Thermal and Barrier Characterizations of Cellulose Esters with Variable Side-Chain Lengths and Their Effect on PHBV and PLA Bioplastic Film Properties

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ABSTRACT: Cellulose esters (CEs) are promising biodegradable substitutes for traditional petroleum-based plastic materials. Research on structure−property relationships of CEs is necessary to evaluate their suitability for industrial applications such as food packaging. Cellulose esters with different side-chain lengths were synthesized and studied. Their thermal and moisture barrier properties were characterized. Cellulose triheptanoate (CTH) was proved to have an optimal moisture barrier (WVTR = 0.31 g·mil/day/in.²) and was used to blend with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polylactic acid (PLA) bioplastics. CTH addition improved the PLA thermal stability, enhanced the ductility, and increased the moisture barrier by 32%, while it decreased the PHBV thermal stability, weakened the ductility, and reduced the moisture barrier by 90%. We demonstrated that by proper choice of the combination of CE and bioplastic, bioplastic blends with unique and useful synergistic properties can be obtained. These blends can potentially be used for commercial applications, such as biodegradable flexible packaging.

1. INTRODUCTION

Concerns over environmental pollution and petroleum depletion have stimulated research on biobased biodegradable plastic materials. A key example is the rapid growth of flexible packaging applications that have resulted in an increased demand for plastic films, which are predominantly petroleum-based and nonbiodegradable under defined conditions. These films are difficult to be recycled as they are often multilayered and contaminated with hard-to-remove residues. The low (<10%) recycling rate has diminished their value since most recycled materials are downcycled ultimately ending up in landfills. Therefore, the packaging industry is seeking alternative bioplastics that meet or exceed cost-performance requirements of current plastics for flexible packaging.

Cellulose has attracted much interest as a biosubstitute for traditional plastics due to its abundance, renewability, and biodegradability. Pristine cellulose has a low moisture barrier and poor thermal processability, limiting its packaging and other industrial applications. Cellulose properties can be improved by derivatization, for example, by esterification or etherification of its hydroxyl groups. Cellulose esters are biodegradable as the ester bonds are enzymatically labile. These cellulose esters, if modified correctly, can be used in food packaging that requires high moisture barrier properties. Typically, a higher DS indicates more substituted hydroxyl groups of the cellulose esters and improved moisture barrier. In addition, cellulose can be added to bioplastic films to improve their barrier and mechanical properties. For example, incorporation of cellulose fibers reduced the water permeability of starch-based bioplastic films by 34% and increased the tensile strength and Young’s modulus; addition of 10 wt % cellulose fibers decreased the water permeability of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) films by 52%; incorporation of 1−5 wt % cellulose nanowhiskers reduced the oxygen permeability of polylactic acid (PLA) films by 90%.

Currently, much of the research on PLA and PHBV bioplastic/cellulose blends focuses on utilizing cellulose fibers/nanocrystals and short side-chain cellulose esters, such as cellulose acetate and cellulose acetate butyrate. In addition, most of the research studies focus on bioplastic blends with a specific cellulose material and very few provide...
guidance on choosing suitable cellulose esters with varying side-chain lengths for bioplastic blending. The side-chain length of cellulose esters plays an important role in determining their thermal, mechanical, barrier, and processing properties and the performance of their bioplastic blends. \(^{10,11}\) Generally, short-chain cellulose esters \((C \leq 6)\), such as cellulose acetate and cellulose butyrate, are commercially available, and their films have acceptable mechanical strength. \(^{12}\) Short-chain cellulose esters usually have narrow processing windows requiring addition of external plasticizers to broaden the temperature gap between melting and thermal degradation. \(^{12}\) They are mainly utilized in fields such as coatings, composites, and laminates. \(^{12}\) In contrast, long-chain cellulose esters \((C > 6)\) have better thermal processability as their long side chains can act as internal plasticizers. \(^{13}\) However, they are not commercially manufactured, and their films have lower strength than short-chain cellulose ester films. \(^{13}\) Therefore, the choice of suitable cellulose esters for bioplastic reinforcement requires a holistic understanding and comprehensive assessment of their structure–property relationship and its effect on their bioplastic-reinforcing performance.

