

Ultrastrong, Hydrostable, and Degradable Straws Derived from Microplastic-Free Thermoset Films for Sustainable Development

Dickens O. Agumba, Duc Hoa Pham, and Jaehwan Kim*

Cite This: *ACS Omega* 2023, 8, 7968–7977

Read Online

ACCESS |



Metrics & More

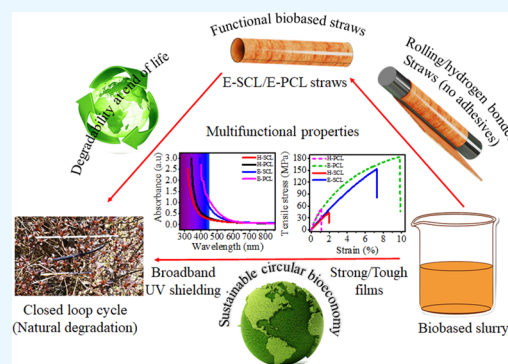


Article Recommendations



Supporting Information

ABSTRACT: Single-use plastics such as straws have caused intricate environmental challenges since they are not readily assimilated into nature at the end of life. Paper straws, on the contrary, become soggy and collapse in drinks resulting in an obnoxious user experience. Here, all-natural, biocompatible, degradable straws and thermoset films are engineered by integrating economical natural resources—lignin and citric acid—into edible starch and poly(vinyl alcohol), making them the casting slurry. The slurries were cast on a glass substrate, partially dried, and rolled on a Teflon rod to fabricate the straws. The straws are perfectly adhered at the edges by the strong hydrogen bonds from the crosslinker—citric acid—during drying, thus eliminating the need for adhesives and binders. Further, curing the straws and films in a vacuum oven at 180 °C results in enhanced hydrostability and endows the films with excellent tensile strength, toughness, and ultraviolet radiation shielding. The functionality of the straws and films surpassed paper and plastic straws, making them quintessential candidates for all-natural sustainable development.



INTRODUCTION

Plastics possess a unique balance of attractive properties—low cost, durability, high versatility, and strength—making them ubiquitous materials for daily use.^{1–3} If the prevailing trends of plastic production and consumption continue, the Anthropocene era will be inevitable. In parallel, a growing global concern has arisen as immense volumes of plastic waste have caused considerable environmental damage.⁴ Among the key players in white pollution are plastic straws since they are single-use and have become an integral part of life.^{4,5} The huge consumption of these straws has seen exponential growth in discarded plastic straws, adding to the environmental load and negatively impacting aquatic, plant, and human life. On the remedies to plastic pollution, approaches best exemplified by reducing, reusing, and recycling the massive volumes of plastics have faced poor progress and success⁶ as plastics take centuries to degrade during their service and end of life.^{7–9} Once disposed of, plastic straws may end up in unwanted places such as the oceans and landfills, negatively impacting life forms via the release of dioxins and microplastic pollutants.^{10–14} With plastic pollution being significant to all life forms on earth¹⁵ and projected to surpass our waste management strategies, the search for alternative high-performance and economical bioderived straw sources is necessary to mitigate these challenges.

Toward a sustainable circular bioeconomy, scientists and engineers have explored a wide variety of materials with great potential for reducing plastic consumption.¹⁶ Among the key alternative materials for plastic straws are plant-based materials

giving rise to paper straws. These straws are sustainable and have a low carbon footprint. On the other hand, paper straws suffer from limited mechanical performance, are unsuitable for carbonated drinks, and often become soggy and collapse, translating into an obnoxious user experience. The limited stability of paper straws when wet may further impart unfavorable flavors to beverages or nasty feelings in the mouth.¹⁶ Besides, the compensation for hydrophilicity of the straws requires binders and wax for hydrophobic coating, which adds to the processing time and cost. Among other alternatives, metal straws lend the feeling of alleviating plastic waste, but the use of metal straws itself establishes new problems. The disposal rate of metal straws may be lower than plastic counterparts, but in the long run, the high energy cost for production and colossal volumes of carbon(IV) oxide emissions are guaranteed. If we trail the path to produce metal straws—from ore mining to the final straw—a fair amount of energy will certainly be spent. According to a recent study, the fabrication of a single stainless steel straw produces over 271% (>3.7 times) carbon(IV) oxide emissions as compared to plastic counterparts.¹⁷ Further, mining raw materials such as

Received: December 6, 2022

Accepted: February 8, 2023

Published: February 16, 2023



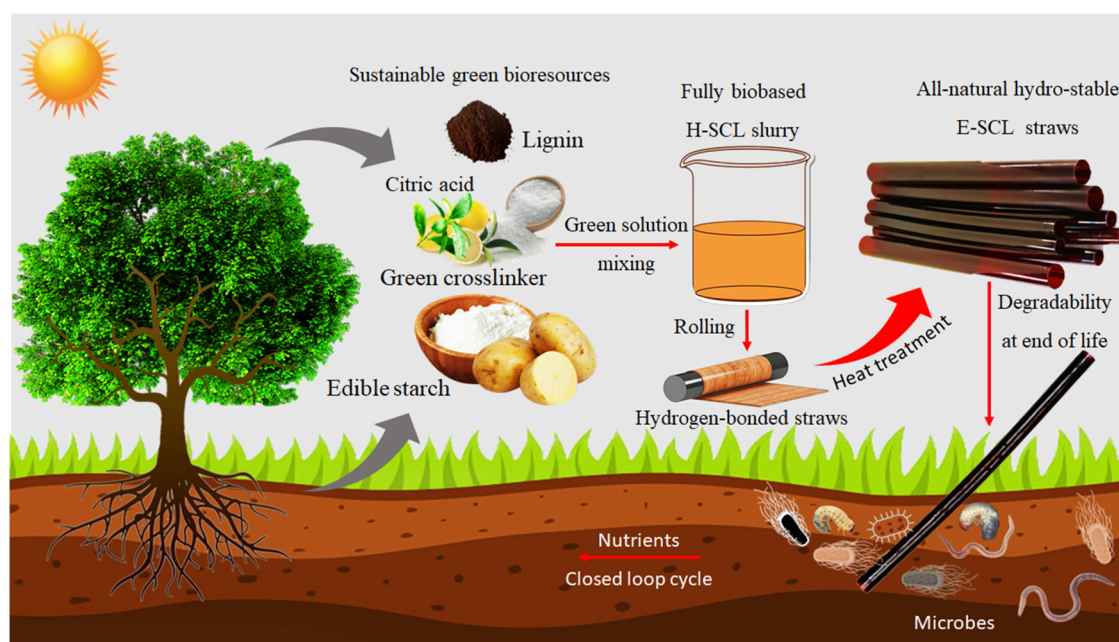


Figure 1. All-natural hydrostable straw fabrication scheme, curing, and closed-loop degradability cycle at the end of life.

nickel, chromium, and iron is energy-intensive and degenerates the landscape through deforestation, erosion, and deposition of spoils and tailings.¹⁸ Owing to the above challenges, polylactic acid (PLA) as a biodegradable engineering plastic may be an appropriate replacement for metal and plastic straws. The major drawbacks of PLA straws are their high cost arising from exorbitant raw materials, stringent degradation conditions unlike plant-based materials, and poor thermal resistance,^{19,20} making them unsuitable for beverages served at elevated temperatures. With the growth of plastic straw production and consumption surpassing any other engineering material,² alternative bioderived, biodegradable, and microplastic-free replacements are urgently needed²¹ for sustainable development. Unlike nonbiodegradable synthetic plastics, these alternative resources must be versatile in innumerable applications and readily assimilated in nature.

