1° ($1\bar{1}0$) and 20.1° (110). These results reveal that the cellulose I crystalline structure was completely disappeared and cellulose macromolecules were recrystallized as cellulose II after dissolution in ILs followed by regeneration in deionized water. In addition, the crystallinity of regenerated films decreased compared with raw xylose residue.

Fig. 3 (a) FTIR spectra and (b) XRD patterns of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

UV-blocking and water vapor barrier performance

The UV blocking capability are important for broadening the films' potential applications. Fig. 4a shows the optical properties of regenerated films based on cellulose and xylose residue. As can be seen, F-Cell exhibited a high transmittance of 90.1% at 600 nm. The as-prepared xylose residue films of F-4.4, F-9.6, F-19.5 and F-29.7 exhibited relatively lower transmittances of 86.6%, 75.9%, 68.7% and 50.6% at 600 nm, respectively due to the increased content of lignin. Long wavelength UVA with strong penetrating ability, affecting the human health; UVB, in contrast, with shallower penetration depth, also cause much harmful impact and potential risk of skin cancer(Ling et al. 2020). As expected, all the xylose residue films showed excellent UV blocking capability in both UVA and UVB range, when compared to the F-Cell. The UVB and UVA blocking percentage for each film are presented in Fig. 4b. F-Cell had a relatively low value of UV blocking capacity (barely 17.0% for UVB and 14.1% for UVB) owing to the absence of functional groups for UV shielding. A striking difference was noted that as-prepared xylose residue films, including F-9.6, F-19.5 and F-29.7, showed strong UV blocking performance. Tuning the films by different content of lignin lead to the different UV blocking capability. The UVB blocking performance for F-4.4, F-9.6, F-19.5, and F-29.5 were 68.6%, 98.4%, 99.2%, and 99.2%, respectively. The UVA

blocking performance also exhibited similar results for F-4.4 (47.1%), F-9.6 (87.6%), F-19.5 (93.9%), and F-29.5 (98.2%). This may be related to the phenylpropane-based structure or hydroxyphenyl groups of lignin in ultraviolet region(Li et al. 2019a). Taken together, these results suggest that the xylose residue films have promising prospects for application in UV blocking.

Fig. 4 (a) Optical transmission spectra and (b) UV blocking rate of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Water vapor permeability (WVP) is another important parameter of films for various fields. Especially for food packaging applications, the value of WVP should be as low as possible to maintain the food quality. Table 1 shows the WVP of films with different lignin content. The results implied that the WVP of xylose residue films were lower than that of pure cellulose film. With the increase of lignin content, the regenerated xylose residue films exhibited a better barrier property. This result could be explained by the intermolecular interaction between lignin and cellulose that hindered the way for water vapor to diffusion(Shankar et al. 2015). Furthermore, the laminated structures mentioned by SEM images could also result in less permeation of water vapor.

Table 1 Water vapor permeability of regenerated cellulose and xylose residue films

Sample	WVP
	($\times 10^{-11} \text{ g} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{mmHg}^{-1}$)
F-Cell	3.36 ± 0.37
F-4.4	2.76 ± 0.11
F-9.6	2.71 ± 0.26
F-19.5	2.67 ± 0.37
F-29.7	2.17 ± 0.10

Surface wettability, tensile properties, and thermal stability

The surface wettability and hydrophobicity are significant for substrates toward wide applications. Herein, the surface wettability of different films was investigated by contact angle and shown in Fig. 5. The F-Cell showed a WCA of 66.8° , while the xylose residue films of F-4.4, F-9.6, F-19.5, and F-29.7 showed a WCA of 72.3° , 76.2° , 80.5° and 86.4° , respectively. The increase of hydrophobicity of xylose residue films was mainly due to the aromatic structure and the fewer hydroxyl groups of lignin compared to cellulose(Llevot et al. 2016). Moreover, amount of lignin in films can hinder the formation of hydrogen bonding from the free hydroxyl group and water molecules(Bian et al. 2018). In addition, the WCA of prepared xylose residue films was constant as the time increased, which proved the excellent stability of films' surface structure.