It can be postulated that the short-chain and long-chain cellulose esters have varying thermal and physical performance and they are likely to perform differently as bioplastic-blended films. In this study, the thermal and barrier properties of short-chain length (cellulose triacetate, CTA, and cellulose tributyrate, CTB) and long-chain length cellulose esters (cellulose triheptanoate, CTH, and cellulose tridecanoate, CTD) were investigated. The effect of their addition on the barrier, thermal, and mechanical properties of PHBV and PLA bioplastic films was studied to provide information about the suitability of cellulose esters with different side-chain lengths for film packaging applications, either as a matrix material or as property-reinforcing materials for other bioplastics.

2. RESULTS AND DISCUSSION

2.1. NMR Analysis of Cellulose Esters. Cellulose esters CTB, CTH, and CTD were synthesized, and CTA was purchased since it is readily commercially available. The structures and DS of CTB, CTH, and CTD were analyzed by proton nuclear magnetic resonance spectroscopy \((^1\text{H NMR, Figure 1})\). The \(^1\text{H NMR} \) spectra showed typical chemical shifts of cellulose esters. Peaks with chemical shifts between 3.0 and 5.5 ppm were observed for the methine (\(\text{CH}\)) and methylene \((\text{CH}_2)\) protons on the oxygen atom. Seven of these diagnostic peaks were observed as expected. Signals with chemical shifts between 0.5 and 2.5 ppm were observed for the methyl \((\text{CH}_3)\) and methylene \((\text{CH}_2)\) protons on the carbon chains of the esters. For tributyrate, seven protons were present in each ester chain; thus, 21 protons in total were expected in the 0.5–2.5 ppm region, and 20.4 protons were observed by \(^1\text{H NMR}\) analysis, yielding DS \((\text{CTB}) = 3 \times (20.4/21) = 2.9\). Similarly, in triheptanoate, 39 protons were expected, and 39 protons were observed, thus DS \((\text{CTH}) = 3 \times (39/39) = 3.0\). In tridecanoate, 57 protons were expected, and 57 protons were observed; thus, DS \((\text{CTD}) = 3 \times (57/57) = 3.0\).

2.2. Side-Chain Length Affected the Thermal Transition of Cellulose Esters. CTA had a glass transition \((T_g)\) at approximately 62 °C while the other three cellulose esters had no discernable \(T_g\) (Figure 2), suggesting that a larger substituent on the cellulose backbone restricted backbone mobilities. \(^{14}\) CTB, CTH, and CTD had a lower melting temperature \((T_m \sim 80 \text{ °C})\) than CTA. This is likely because cellulose esters with longer side chains that are in close proximity can organize through hydrophobic interactions, disturbing the crystallization of the cellulose backbone and forming new crystals with a lower melting temperature. \(^{14,15}\) The similar \(T_m\) of CTB, CTH, and CTD indicates that the difference between their chain lengths was not adequate to affect \(T_m\). Additionally, CTB and CTD had a higher degree of crystallinity than CTA and CTH (Table 1). Furthermore,

![Figure 1. \(^1\text{H-NMR}\) spectra of (A) CTB, (B) CTH, and (C) CTD.](https://doi.org/10.1021/acsomega.1c03446)

![Figure 2. Thermal transitions of cellulose esters determined from the second differential scanning calorimetry (DSC) heating scan at 10 °C/min.](https://doi.org/10.1021/acsomega.1c03446)

| Table 1. Thermal Properties of Cellulose Esters |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| samples         | \(T_m\) (melting, °C) | \(T_p\) (peak degradation, °C) | \(T_d\) (onset degradation, °C) | \(X\) (crystallinity, %) |
| CTA             | 203.42          | 382.31          | 358.93          | 8.78           |
| CTB             | 82.46           | 385.78          | 357.37          | 15.89          |
| CTH             | 81.32           | 384.78          | 355.45          | 11.32          |
| CTD             | 80.77           | 385.58          | 356.78          | 16.76          |