Currently, plastic straws bear the brunt of the backlash, though the scourge of such single-use plastics lies in our sheer reliance on them. Tackling this plastic pollution will demand a change in material selection and design. Among the key materials capable of mitigating white pollution, starch presents a sensible alternative since its readily available, economical, nontoxic, biocompatible, biodegradable, and microplastic-free,²² thus translating to a low-waste ecosystem. Following these merits, starch has been extensively used as a food additive,²³ strengthening paper,²⁴ warp sizing, optics, and packaging.^{25–27} In the fight against white pollution, the utilization and transformation of starch into versatile high-strength green materials such as straws is not profitable owing to the suboptimal performance of the resultant products.²² Other biocompatible and biodegradable polymers, such as poly(vinyl alcohol) (PVA), may act as alternatives for starch but are limited by their functionality. Although starch and PVA straws or products may be readily assimilated at the end of their life cycles, their low mechanical properties, hydrophilicity, and low durability while in service have been limited.^{28–32} Polymer fillers or reinforcements such as cellulose and lignin have been used to overcome limitations in the strength of

various materials. Lignin, a nontoxic polymer, possesses an aromatic ring that favors the engineering of advanced thermosets with desirable mechanical, chemical, and thermal properties. As a waste material from paper or pulping processes and a side stream of bioethanol and biorefinery concepts, lignin presents a salient sustainable material for synthesizing hydrostable advanced materials. However, the complex structure, free hydroxyl group, brittleness, and poor solubility of lignin have mainly resulted in disdain and incineration of the product as a fuel source. On the other hand, modifying lignin^{33–36} to enhance its reactivity may aid in making microplastic-free sustainable high-strength straws and multifunctional materials from starch and PVA.

In this work, we propose a simple, scalable, low-cost, and binder-free fabrication strategy for advanced microplastic-free straws and films from edible starch, citric acid, and lignin, readily available and economical resources as opposed to energy-intensive cellulose-based straws. The casting slurry (Figure 1) was made by blending starch and lignin, followed by citric acid as a crosslinker. By doctor blading and roll-up of the partially dry films on a Teflon rod, the straws adhere at the edges in a binder-free approach through the newly formed hydrogen bonds between starch, citric acid, and lignin (H-SCL straw). Similarly, hydrogen-bonded-poly(vinyl alcohol)—citric acid—lignin (H-PCL) straws were fabricated by following the above approach. We believe integrating economical resources such as lignin and citric acid into starch and PVA could help lower the production cost of such straws. When H-SCL and H-PCL straws and films are cured at 180 °C, strong and hydrostable straws and films of esterified-starch-citric acid-lignin and poly(vinyl alcohol)-citric acid-lignin (E-SCL and E-PCL) surpassing the strength of synthetic plastics and products were produced. Unlike synthetic plastics, our methodology utilizes a green solution mixing approach (water-based), and the straws can naturally degrade, demonstrating a fascinating closed-loop cycle aspect (Figure 1).

Further, the straws and films are mechanically robust in the dry and wet state and are hydrostable during service, disclosing

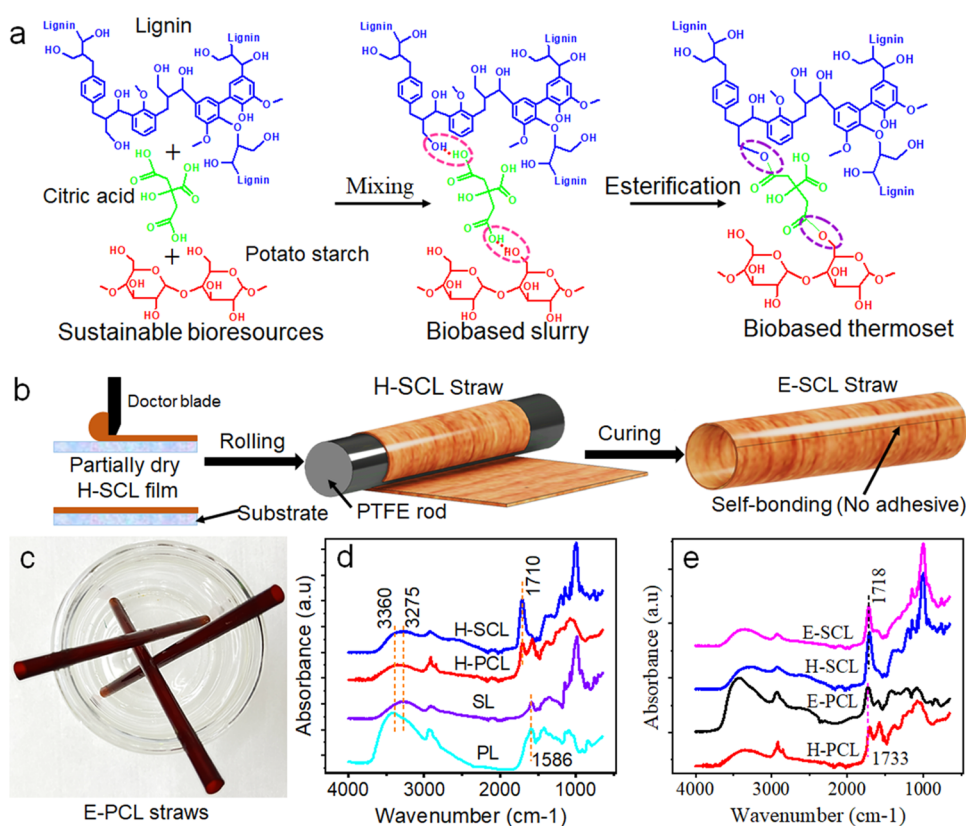


Figure 2. (a) Synthesis of H-SCL slurry and E-SCL thermoset films from sustainable resources, (b) doctor blade casting of H-SCL films and rolling to fabricate hydrogen and ester-bonded straws, (c) fabricated E-PCL straw, (d) FTIR spectra of the hydrogen-bonded films, and (e) FTIR spectra of the esterified thermoset films.

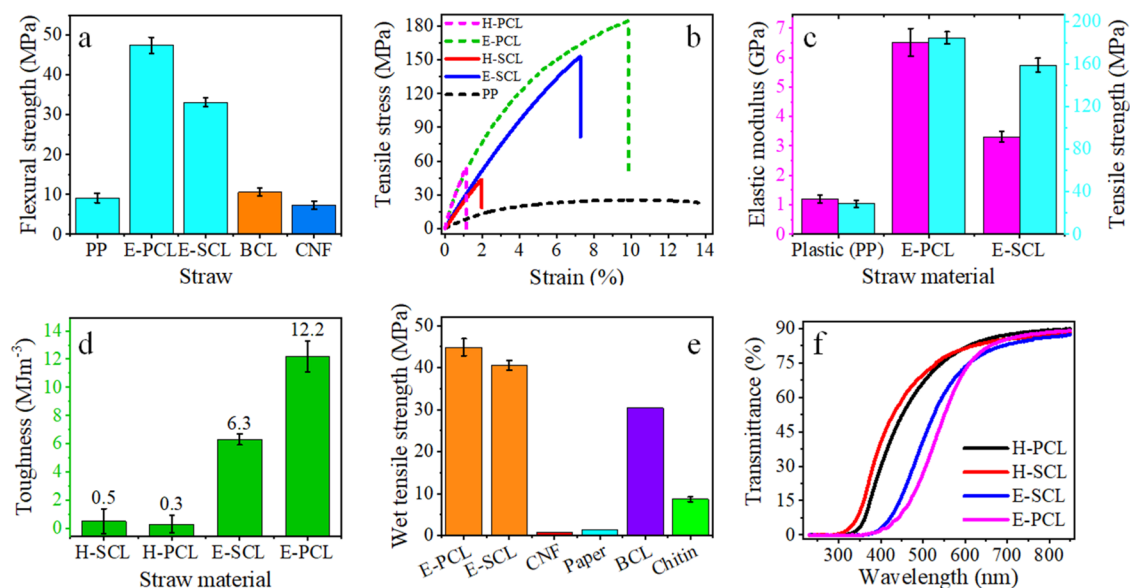


Figure 3. (a) Flexural properties of E-PCL and E-SCL straws in comparison to PP, BCL, and CNF straws, (b–e) tensile properties of hydrogen-bonded and esterified films compared to PP, CNF, paper, BCL, and chitin-based films, and (f) optical properties of H-SCL, H-PCL, E-SCL, and E-PCL films.