Fig. 5 The WCA of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

The mechanical properties like strength and toughness of films were further tested to ensure that the films have sufficient physical performance. The stress-strain curves of the regenerated cellulose film and xylose residue films are shown in Fig. 6a. The mechanical properties including tensile strength, tensile strain, and toughness of as-prepared films are also summarized in Supplementary Table S1. As can be seen, the F-Cell had a tensile stress of 70.63 ± 2.91 MPa, which attributed to the original great performance of native cellulose fiber. For four xylose residue films of F-4.4, F-9.6, F-19.5 and F-29.7, they had relatively lower tensile strength of 66.49 ± 5.28 MPa, 54.95 ± 0.18 MPa, 45.86 ± 1.89 MPa and 42.27 ± 2.39 MPa, respectively. These results suggested that lignin have a negative impact on the film's tensile strength, which may be due to the lignin's interference of hydrogen bonding formation between cellulose fibers in composite films(Bian et al. 2018). However, the tensile strength of obtained

xylose residue films is higher than that of commercial petroleum-based films (such as PE and PP), which exhibited tensile strengths of 20-40 MPa(Li et al. 2019b). In Fig. 6b, the xylose residue films possessed a lower toughness but much higher stiffness compared with F-Cell, which may be attributed to the rigid structure of lignin. From the SEM images in Fig. 2h-i, the poor mechanical strength of xylose residue films might be relevant to their layered structures caused by the hydrophobicity of lignin particles. In addition, low crystallinity shown in XRD patterns could be another reason for the poor mechanical performance results(Harris and Lee 2008). Therefore, various films with tunable UV-blocking and mechanical properties via tunable delignification and regeneration could be obtained and used in different application.

Fig. 6 (a)Tensile stress-strain curves and (b) toughness comparison of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

The thermal stability of the regenerated films was investigated using TGA and DTG analysis under a nitrogen atmosphere. As Fig. 7a shows, all the films exhibited two steps of degradation. The first weight loss occurred below 200 °C due to the release of water. In the range of 200-600 °C, the rate of decomposition and mass weight of regenerated films were maximum, which was mainly due to the degradation of cellulose. Evidently, the amount of remaining solid residue at 600 °C of the five regenerated films were 15.52%, 17.88%, 18.02%, 21.57%, and 25.41%, respectively, which implied that the thermal stability of the xylose residue films was improved with the increase of lignin content. Besides, the T_{onset} (the temperature at onset of the decomposition of polymer), T_{max} (the maximum weight loss temperatures), and the residue values of the films were determined from the DTG curves as shown in Table 2. Obviously, F-29.7 showed the highest T_{onset} of 251.42 °C and T_{max} of 345.99 °C compared to other films, indicating that lignin has a positive effect on the thermal behavior of films(Sadeghifar et al. 2016). The increased thermal stability of films makes the xylose residue films a promising candidate for applications in electronic, energy, sensing, and other high-tech fields.

Fig. 7 (a)TGA and (b) DTG curves of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Table 2 Thermal characteristics of TG curves in Fig. 7

Curve	F-Cell	F-4.4	F-9.6	F-19.5	F-29.7
T_{onset} (°C)	243.88	246.55	249.31	250.00	251.42
T_{max} (°C)	340.81	338.96	343.87	343.95	345.99
Residue (wt%) at 600 °C	15.52	17.88	18.02	21.57	25.41

Conclusion

In summary, the biodegradable and flexible UV-blocking films have been fabricated based on xylose residue via the top-down tunable delignification and regeneration. Taking advantage of the original lignin, the obtained xylose residue films possessed excellent UV-blocking property (68.6-99.2% for UVB and 47.1-98.2% for UVA) and great optical transmittance (50.6-86.6%). They also exhibited enhanced water vapor barrier property, surface wettability, and thermal stability when compared to pure cellulose films. In addition, the xylose residue films showed a better tensile strength than that of most of petroleum-based films, satisfying the commercial demands. Therefore, our sustainable UV-blocking films based on xylose residue have great potential and prospects for diverse applications, such as flexible electronics, food packaging, and windshields. This work provides a new perspective on converting xylose residue directly to high value-added functional materials.

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273

274 **Appendix A. Supplementary data**

275 Effect of reaction time on the delignification of xylose residue; the mechanical properties of as-prepared
276 regenerated cellulose film and xylose residue films. (PDF)

277

278 **Compliance with ethical standards**

279 Conflict of interest: The authors declare that they have no conflict of interest.

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385 **Graphical abstract**

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Figures

Figure 1

The schemes showing the fabrication process of xylose residue films

Figure 2

(a-c) Photos of F-Cell, F-9.6, and F-29.7 placed close to the printed pattern underneath. (d-f) The surface morphologies of F-Cell, F-9.6, and F-29.7. (g-i) The cross-sectional morphologies of F-Cell, F-9.6, and F-29.7

Figure 3

(a) FTIR spectra and (b) XRD patterns of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Figure 4

(a) Optical transmission spectra and (b) UV blocking rate of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Figure 5

The WCA of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Figure 6

(a) Tensile stress-strain curves and (b) toughness comparison of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

Figure 7

(a) TGA and (b) DTG curves of F-Cell, F-4.4, F-9.6, F-19.5, and F-29.7

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