\(^{a-b}\) Means showing different letters are significantly different at \(\alpha = 0.05\) according to one-way ANOVA and Tukey’s HSD analysis.
CTH had the sharpest melting peak among the samples, indicating a narrower distribution of the crystals. This different crystallization behavior of the cellulose esters with different side-chain lengths affected their barrier properties and bioplastic-reinforcing performance, as will be discussed in Sections 2.4 and 2.5.

**2.3. Side-Chain Length Affected the Thermal Degradation of Cellulose Esters.** The four cellulose esters showed different thermal degradation behaviors (Figure 3A,B). CTB, CTH, and CTD had a single stage of thermal degradation between 200 and 400 °C, while CTA had a two-stage degradation at 200–400 °C and 500–800 °C. The thermal degradation of cellulose esters at 200–400 °C could be attributed to pyrolitic decomposition of the polymer chain skeleton, and the degradation at 500–600 °C is caused by carbonization of the degradation products or by degradation of a new cross-linked material formed in the first degradation stage via reactions between hydroxyl and carboxylic acid groups formed through chain scission. Additionally, CTA, CTB, and CTH had a larger and sharper degradation peak than CTD, indicating their rapid and vigorous decomposition.

Finally, the difference between the peak degradation temperature and the melting temperature \( (T_d - T_m) \) of the samples were 178.9, 303.3, 303.5, and 304.8 °C for CTA, CTB, CTH, and CTD, respectively. As cellulose has poor processability partially due to its degradation at temperatures slightly above its melting point, the enlarged \( T_d - T_m \) of CTB, CTH, and CTD compared with CTA can help improve the processability of the cellulose esters through expanding the processing temperature range and broadening the processing window.

**2.4. Side-Chain Length Affected the Moisture Barrier of Cellulose Esters.** CTH had the lowest WVTR (highest moisture barrier) while CTD had the highest WVTR (lowest moisture barrier) among the four cellulose ester samples (Figure 4). This result is different from a previous study where WVTR usually decreased with increasing side-chain lengths, mainly due to the increasing hydrophobicities of the substituent groups. One possible explanation is that the side chains act as protruding spacers, which separate cellulosic chains. Therefore, the longer the side chains, the more the cellulose chains are spread out, increasing the free volume in the cellulose matrix, resulting in greater moisture diffusion and therefore higher water vapor transmission. However, in this study, the water vapor transmission did not show significant dependence on the crystallinity of the cellulose esters. One possible explanation is that the gas/vapor permeability only decreases at higher crystallinity (>60%) and minimally changes at lower crystallinity (21–58%).

The degree of crystallinity is another important factor affecting the cellulose ester moisture barrier property. Usually, higher crystallinity leads to a better moisture barrier as high-crystalline regions are inaccessible to water molecules. However, in this study, the water vapor transmission did not show significant dependence on the crystallinity of the cellulose esters. One possible explanation is that the gas/vapor permeability only decreases at higher crystallinity (>60%) and minimally changes at lower crystallinity (21–58%).

CTH with a WVTR of 0.32 g·mil/day/in. had a better moisture barrier compared to PHBV and PLA bioplastics, which have a WVTR of 1.98 and 0.41 g·mil/day/in., respectively. Therefore, CTH was selected to be incorporated into PHBV and PLA bioplastics to improve their moisture barrier (discussed in Section 2.5), broadening their industrial applications such as high barrier-flexible food packaging applications.