a remarkable balance between functionality, durability, and degradability at the end of life, which can hardly be provided by hydrophilic cellulose or conventional plastic straws. These hydrostable, fully biobased, and biodegradable straws and films can substantially reduce the environmental waste footprint generated by conventional synthetic plastics such as poly-

propylene (PP) and act as drivers for a sustainable bioeconomy.

RESULTS AND DISCUSSION

H-SCL slurry was synthesized using a facile solution mixing approach directly from economical and abundant resources—

Table 1. Mechanical Properties of E-SCL, E-PCL, and PP Films Contrasted with Previous Reports

straw films	σ_{tensile} (MPa)	ϵ_{break} (%)	E (GPa)	σ_{flexural} (MPa)	reference
E-SCL	158.8 \pm 6.5	7.3 \pm 0.2	3.3 \pm 0.2	33.1 \pm 1.1	this work
E-PCL	184.5 \pm 5.6	9.9 \pm 0.8	6.5 \pm 0.5	47.4 \pm 2.0	this work
PP	28.6 \pm 3.3		1.2 \pm 0.1	9.1 \pm 1.2	this work
LCS ^a	127.2	\leq 4	5.94	62.22	1
Ch-20A ^b	143.4 \pm 9.61	\leq 4.2	8.5 \pm 0.41	13.3 \pm 0.86	3
CL ^c	30.2	\leq 9	\leq 1.2	10.6 \pm 1.0	39
BCL ^d	75.2	\leq 4	2.8	9.85 \pm 0.3	39
CH ^e	70	10.2	1	6.9 \pm 0.8	40
CNF ^f	\leq 59	2.4	2.3	7.3 \pm 1.0	40
BC/A ^g	420.5 \pm 31.3	\leq 11.5	\leq 5	35.3 \pm 3.9	42

^aLignocellulose. ^bChitin-based. ^cCellulose lignin. ^dBaked cellulose lignin. ^eCellulose hybrid fibers. ^fCellulose nanofiber. ^gBacterial cellulose/alginate-coated.

edible potato starch, citric acid, and kraft lignin. The potato starch serves as a film-forming agent, lignin—typically an incinerated waste resource—provides the required reinforcement for added strength and stiffness, while the citric acid is a crosslinker endowing the slurry with numerous hydrogen and ester bond linkages, as depicted in Figure 2a.

The slurry was cast on a glass substrate by doctor blading technique and partially dried, giving rise to highly flexible films that can be readily processed into H-SCL straws by rolling on a Teflon rod, as portrayed in Figure 2b. The straws are effectively adhered to the edges by the newly created hydrogen bonds during drying, thus eliminating the need for extra binders or adhesives. The strong ester bonds formed on curing further boosted the bond strength, and the straws portrayed no evidence of edge delamination (Figure 2c). Figure 2d shows FTIR spectra of H-PCL and H-SCL films. The starch-lignin (SL) and PVA-lignin (PL) films are included for comparison. The peaks at 3360 and 3275 cm^{-1} correspond to the $-\text{OH}$ peak stretching of aliphatic and aromatic chains, while the band at 1586 cm^{-1} denotes the merging of the hydrogen bonding of starch and PVA and the aromatic skeletons of lignin, respectively.³⁷ The sharp peak at 1710 cm^{-1} is attributed to the stretching mode of the carbonyl group and hydrogen bonding between hydroxyl and carboxylic groups. Further, the peak at 1710 cm^{-1} shifts to a higher wavenumber of 1718 and 1733 cm^{-1} (Figure 2e) after heat treatment of H-SCL and H-PCL, respectively, and this occurrence implies successful ester bond formation.^{37,38} The esterified films are thermosets, which are hydrostable, thermally stable, mechanically robust, biocompatible, and biodegradable.

Mechanical properties are crucial in determining the efficacy of the straws and establishing their service life. In this regard, we evaluated the flexural properties of E-SCL and E-PCL straws following a previous report.³⁹ Figure 3a shows the flexural properties of E-SCL and E-PCL straws in comparison with PP straws, baked cellulose lignin (BCL) straws,³⁹ and cellulose nanofiber (CNF) straws,⁴⁰ respectively. E-SCL and E-PCL straws displayed a record high flexural strength of 33.1 \pm 1.1 and 47.4 \pm 2.0 MPa, respectively. The PP and the recently reported BCL and CNF straws exhibit a flexural strength of 9.1 \pm 1.2, 10.6 \pm 1.0, and 7.3 \pm 1.0 MPa, respectively. Thus, E-SCL and E-PCL straws are over 3.6 and 5.2 times stronger than the PP straws and 3.2 and 4.4 times stronger than the previously reported BCL straws. Despite the excellent flexural strength of LCS¹ shown in Table 1, the raw materials require prolonged processing time and involve the use of toxic chemicals. Nonetheless, the fabrication process of our straws is

simple, economical, and scalable, thus presenting a sensible route for the commercialization and replacement of synthetic plastics.

Regarding ecological waste footprints, we hypothesize that E-SCL and E-PCL straws may help alleviate microplastic pollution and present more eco-friendly straw alternatives, given their biobased nature. In a recent report, high bending strength (35.3 \pm 3.9 MPa) and microplastic-free bacterial cellulose/alginate straws⁴¹ were more effective than their plastic counterparts. Though the straws have comparable performance, E-PCL straws are 134.4% superior in flexural strength. In terms of simplicity, cellulose production by mechanical and biosynthesis approaches is energy-intensive, costly, and various processes and parameters are involved,⁴² making bacterial cellulose/alginate-coated (BC/A) straw fabrication time-consuming. Furthermore, the straws require a layer of alginate coating to compensate for their hydrophilicity. In contrast to the recently reported lignocellulose straws (LCS)¹ and Chitin-based straws,³ the processing and fabrication time for the straws is cumbersome. Based on these aspects, E-SCL straws may provide a simpler, cost-effective, and scalable approach in microplastic-free straw manufacturing since starch is relatively cheap compared to cellulose.

Further, we characterized the tensile properties of H-SCL, E-SCL, H-PCL, and E-PCL films (Figure 3b–d) and compared them to the commercial PP films (Figure 3b,c) and recent reports (Table 1) to ascertain their performance and viability in functional scenarios. H-SCL and E-PCL films displayed a brittle failure mechanism with a tensile strength of 43.5 and 54.8 MPa, respectively. These films have high strength and stiffness as compared to PP. In parallel, the brittleness limits the functionality of the films as a straw material. Meanwhile, the heat treatment of H-SCL and H-PCL introduced remarkable improvements in strength, elastic modulus, and toughness. E-SCL and E-PCL films displayed a record high tensile strength of 158.8 \pm 6.5 and 184.5 \pm 5.6 MPa with Young's modulus of 3.3 \pm 0.2 and 6.5 \pm 0.5 MPa, respectively.