**2.5. Addition of Cellulose Ester Affected the Bioplastic Thermal Transition Properties.** The blend of PHBV and 10 wt % CTH had thermal transitions, that is, glass and melting transitions, resembling those of PHBV (Figure 5A). The characteristic melting peak of CTH (at around 80 °C) was not observed in the blend, indicating miscibility between PHBV and CTH. The PHBV/CTH blend had slightly lower crystallinity (by approximately 6.7%) and lower crystallization temperature (by around 3 °C) than PHBV (Figure 5A,B), suggesting that CTH addition restricted PHBV crystallization. Additionally, the blend had a slightly sharper
peak than PHBV, indicating that the blend had improved uniformity of spherulite sizes and order of molecular structures. The effect of CTH addition on restricting PHBV crystallization is likely caused by the dynamic heterogeneity, that is, different molecular chain mobilities, of PHBV and CTH rather than the miscibility gap between the two components. It is generally believed that cellulose esters (both in the solid state and in solution) are rigid extended helices or ribbons, while PHBV is generally random coils with good molecular mobility. As a result, the rigid CTH molecular chains hinder the mobility of PHBV chains and cause restricted PHBV crystallization.27 Similarly, previous research on blends from PHBV and cellulose fillers, such as nanocrystalline cellulose, cellulose nanocrystals, cellulose nanofibers, and cellulose nanowhiskers, also suggested that cellulose fillers can restrict PHBV chain mobility through interfacial molecular chain interactions and result in decreased PHBV crystallinity in some cases.28 In addition, the crystal cellulose fillers (at a low concentration of <1%) can provide heterogeneous nucleation sites and act as an effective nucleation agent for PHBV crystallization, increasing the PHBV crystallization temperature and crystallization rate.29−30

The crystallization-restricting effect of CTH addition on PLA is more significant than PHBV (Figure 5C,D). Pristine PLA showed a double melting behavior, which is related to mechanisms such as the formation of multiple crystal structures and lamellar populations with different thicknesses or perfection.6,31 The PLA melting peak at a lower temperature (around 55 °C) could be attributed to the less perfect or disordered α′-form while the one at a higher temperature (around 150 °C) could be attributed to the more perfect α-form.32 During the DSC heating scan, the less perfect α′-form crystals can melt and evolve into more perfect crystals before remelting at a higher temperature.32 Furthermore, PLA had an exothermic peak at 125 °C, which is related to its cold crystallization transition. Cold crystallization occurs when heating a polymer sample that has previously been rapidly cooled and had no time to crystallize.33 When the heating temperature is above its glass transition temperature, small crystallites form at relatively low temperatures.34 CTH addition diminished both melting and cold crystallization transitions of PLA, indicating its crystallization-restricting effect due to (i) restricting the mobility of PLA chains, causing diminished melting peak and reduced crystallinity; (ii) the restricted PLA chain mobility make it difficult for the disordered α′-form crystals to be transformed into highly ordered α-form crystals, causing diminished cold crystallization; (iii) the PLA polymer fraction decreased as a function of CTH in the blends.32,34 This result is different from previous research on the blend of PLA and crystal cellulose fillers where cellulose (when added at a small amount of < 0.3 wt %) acted as a nucleating agent and promoted PLA crystallization by enhancing the cold crystallization transition and accelerating the crystallization rate.32,34 When added at high amounts (>0.3−0.7 wt %), the crystal cellulose fillers aggregated in the PLA matrix and showed a decreased crystallization-enhancing effect.32 The PLA/CTH blend in this study had significantly reduced crystallinity and is almost amorphous. The single thermal transition of the blend suggested good compatibility between CTH and PLA and plasticity of the blends, which can potentially improve the processability. The change in the crystallization behavior of PHBV and PLA caused by CTH addition will further affect the physical and mechanical properties of the bioplastics, as discussed in Sections 2.6 and 2.7 below.

2.6. Addition of Cellulose Ester Affected the Bioplastic Thermal Degradation Properties. TGA was also performed to study the thermal stability and decomposition of
the PHBV and PLA bioplastics and their CTH blends, which can provide important information on their suitable thermal processing conditions. The film from the PHBV/CTH blend had a two-stage thermal degradation (Figure 6). The first stage between 250 and 320 °C was associated with PHBV degradation and the second stage between 350 and 420 °C was caused by CTH degradation. The two distinct degradation stages reflected the dynamic heterogeneity between PHBV and CTH, as supported by the DSC analysis. The ratio of the weight losses of the two stages was consistent with the amount of CTH (10 wt %) in the randomly selected blend sample, suggesting a homogeneous distribution of CTH within the PHBV matrix. Addition of CTH slightly decreased the onset and peak degradation temperatures of PHBV by 4 and 7 °C, respectively. The film from the PLA/CTH blend had a single-stage degradation with slightly higher onset and peak temperatures ($T_o = 352 ^\circ C$ and $T_p = 379 ^\circ C$) than pristine PLA ($T_o = 348 ^\circ C$ and $T_p = 376 ^\circ C$). The single degradation stage of the blend indicated good compatibility between PLA and CTH, as supported by the DSC analysis. This result is similar to previous research on the PLA/crystal nanocellulose blend where cellulose addition slightly increased the PLA thermal stability. To summarize, PLA/CTH blends had better thermal stability than the PHBV/CTH blend.

2.7. Incorporation of Cellulose Ester Improved the PLA Moisture Barrier. Addition of 10 wt % CTH reduced the WVTR of PLA from 0.41 to 0.28 g·mil/day/in.$^2$, indicating an improved PLA moisture barrier by 32%, while the addition decreased the PHBV moisture barrier by 90% (Figure 7). The moisture barrier of a bioplastic blend mainly depends on the molecular structures of the blend components, such as polarity, crystallinity, intermolecular forces, and chain segmental mobility, and the status of the interphase mixing in the blend, such as the distribution, amount of the multiphases, and the nature and magnitude of the component interactions. Generally, increased polarity, high crystallinity of the blend components, and good interphase interactions lead to a good moisture barrier.

However, in our study, although CTH addition reduced the crystallinity of both PHBV and PLA, the moisture barrier effect differed between the two bioplastics, that is, CTH addition reduced the PHBV moisture barrier while increased the PLA moisture barrier. Potential explanations are as follows: (i) the two bioplastics have different physical structures: PHBV is highly crystalline (crystallinity > 60%) and PLA is mostly amorphous (crystallinity <10%). Therefore, the effect of crystallinity decrease on the PHBV moisture barrier, which counteracted the moisture barrier reinforcing effect of CTH, is more significant than in PLA; (ii) the PLA/CTH blend has better interphase interactions than the PHBV/CTH blend, as supported by the DSC and TGA results (the PLA/CTH blend had good compatibility while the PHBV/CTH blend displayed dynamic heterogeneity), which could cause the interphase regions to show higher water vapor sorption than the adjoining phases. Similar results of the incorporation of cellulose esters (cellulose acetate) weakening the PHBV moisture barrier were previously reported. Although previous research on the PLA/cellulose acetate blend reported that cellulose acetate increased the water absorption of PLA, cellulose acetate had higher hydrophilicity (lower DS, ~0.9) and shorter side chains than CTH in this study.

2.8. Addition of Cellulose Ester Affected the Bioplastic Mechanical Properties. Overall, the PLA films had a lower tensile strength and a higher tensile strain than PHBV films, suggesting that PLA is more ductile than PHBV (Figure 8). Addition of 10 wt % CTH decreased the tensile strength of the PHBV film by approximately 50%, likely due to the
decreased crystallinity and inadequate compatibility of the PHBV/CTH blend. This result is different from previous research on PHBV/nanocrystal cellulose, where cellulose addition improved both the PHBV tensile strength and the modulus, likely due to the crystallization-promoting effect of the nanocrystal cellulose fillers. CTH addition had no significant effect on the PHBV tensile strain. A similar result of addition of cellulose ester decreasing the bioplastic strength was reported for the polyhydroxyalkaonate (PHA)/cellulose acetate blend. CTH addition had no significant effect on the PLA tensile strength yet improved the PLA tensile strain by 24%. This can be explained by the good compatibility between PLA and CTH as well as the increase in the amorphous nature of the blend, as supported by the DSC analysis. The improved ductility of the PLA/CTH blend, which is similar to that of polypropylene (tensile strain about 100%) makes it promising for flexible packaging applications.