In contrast to the PP films, E-SCL and E-PCL films revealed an enhancement in strength by over 556.0 and 646.2%, respectively, making the all-natural films more suitable for straw fabrication and advanced applications. Strikingly, it is worth noting that the toughness of E-SCL and E-PCL (Figure 3d) were superior by over 1260 and 4066.6% to H-SCL and H-PCL films. This exceptional enhancement of the mutually exclusive strength and toughness is ascribed to the heat treatment, which transforms the carboxyl and hydroxyl groups into strong ester bonds,^{37,38} as validated by FTIR spectra in

Figure 1d. This work shows that simple heat treatment approaches can fabricate strong and crack-resistant materials exhibiting enhanced failure strain (Figure 3b). Further, the tensile strength of E-SCL and E-PCL films surpassed those of previous reports, except for BC/A films, as depicted in Table 1. Thus, the desirable strength and flexibility of E-SCL and E-PCL films make them an excellent choice for straw materials that can substitute PP straws and aid in alleviating the environmental waste load and mass pollution caused by synthetic plastics.

The wet tensile strength is an equally important parameter that defines the application field of material. Materials such as paper require chemical agents such as wet-strength resins to enhance their wet strength. From Figures 3e and S1 and Table S1, E-SCL and E-PCL films display a wet strength of 40.6 ± 1.1 and 44.8 ± 2.0 MPa discretely after 2 h of water immersion. In the previous report,³⁹ BCL straw films were immersed in water for only 30 min, even though E-SCL and E-PCL films still showed superior performance. For an improved user experience, a straw material should maintain a high wet strength for longer since some users may prefer to take longer during leisure. The CNF, paper, and cellulose lignin (CL) straws portrayed in Figure 3e and Table S1 display an inferior wet strength, revealing that the straws will become soggy and collapse in drinks, translating into a poor user experience. Furthermore, the poor wet strength may impart negative flavors and nasty feelings in the mouth while using such straws. Though BC/A⁴¹ straws were shown to be more suitable for various drinks such as cola, the compensation of wet strength using a layer of alginate coating and binder makes the processing time-consuming. In addition, the fabrication of the reported ultra-strong LCS¹ requires a long processing time and toxic chemicals. The straws in this work do not require the use of binders and wet strength compensation agents and are also derived from economical resources such as starch, lignin, and citric acid.

The functional performance of H-SCL, H-PCL, E-SCL, and E-PCL films as UV shielding materials was evaluated by utilizing a dual-beam spectrophotometer. The films display an outstanding UV performance and optimum transparency in the visible region, as shown in Figures 3f and S2. The average UV shielding/absorption capacity for UVA (315–400 nm) and UVB (290–315 nm) by the films was evaluated from eqs 1 and 2 to determine their efficacy in UV radiation shielding applications (where n is the overall number of quantities and $i = 0, 1, 2, 3, \dots$).

$$\text{UVB}_{T_{\text{avr}}} = \frac{1}{n} \sum_{n=1}^{i=0} T_{5i+290} \quad (1)$$

$$\text{UVA}_{T_{\text{avr}}} = \frac{1}{n} \sum_{n=1}^{i=0} T_{5i+315} \quad (2)$$

Considering the data in Table 2, H-SCL and H-PCL absorb over 99% UVB while E-SCL and E-PCL absorb broadband (100%) UVB radiation. The strong UVB absorption by the hydrogen-bonded films is due to the aromatic nature of lignin that confers UV shielding. On the other hand, it was noted that the color of the films changed from light brown to dark brown after the heat treatment. It is known that dark colors provide better UV absorption than light colors,^{43,44} and this explains the broadband UVB shielding by E-SCL and E-PCL films.

Table 2. Average UV Shielding Properties of H-SCL, H-PCL, E-SCL, and E-PCL Films

UV radiation	average transmittance, % T_{avr} (UV absorbance = $100 - \%T_{\text{avr}}$)			
	H-SCL	H-PCL	E-SCL	E-PCL
UVB	0.68	0.02	0	0
UVA	21.1	12.15	0.54	0.44

Analogous observations were made on the UVA shielding properties of the films, whereby E-SCL and E-PCL films revealed over 99% shielding capacity in combination with high visible transparency. The multifunctional nature of E-SCL and E-PCL films disclose their versatility and potential in substituting synthetic or petroleum-based plastics. The enhanced UV shielding and strength of the films make them suitable for automobile and structural window coatings and the protection of cultural relics in museums and greenhouse plants.⁴⁵

Straws are used for convenience when consuming beverages; thus, they can be soggy and collapse in the drink. Moisture sorption can significantly impact material characteristics⁴⁴ and must be considered depending on the application fields. The moisture uptake by starch-soluble (SS), starch-lignin (SL), H-SCL, H-PCL, E-SCL, and E-PCL was evaluated by fully immersing the films in DI water for 24 h. From Figure 4a,b, H-SCL is shown to absorb over 100% moisture and reaches an equilibrium after about 2 h. The slight reduction in weight gain after 24 h of immersion was linked to the partial dissolution of lignin and citric acid from the films. However, H-PCL absorbed over 500% moisture without evidence of saturation after 24 h, revealing its hydrophilic nature. The heat treatment of H-SCL and H-PCL resulted in a remarkable decrease in moisture absorption by over 178.5% (E-SCL) and 196.3% (E-PCL). It shows that the esterified network is more compact and can significantly reduce moisture uptake and enhance the hydrostability of the straws.

The wetting characteristics of the films (Figure 4c) were also studied using a contact angle goniometer. Starch-lignin (SL) and PVA-lignin (PL) films recorded the lowest water contact angle (WCA) of 48.3 ± 0.9 and $29.5 \pm 2.9^\circ$, respectively. These films are endowed with more hydroxyl groups on their surfaces, thus the low hydrophobicity. The incorporation of citric acid into the films resulted in improved WCA, as evident in Figure 3c. This phenomenon shows that the crosslinked structure has limited free hydroxyl groups to interact with water molecules on the surface (Figure 2a). Furthermore, great improvements in the hydrophobic performance surpassing the previous report¹ were attained upon heat treatment due to the dense network structure formed during the esterification reaction. To gain more insights into the improved hydrophobic performance of E-SCL and E-PCL, we investigated the changes in the morphology of the films via SEM, with the results depicted in Figure 4d. H-SCL and H-PCL films displayed a smooth surface with a brittle failure characteristic, as evident in Figure S1, whereas dimpled structures were apparent on E-SCL (Figure 4d) and E-PCL (Figure 4f) films. The dimpled features are attributed to moisture liberation during heat treatment.^{37,38} The classical wetting theory has established that surface roughness or anomalies triggered by hierarchical structures is a prerequisite for hydrophobic modification and self-cleaning.^{46,47} Besides the compact structure from the

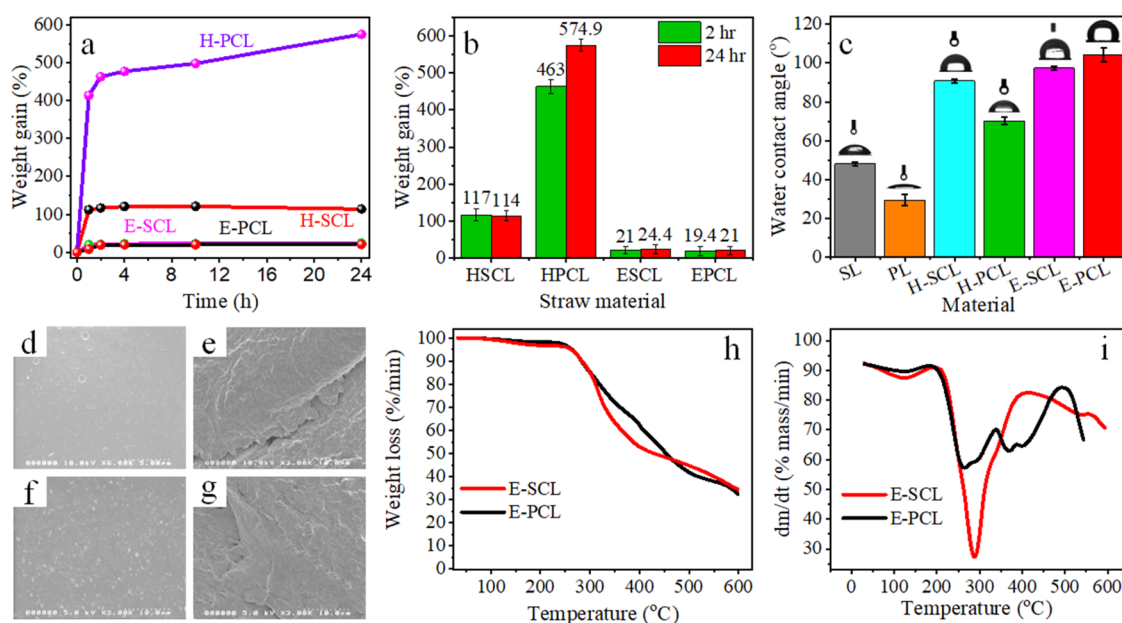


Figure 4. (a) Weight gain of H-SCL, H-PCL, E-SCL, and E-PCL films versus time, (b) wetting analysis of SL, PL, H-SCL, H-PCL, E-SCL, and E-PCL films, (c) water contact angle of SL, PL, H-SCL, H-PCL, E-SCL, and E-PCL films, (d–g) surface and cross-sectional morphology of E-SCL (d, e) and E-PCL (f, g) respectively, and (h, i) thermogravimetric analysis and derivative weight loss of E-SCL and E-PCL films.

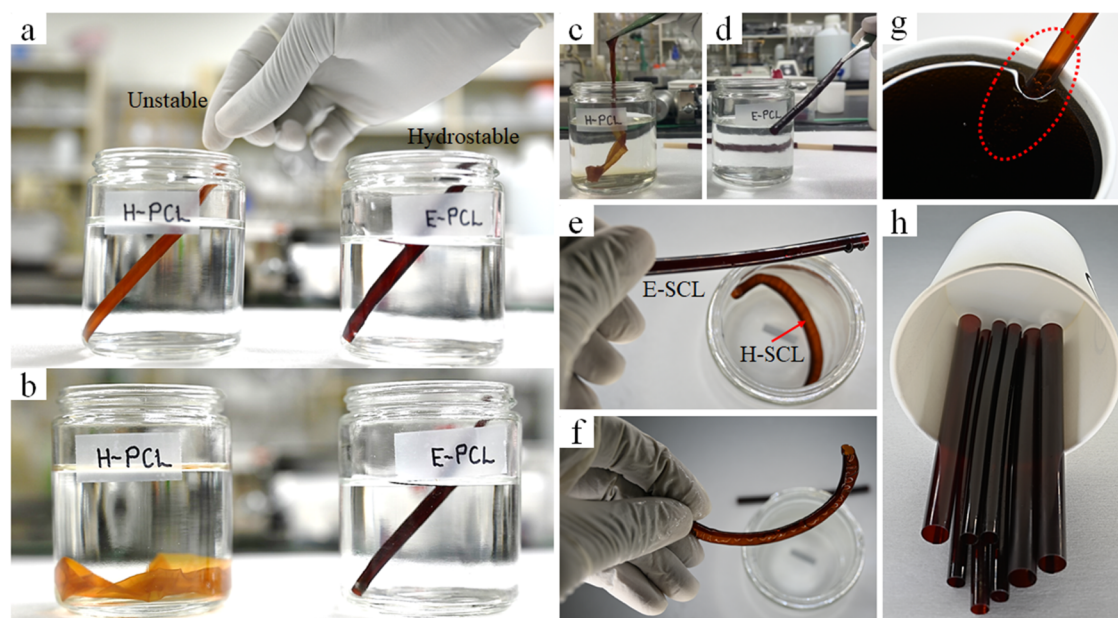


Figure 5. (a–f) Hydrostability of H-SCL, H-PCL, E-SCL, and E-PCL straws, (g) functionality of H-SCL straw in a cola drink, and (h) mass-produced E-SCL straws of different sizes and diameters.

excellent degree of crosslinking after heat treatment, we suspect the dimpled surface ameliorated the WCA of the films.

Figure 4h,i depicts the thermal degradation behavior of E-SCL and E-PCL straws. The onset of degradations for E-SCL and E-PCL occurred at 202.3 and 189.1 °C, while their maximum degradations were 288.3 and 265.8 °C. Moreover, the degradation of the esterified straws is 146.4% (E-SCL) and 130.2% (E-PCL), superior to the hydrogen-bonded straws, as evident in Figure S3 and Table S2. The enhanced thermal stability shows that the straws can be used in various beverages at different temperatures. Compared to PP straws, our straws will not generate harmful microplastics.

Hydrostability of paper straws has adversely impacted their performance, commercialization, and continued use.⁴⁸ Therefore, we analyzed the hydrostability of H-PCL, H-SCL, E-PCL, and E-SCL straws by immersing them in normal and hot water maintained at 95 °C to show their superiority over paper straws and to establish their potential for replacing plastic and paper straws. H-PCL straw became soggy, swollen, and collapsed in the water after a few minutes, as shown in Figure 5a,b and Video S1. The resultant amorphous structure became unstable, intertwined in water, and could no longer be considered a straw.

On the other hand, H-SCL straws displayed a swollen warped structure (Figure 5e,f), indicating that the straws are

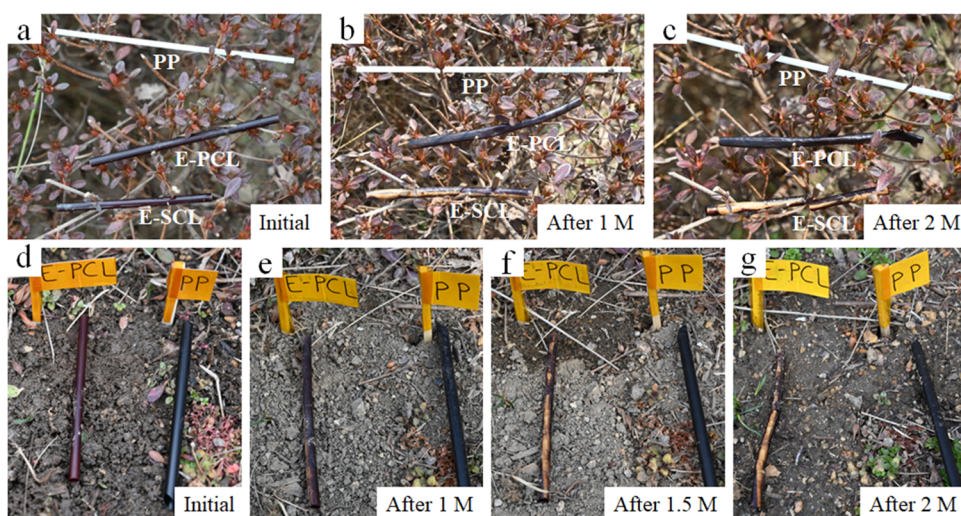


Figure 6. (a–c) Natural degradation of E-SCL and PP straws supported by a tree, and (d–g) E-PCL straws in contrast to PP straws placed on the surface of the soil.