3. CONCLUSIONS

Cellulose esters with different side-chain lengths (C1, C3, C6, and C9) were studied and those of C3−C9 decreased the melting temperature and increased the crystallinity compared with cellulose triacetate (C1). CTH exhibited the highest moisture barrier among the investigated cellulose esters and was used to reinforce bioplastics PHBV and PLA through blending. The incorporation of CTH had varying effects on different bioplastics. CTH proved to be an efficient performance-reinforcing material for PLA as it significantly restricted PLA crystallization and improved PLA plasticity, moisture barrier, and ductility. In contrast, CTH had no significant effect on PHBV thermal properties and decreased PHBV tensile strength by approximately 50% and increased PHBV water vapor permeability by around 90%. This variable effect of CTH addition was caused by the different physical structures of the two bioplastics: PHBV is highly crystalline, while PLA was mostly amorphous. This result can provide insight into future research on reinforcing bioplastic materials using cellulose esters. The PLA/CTH blend with improved moisture and ductility can have potential applications in flexible packaging. Future research on the compatibility and biodegradability of the PLA/CTH blend and thermal processability via traditional plastic processing techniques is needed.

4. MATERIALS AND METHODS

4.1. Materials. A cellulose microcrystalline was purchased from Crescent Chemical Co., Inc. (Islandia, NY, USA) and was used as received to prepare cellulose esters. CTA, LiCl, N,N-dimethyl acetamide (DMAc), acid chloride, CH2Cl2, and MgSO4 were purchased from Sigma-Aldrich (St. Louis, MO, USA). PHBV with about 2 mol % of hydroxyvalerate (HV) content was purchased from Tianan Biological Material Co. (Ningbo, China). PLA (4043, film grade) was purchased from NatureWorks (Minnetonka, MN, USA).

4.2. Methods. 4.2.1. Sample Preparation. To prepare cellulose esters with different side-chain lengths (Figure 9), cellulose (1.0 g, 6.2 mmol glucose units, 1 equiv) and LiCl (1.0 g, 100 wt %) were mixed in a round-bottom flask, heated to 110 °C, stirred for 1 h under vacuum, and then cooled to room temperature. With slow back-filling with N2 followed by the addition of DMAc (30 mL), pyridine (2.0 mL, 24.7 mmol, 4 equiv) and acid chloride (24.7 mmol, 4 equiv) were added under N2. The reaction mixture was vigorously stirred at 110 °C for 16 h. Then it was cooled to room temperature and

Figure 8. Tensile properties of bioplastics (A) PHBV and (B) PLA and their blends with 10 wt % CTH.

Figure 9. Synthesis of cellulose esters with different side-chain lengths.
quenched by the addition of excess water. Cellulose ester was collected by filtration (a solid cannot be filtered), washed with water, and dissolved in CHCl3; the solution was dried over anhydrous MgSO4, the drying agent was removed by filtration, and the solution was concentrated by rotary evaporation of the solvent to provide a residue, which was dissolved in a minimal amount of CHCl3 to obtain a viscous yellow syrup. The final cellulose ester product was obtained by adding the syrup to vigorously stirred methanol (150 mL), which was followed by filtration and drying at a reduced pressure to give an 80–95% yield. Cellulose esters including CTB (2), CTH (3), and CTD (4) were obtained. CTA (1) is commercially available.