unsuitable for sipping beverages. By contrast, E-PCL and E-SCL straws (Figure 5d,e) were hydrostable for over 30 min and 24 h in hot water and normal water, respectively, revealing that the reconstructed ester-bonded straw network is strong and water-resistant. Interestingly, the hydrogen and ester-bonded straws displayed no evidence of delamination in water, justifying the strong bonding at the edges (Video S1 and Figure S4). Recently, it was shown that paper straws were not suitable for cola drinks due to the generation of air bubbles when immersed in the drink.⁴¹ H-SCL straws (Figure 5g) and E-SCL straws (Video S2) were also tested on a cola drink to check their suitability over paper straws. H-SCL straws generated air bubbles on the drink's surface and inside the straw, which shows that the straws could alter the taste and user experience. However, no air bubbles were generated when E-SCL straws were used in cola drinks, displaying they are functional and quintessential candidates for replacing plastic straws. Even though LCS¹ and Ch-20A³ straws were hydrostable, the straws absorbed over 60 and 53.6% of water in 120 min and 5 h, respectively. These findings show that our E-SCL and E-PCL straws and thermoset films are more hydrophobic and hydrostable for longer periods, as evident in Figure 4a–c. The low water uptake by E-SCL and E-PCL thermoset films shows that the products, including straws, can offer extended service life translating to customer satisfaction.

To ascertain the suitability of our straws for mitigating global pollution by these single-use plastics, we further investigated the natural degradability of E-SCL and E-PCL straws and compared them with PP straws under similar conditions. Figure 6a–c depicts the natural degradation of E-SCL and PP (white color) straws supported on a tree for 2 months, while Figure 6d–g represents the degradability of E-PCL and PP (black color) straws placed on the surface of the soil over 2 months in the same natural environment. E-SCL and E-PCL straws display an analogous degradation trend, with discoloration after 1 month and disintegration into fragments occurring after about 2 months. During the degradation, delamination, and collapse of the inner wall of the straws were not apparent. In contrast, the PP straws exhibited no signs of degradation for over 2 months, showing that E-SCL and E-PCL straws have a unique advantage of functionality and degradability against the nondegradable PP straws. Moreover,

our fully biobased and functional straws and advanced films may act as drivers for mitigating plastic pollution.

CONCLUSIONS

This report demonstrates a facile yet economical approach to manufacturing strong, tough, scalable, biodegradable, and hydrostable straws and films. Our methodology involves the simultaneous integration of lignin and citric acid into biobased and biocompatible starch and poly(vinyl alcohol), respectively, to synthesize hydrogen-bonded biobased slurries (H-SCL and H-PCL). The lignin provided the necessary reinforcement, while citric acid endowed the crosslinked network with numerous hydrogen and ester bonding interactions. By doctor blade casting of the slurries, rolling of the resultant films on a Teflon rod, and heat treatment, strong, tough, and hydrostable straws and multifunctional films that can substitute plastic and paper straws were fabricated. The resultant E-SCL and E-PCL straws demonstrated a high bending strength of 33.1 ± 1.1 and 47.4 ± 2.0 MPa, respectively, and were shown to be hydrostable for over 24 h. Also, E-SCL and E-PCL films displayed a record high tensile strength of 158.8 ± 6.5 and 184.5 ± 5.6 MPa, respectively. Furthermore, the films exhibited broadband UV shielding, while the straws displayed a unique balance of functionality and degradability at the end of life, making them quintessential candidates for plastic straw replacement. This green, economical, and scalable manufacturing process and the final products also demonstrate a closed-loop cycle, offering new avenues to engineer biobased, hydrostable, strong, UV shielding, and biodegradable materials from economical and sustainable biomass.

EXPERIMENTAL SECTION

Materials. Lignin (kraft) with a sulfur content of $\leq 3.6\%$ and an average molecular weight of 10 000 g/mol, citric acid (99%), starch-soluble ($M_w = 342.3$ g/mol), and poly(vinyl alcohol) (99% hydrolyzed) were purchased from Sigma-Aldrich (St. Louis, MO).

Preparation of H-SCL, H-PCL, E-SCL, and E-PCL Films and Straws. The starch (7 wt %) was gelatinized at 80 °C in a neck flask for 3 h, while PVA was dissolved in deionized water at 90 °C for 3 h. The resultant solutions were homogenized

using a sonicator (HD 2200, Bandelin electronic Co., Berlin, Germany) at 72% power for 10 min. Similarly, kraft lignin (7 wt %) and citric acid (7 wt %) were dissolved in deionized water for 3 h and 15 min, respectively. The lignin solution was homogenized using a sonicator at 72% power for 15 min. The starch-soluble, PVA, and lignin solutions were centrifuged at 11 000 rpm to remove undissolved particles. To prepare the H-SCL slurry, starch, citric acid, and lignin were mixed in a ratio of 51:9:40, while the H-PCL slurry was synthesized by blending PVA, citric acid, and lignin in a ratio of 45.5:24.5:30. The solutions were mixed using a magnetic stirrer for 1 h, then homogenized at 72% power for 10 min, and finally degassed. The degassed slurry was cast on a glass substrate using a doctor blade and partially dried to form a flexible film that could be easily rolled into straws on a Teflon rod. The partially dry films can easily be bonded at the edges without needing binders and adhesives. The films and rolled straws were fully dried in a dry oven and cured in a vacuum oven at 180 °C to form esterified straws and films.

Mechanical Properties. The flexural properties of the straws and tensile properties of the dry and wet films were characterized using tensile test equipment (T0-102, TESTONE, South Korea). The films and straws had comparable thicknesses and outer (5.1 mm) and inner diameters (4.7 mm), which were analogous to the PP straws. The flexural properties of the straws were determined in line with a previous study using eq 3

$$\sigma_{\text{straw}} = \frac{M \cdot y}{I} = \frac{P \times \frac{l}{4} \times y}{\frac{\pi[(R)^4 - (r)^4]}{4}} \quad (3)$$

where M represents the maximum bending moment, y is the maximum distance from the center of straw/tube ($y = r$), I is the moment of inertia of the cross section, l is the support span, R is the outer radius of the straw, and r is the inner radius of the straw.

Tensile tests were conducted at a crosshead speed of 2.4 mm/min. The samples were first dipped in water for 3 h for the wet tensile tests.

Characterization. The chemical interaction of the films was investigated by Fourier transform infrared spectroscopy equipped with an attenuated total reflection accessory (FTIR, Excalibur FTS 3000, Bio-Rad, Hercules). The surface and cross-sectional morphology of the films was studied by scanning electron microscopy (SEM, Hitachi, S-4300, Japan). A dual-beam optical spectrophotometer (Mega 900, Scinco, South Korea) was used to evaluate the optical properties of the films. For uniformity and comparison, the films had equal thickness (24.1 μm). The moisture absorption by the films was characterized per the ASTM D570 standard. The samples were fully submerged in water for a specified period, removed, patted dry with a lint-free wiper, and weighed. The water contact angle of the films was acquired by an optical tensiometer (GSA, Surfactech Co., South Korea). The film samples were secured on a glass slide, and the WCA was automatically computed from a single droplet (13.65 \pm 0.02 μL). The straws were immersed in water at room temperature for the hydrostability tests and monitored for 24 h.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07797>.

Wet tensile strength of E-SCL and E-PCL films (Figure S1 and Table S1). UV-radiation capacity of H-SCL, H-PCL, E-SCL, and E-PCL (Figure S2). Thermal degradation of H-SCL, H-PCL, E-SCL, and E-PCL (Figure S3 and Table S2). Photographs and hydrostability analysis of E-SCL and H-SCL straw (Figure S4) (PDF)

Video S1 (MP4)

Video S2 (MP4)

■ AUTHOR INFORMATION

Corresponding Author

Jaehwan Kim – Creative Research Center for Nanocellulose Future Composites, Inha University, Incheon 22212, Republic of Korea; orcid.org/0000-0002-6152-2924; Phone: +82-32-860-7326; Email: jaehwan@inha.ac.kr; Fax: +82-32-832-7325

Authors

Dickens O. Agumba – Creative Research Center for Nanocellulose Future Composites, Inha University, Incheon 22212, Republic of Korea

Duc Hoa Pham – Creative Research Center for Nanocellulose Future Composites, Inha University, Incheon 22212, Republic of Korea

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsomega.2c07797>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The National Research Foundation of Korea supported this research through the Creative Research Initiatives Program (NRF-2015R1A3A2066301).

■ REFERENCES

- (1) Dong, T.; Chen, W.; Cai, C.; Bai, F.; Zhou, Z.; Wang, J.; Li, X. Water-Stable, Strong, Biodegradable Lignocellulose Straws Replacement for Plastic Straws. *Chem. Eng. J.* **2023**, *451*, No. 138970.
- (2) Roland, G.; R, J. J.; Lavender, L. K. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2022**, *3*, No. e1700782.
- (3) Chen, C.; Wu, Q.; Wan, Z.; Yang, Q.; Xu, Z.; Li, D.; Jin, Y.; Rojas, O. J. Mildly Processed Chitin Used in One-Component Drinking Straws and Single Use Materials: Strength, Biodegradability and Recyclability. *Chem. Eng. J.* **2022**, *442*, No. 136173.
- (4) Gao, A. L.; Wan, Y. Life Cycle Assessment of Environmental Impact of Disposable Drinking Straws: A Trade-off Analysis with Marine Litter in the United States. *Sci. Total Environ.* **2022**, *817*, No. 153016.
- (5) Roy, P.; Ashton, L.; Wang, T.; Corradini, M. G.; Fraser, E. D. G.; Thimmanagari, M.; Tiessan, M.; Bali, A.; Saharan, K. M.; Mohanty, A. K.; Misra, M. Evolution of Drinking Straws and Their Environmental, Economic and Societal Implications. *J. Cleaner Prod.* **2021**, *316*, No. 128234.
- (6) Bartl, A. Moving from Recycling to Waste Prevention: A Review of Barriers and Enablers. *Waste Manage. Res.* **2014**, *32*, 3–18.
- (7) Urbanek, A. K.; Rymowicz, W.; Mironczuk, A. M. Degradation of Plastics and Plastic-Degrading Bacteria in Cold Marine Habitats. *Appl. Microbiol. Biotechnol.* **2018**, *102*, 7669–7678.