Films from cellulose esters and bioplastics (PHBV and PLA) and blends of bioplastics with CTH (10 wt %, determined from a preliminary blending trial) were prepared by solvent casting (Table 2). Cellulose esters were dissolved in acetone, and bioplastic pellets were dissolved in chloroform. The solution (bioplastic solution alone for the bioplastic film; premixed bioplastic solution and CTH solution for the film of bioplastic/CTH blend) was poured into a glass Petri dish and left in a fume hood overnight to evaporate the solvent to obtain the film sample.

4.2.2. Thermal Transition Measurement—DSC Analysis. The thermal transitions of the film samples were measured using a previously described procedure using a TA Instruments Discovery DSC 2500 (New Castle, DE, USA). The samples were first heated from room temperature to 200 °C at 10 °C/min, held for 4 min to remove thermal history of the samples, cooled to −85 °C, held for 4 min, and reheated to 200 °C at 10 °C/min. The melting temperature (Tm) of the samples was determined at the peak value of the endotherms of the heat capacity changes (0–20 J/g) from the second heat scan. Xc of the samples was obtained by dividing the enthalpy of fusion (ΔHfus determined from the area under the endotherms using TRIOS Software v4.1.1.33073) by the enthalpy value of a theoretically 100% crystalline sample material.

4.2.3. Thermal Degradation Measurement—TGA. The thermal degradation properties of the samples were measured using a TA Instruments Discovery TGA 550 (New Castle, DE, USA). Samples were heated under nitrogen from room temperature to 500 °C at 20 °C/min. The extrapolated onset (Tonset) and peak (Tpeak) degradation temperatures were determined from the weight loss and derivative thermograms, respectively, using TRIOS Software v4.1.1.33073.

4.2.4. Moisture Barrier Measurement—WVTR Measurement. WVTR of the samples was determined according to ASTM E96/E96M-16 using a dynamic vapor sorption instrument from Surface Measurement Systems Ltd. (Allentown, PA, USA). A disk test specimen (thickness 0.05 mm and diameter 7 mm) was used in a Payne cell with an opening area of 0.024 in.2 (15.54 mm2) for water vapor transport. The Payne cell was sealed with the film sample, filled with a drying agent, and placed in a chamber at 40 °C and 90% RH for 24 h for testing. The WVTR was calculated as

\[ \text{WVTR}_{\text{original}} = G / A \]

where G is the change in mass (g) of the drying agent, t is the testing time (day, i.e., 24 h), A is the area (in.2) that the water vapor diffused through the test specimen via the cell opening, and WVTRoriginal is the rate of water vapor transmission (g/day/in.2). The reported WVTR data in this study were normalized by thickness, that is, WVTR (g/mil/day/in.2) = sample thickness (mil) × WVTRoriginal (g/day/in.2).

4.2.5. Mechanical Characterization. The tensile strength and tensile elongation at break of the film samples were measured according to ASTM D882-12 using an Instron 5542 equipped with a Bluehill v. 2.17 software package (Norwood, MA, USA) at a speed of 50 mm/min and an initial gap separation of 50.8 mm over five replicates.

Table 2. Prepared Bioplastic-Blended Film Samples

| samples | side-chain length | formula |
|---------|------------------|---------|
| CTA     | –CO–CH2           | cellulose triacetate (1) |
| CTB     | –CO–(CH2)–       | cellulose tributyrate (2) |
| CTH     | –CO–(CH2)–       | cellulose triheptanoate (3) |
| CTD     | –CO–(CH2)–       | cellulose tridecanoate (4) |
| PLA     | N/A              | polyactic acid |
| PLA/CTH/10 | N/A          | PLA (90 wt %) + CTH (10 wt %) |
| PHBV    | N/A              | poly(3-hydroxybutyrate-co-3-hydroxyvalerate) |
| PHBV/CTH/10 | N/A            | PHBV (90 wt %) + CTH (10 wt %) |

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03446

Notes

The authors declare no competing financial interest.

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