- (8) Gewert, B.; Plassmann, M. M.; MacLeod, M. Pathways for Degradation of Plastic Polymers Floating in the Marine Environment. *Environ. Sci.: Process Impacts* **2015**, *17*, 1513–1521.
- (9) Zeenat; Elahi, A.; Bukhari, D. A.; Shamim, S.; Rehman, A. Plastics Degradation by Microbes: A Sustainable Approach. *J. King Saud Univ. – Sci.* **2021**, *33*, No. 101538.
- (10) Alfaro-Núñez, A.; Astorga, D.; Cáceres-Farías, L.; Bastidas, L.; Soto Villegas, C.; Macay, K. C.; Chistensen, J. H. Microplastic Pollution in Seawater and Marine Organisms across the Tropical Eastern Pacific and Galápagos. *Sci. Rep.* **2021**, *11*, No. 6424.
- (11) Koelmans, A. A.; Bakir, A.; Burton, G. A.; Janssen, C. R. Microplastic as a Vector for Chemicals in the Aquatic Environment: Critical Review and Model-Supported Reinterpretation of Empirical Studies. *Environ. Sci. Technol.* **2016**, *50*, 3315–3326.
- (12) Mohamed Nor, N. H.; Kooi, M.; Diepens, N. J.; Koelmans, A. A. Lifetime Accumulation of Microplastic in Children and Adults. *Environ. Sci. Technol.* **2021**, *55*, 5084–5096.
- (13) Lambert, S.; Wagner, M. Microplastics are Contaminants of Emerging Concern in Freshwater Environments: An Overview. In *Freshwater Microplastics: Emerging Environmental Contaminants?*; Springer International Publishing: Cham, 2018; pp 1–23.
- (14) Verma, R.; Vinoda, K. S.; Papireddy, M.; Gowda, A. N. S. Toxic Pollutants from Plastic Waste- A Review. *Procedia Environ. Sci.* **2016**, *35*, 701–708.
- (15) Evode, N.; Qamar, S. A.; Bilal, M.; Barceló, D.; Iqbal, H. M. N. Plastic Waste and Its Management Strategies for Environmental Sustainability. *Case Stud. Chem. Environ. Eng.* **2021**, *4*, No. 100142.
- (16) Jonsson, A.; Andersson, K.; Stelick, A.; Dando, R. An Evaluation of Alternative Biodegradable and Reusable Drinking Straws as Alternatives to Single-Use Plastic. *J. Food Sci.* **2021**, *86*, 3219–3227.
- (17) Chang, L.; Tan, J. An Integrated Sustainability Assessment of Drinking Straws. *J. Environ. Chem. Eng.* **2021**, *9*, No. 105527.
- (18) Žibret, G.; Gosar, M.; Miler, M.; Alijagić, J. Impacts of Mining and Smelting Activities on Environment and Landscape Degradation-Slovenian Case Studies. *Land Degrad. Dev.* **2018**, *29*, 4457–4470.
- (19) Farah, S.; Anderson, D. G.; Langer, R. Physical and Mechanical Properties of PLA, and Their Functions in Widespread Applications - A Comprehensive Review. *Adv. Drug Delivery Rev.* **2016**, *107*, 367–392.
- (20) Lim, L.-T.; Auras, R.; Rubino, M. Processing Technologies for Poly(Lactic Acid). *Prog. Polym. Sci.* **2008**, *33*, 820–852.
- (21) Mundt, D.; Carl, S.; Harhoff, N. A Field Experiment on Reducing Drinking Straw Consumption by Default. *Front. Psychol.* **2020**, *11*, No. 565537.
- (22) Soykeabkaew, N.; Thanomsilp, C.; Suwantong, O. A Review: Starch-Based Composite Foams. *Composites, Part A* **2015**, *78*, 246–263.
- (23) Mason, W. R. Starch Use in Foods. In *Food Science and Technology*, 3rd ed.; BeMiller, J.; Whistler, R. B. T.-S., Eds.; Academic Press: San Diego, 2009; Chapter 20, pp 745–795.
- (24) Maurer, H. W. Starch in the Paper Industry. In *Food Science and Technology*, 3rd ed.; BeMiller, J.; Whistler, R. B. T.-S., Eds.; Academic Press: San Diego, 2009; Chapter 18, pp 657–713.
- (25) Żolek-Tryznowska, Z.; Holica, J. Starch Films as an Environmentally Friendly Packaging Material: Printing Performance. *J. Cleaner Prod.* **2020**, *276*, No. 124265.
- (26) Singaram, A. J. V.; Guruchandran, S.; Bakshi, A.; Muninathan, C.; Ganesan, N. D. Study on Enhanced Mechanical, Barrier and Optical Properties of Chemically Modified Mango Kernel Starch Films. *Packag. Technol. Sci.* **2021**, *34*, 485–495.
- (27) Onyeaka, H.; Obileke, K.; Makaka, G.; Nwokolo, N. Current Research and Applications of Starch-Based Biodegradable Films for Food Packaging. *Polymers* **2022**, *14*, No. 1126.
- (28) Ko, H. U.; Zhai, L.; Park, J. H.; Lee, J. Y.; Kim, D.; Kim, J. Poly(Vinyl Alcohol)-Lignin Blended Resin for Cellulose-Based Composites. *J. Appl. Polym. Sci.* **2018**, *135*, No. 46655.
- (29) Chaléat, C.; Halley, P. J.; Truss, R. W. *Mechanical Properties of Starch-Based Plastics*; Halley, P. J.; Avérous, L. B. T.-S. P., Eds.; Elsevier: Amsterdam, 2014; Chapter 7, pp 187–209.
- (30) Lai, D. S.; Adnan, S. A.; Osman, A. F.; Ibrahim, I.; Haq, H. Mechanical Properties of Thermoplastic Starch Biocomposite Films with Hybrid Fillers. *J. Phys.: Conf. Ser.* **2021**, *2080*, No. 012011.
- (31) Musa, B. H.; Hameed, N. J. Study of the Mechanical Properties of Polyvinyl Alcohol/Starch Blends. *Mater. Today Proc.* **2020**, *20*, 439–442.
- (32) Esmaeli, M.; Pircheraghi, G.; Bagheri, R. Optimizing the Mechanical and Physical Properties of Thermoplastic Starch via Tuning the Molecular Microstructure through Co-Plasticization by Sorbitol and Glycerol. *Polym. Int.* **2017**, *66*, 809–819.
- (33) Sawamura, K.; Tobimatsu, Y.; Kamitakahara, H.; Takano, T. Lignin Functionalization through Chemical Demethylation: Preparation and Tannin-Like Properties of Demethylated Guaiacyl-Type Synthetic Lignins. *ACS Sustainable Chem. Eng.* **2017**, *5*, 5424–5431.
- (34) Podschun, J.; Saake, B.; Lehnen, R. Reactivity Enhancement of Organosolv Lignin by Phenolation for Improved Bio-Based Thermosets. *Eur. Polym. J.* **2015**, *67*, 1–11.
- (35) Nikafshar, S.; Zabihi, O.; Moradi, Y.; Ahmadi, M.; Amiri, S.; Naebe, M. Catalyzed Synthesis and Characterization of a Novel Lignin-Based Curing Agent for the Curing of High-Performance Epoxy Resin. *Polymers* **2017**, *9*, No. 266.
- (36) Jiang, X.; Liu, J.; Du, X.; Hu, Z.; Chang, H.; Jameel, H. Phenolation to Improve Lignin Reactivity toward Thermosets Application. *ACS Sustainable Chem. Eng.* **2018**, *6*, 5504–5512.
- (37) Agumba, D. O.; Kumar, B.; Latif, M.; Panicker, P. S.; Pham, H. D.; Kim, H. C.; Kim, J. High-Performance Esterified-Poly (Vinyl Alcohol)-Citric Acid-Lignin Resin and Its Application to Wet-Spun Nanocellulose Filament-Reinforced Polymer Composite. *Composites, Part A* **2022**, *153*, No. 106735.
- (38) Ko, H.-U.; Kim, J. W.; Kim, H. C.; Zhai, L.; Kim, J. Esterified PVA-Lignin Resin by Maleic Acid Applicable for Natural Fiber Reinforced Composites. *J. Appl. Polym. Sci.* **2020**, *137*, No. 48836.
- (39) Wang, X.; Xia, Q.; Jing, S.; Li, C.; Chen, Q.; Chen, B.; Pang, Z.; Jiang, B.; Gan, W.; Chen, G.; Cui, M.; Hu, L.; Li, T. Strong, Hydrostable, and Degradable Straws Based on Cellulose-Lignin Reinforced Composites. *Small* **2021**, *17*, No. 2008011.
- (40) Wang, X.; Pang, Z.; Chen, C.; Xia, Q.; Zhou, Y.; Jing, S.; Wang, R.; Ray, U.; Gan, W.; Li, C.; Chen, G.; Foster, B.; Li, T.; Hu, L. All-Natural, Degradable, Rolled-Up Straws Based on Cellulose Micro- and Nano-Hybrid Fibers. *Adv. Funct. Mater.* **2020**, *30*, No. 1910417.
- (41) Yang, H.-B.; Liu, Z.-X.; Yin, C.-H.; Han, Z.-M.; Guan, Q.-F.; Zhao, Y.-X.; Ling, Z.-C.; Liu, H.-C.; Yang, K.-P.; Sun, W.-B.; Yu, S.-H. Edible, Ultrastrong, and Microplastic-Free Bacterial Cellulose-Based Straws by Biosynthesis. *Adv. Funct. Mater.* **2021**, *32*, No. 2111713.
- (42) Raghavendran, V.; Asare, E.; Roy, I. *Bacterial Cellulose: Biosynthesis, Production, and Applications*; Academic Press, 2020; Vol. 77, Chapter 3, pp 89–138.
- (43) Dubrovski, P. D.; Golob, D. Effects of Woven Fabric Construction and Color on Ultraviolet Protection. *Text. Res. J.* **2009**, *79*, 351–359.
- (44) Srinivasan, M.; Gatewood, B. Relationship of Dye Characteristics to UV Protection Provided by Cotton Fabric. In *Textile Chemist and Colorist and American Dyestuff Reporter*; American Association of Textile Chemists and Colorists: Research Triangle, NC, 2000; Vol. 32, pp 36–43.
- (45) Lu, J.; Fang, J.; Li, J.; Zhu, L. Engineering Highly Transparent UV-Shielding Films with Disassembled Polydopamine Oligomers as Light Adsorber. *Appl. Surf. Sci.* **2021**, *550*, No. 149284.
- (46) Lm, S. J.; Kim, D.; Kim, Y.; Jeong, S.; Pang, C.; Ryu, S.; Weon, B. M. Hydrophobicity Evolution on Rough Surfaces. *Langmuir* **2020**, *36*, 689–696.
- (47) Zhang, K.; Li, Z.; Maxey, M.; Chen, S.; Karniadakis, G. E. Self-Cleaning of Hydrophobic Rough Surfaces by Coalescence-Induced Wetting Transition. *Langmuir* **2019**, *35*, 2431–2442.
- (48) Gutierrez, J. N.; Royals, A. W.; Jameel, H.; Venditti, R. A.; Pal, L. Evaluation of Paper Straws versus Plastic Straws: Development of a

Methodology for Testing and Understanding Challenges for Paper Straws. *BioResources* 2019, 14, 8345–8363.