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ORIGINAL PAPER

Effect of Simulated Weathering on Physicochemical Properties and Inherent Biodegradation of PLA/PHA Nonwoven Mulches

Elodie Hablot · Sathiskumar Dharmalingam · Douglas G. Hayes · Larry C. Wadsworth · Christopher Blazy · Ramani Narayan

Abstract The effect of simulated weathering on the physicochemical properties and biodegradability of four fully biobased and potentially biodegradable agricultural mulches prepared nonwoven textile technology, consisting of randomly oriented fibers of average diameter 7–16 µm, has been investigated. Two mulches were prepared from polylactic acid (PLA) using spunbond processing, one naturally white and the other black (SB-W and SB-B, respectively), and two via meltblown processing, from 100 % PLA and a 75/25 w/w blend of PLA and polyhydroxyalkanoate [PHA; poly (3-hydroxybutyrate-co-4-hydroxybutyrate); MB-PLA and MB-PLA+PHA, respectively]. SB-W and SB-B possessed higher tensile strength than MB-PLA and MB-PLA+PHA (56.2N, 37.1N, 8.96N, and 3.90N, respectively). Simulated weathering introduced minor changes in physicochemical properties of SBs, but enhanced inherent biodegradability, yielding 68–72 % mineralization in 90 days. Simulated weathering greatly affected the physicochemical properties of the MB mulches, particularly MB-PLA+PHA, which underwent a 95 % loss of tensile strength, 32 % decrease of weight-averaged molecular weight (from 95.4 to 70.5 kDa), and breakage of microfibers, during a 21 days weatherometry cycle. Weathering accelerated the biodegradation of both MB mulches, with the time course of biodegradation and final extent of biodegradation (91–93 % in 90 days) nearly matching the value obtained for the cellulosic positive control. Fourier transform infrared spectroscopy suggested the SB and MB mulches underwent hydrolysis and photodegradative chain scission (Norrish Type II reaction). SB nonwovens may prove useful as biobased and compostable materials for multi-season mulching, and other long-term agricultural applications, such as for row covers in perennial cropping systems. MB nonwovens may be better suited for more traditional agricultural mulch applications.

Keywords Agricultural mulches · Biodegradability · Polyhydroxyalkanoate · Polylactic acid · Sustainable agriculture · Weathering of plastics

Abbreviations

ATR	Attenuated total reflectance
BDMs	Biodegradable mulches
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
MB	Meltblown (nonwoven materials)
MD	Machine direction
M_w	Weight-averaged molecular weight
PDI	Polydispersity index
PHA	Polyhydroxyalkanoate [poly(3-hydroxybutyrate-co-4-hydroxybutyrate]
PLA	Polylactic acid
SB	Spunbond (nonwoven materials)
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
UV	Ultraviolet

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Introduction

Mulching with plastic was introduced to agriculture in the 1950's and since then has been used successfully throughout the world to increase vegetable and fruit crop productivity, with worldwide usage reaching over 2.6 million metric tonnes in 2004 [1–3]. The main purpose of employing mulches is to reduce weeds and prevent soil erosion. In addition, mulching leads to establishment of a "microclimate" that can enhance management of the soil's moisture level, temperature, nutrients, and physical structure [4]. Traditionally, plastic mulches are films containing non-renewable fossil fuel-based plastics, particularly polyethylene. Concerns have been raised regarding the economic and environmental sustainability of polyethylene mulches, particularly related to their beginning- and end-of-life [3, 5–8]. For the latter, debris and fragments formed from the weathering of polyethylene mulches [due to exposure to sunlight, especially ultraviolet (UV) radiation, and to moisture] are laborious to retrieve ($247/ha [9]), and are readily dispersed in the environment via wind and water, where they present a major hazard to animals via entanglement or ingestion, and persist for years due to poor biodegradability [2, 3, 10].

A solution that could overcome these issues has been stated in a recent review on biopolymers employed in agriculture: "… the best choice appears to be a mulch material with an outdoor service life which matches the crop duration, and which would later be incorporated by the agricultural system" [11]. After the growing season, weathered mulches would be tilled into the soil, where they would undergo complete aerobic mineralization within a reasonable period of time (2 years).

To address this goal, "biodegradable" mulches (BDMs) were developed in the 1980s, and new materials and assessment methods have been developed continually [3, 12]. Common polymeric constituents of BDMs include starches, polybutylene adipate terephthalate (PBAT), polycaprolactone (PCL), polybutylene succinate (PBS) and PBS-co-adipate (PBSA), with mulches most often containing blends of these [3, 12]. Recent studies have demonstrated the loss of mechanical strength and partial conversion into CO_2 for BDMs when buried in soil or placed at the water–air surface [1, 3, 13–18]. But, BDMs also have undesirable attributes, including high price (2.5 × conventional polyethylene mulches) [19], an uncontrollable and unpredictable onset and rate of biodegradation [20], and low biobased content (e.g., PBAT and PBS are mainly derived from fossil fuel feedstocks) [2, 12, 21]. Due to the inclusion of fossil fuel-based components, BDMs have been labelled as "synthetics" and therefore are not allowed for use in US certifiable organic agriculture [8, 22]. In addition, a recent study demonstrated that PBAT-based mulches undergo cross-linking via photodegradation, reducing the extent of mineralization that can be achieved [16]. Therefore, a completely biobased agricultural mulch would be of great interest to the sustainable and organic agricultural communities.

Motivated by this need, the authors have developed novel agricultural mulches of the biopolymers polylactic acid (PLA) and blends of PLA and polyhydroxyalkanoate (PHA), prepared using nonwoven textile technology (Fig. 1) [23]. Nonwovens are sheets, webs, or bats of randomly-oriented micron-sized fibers that are bonded together physically or chemically [23–27]. The molecular structure of the two polymers is also given in Fig. 1. PLA has many attractive attributes as a mulch feedstock relative to other biopolymers: low cost ($2.10/kg) [28], availability in large volumes, and high mechanical strength [12, 29]. However, PLA also has several undesirable materials-related properties, including a high crystallinity and brittleness [12, 29]. In addition, although PLA is well known to be biodegradable under composting conditions, it typically undergoes microbial assimilation in the soil under ambient conditions very slowly [30]. (However, recent reports suggest PLA will undergo biodegradation readily when the soil microbial community is optimized [31, 32]). To address these deficiencies, particularly the enhancement of biodegradability in ambient soil [33], PHA has been incorporated into some of the materials.

Two nonwoven processes have been employed to prepare the mulches: spunbond (SB) and meltblown (MB). SB (spunmelt) nonwovens are prepared in a continuous process consisting of extrusion and spinning of a polymer melt, collection of the fibers on a conveyor belt, followed by heat bonding, and are comprised of strong, thermally point-bonded webs of continuous filaments with fiber diameters of 12–15 μm [23–27]. SB mulches have been shown to be robust for long-term agricultural uses, undergoing minimal deterioration during recently conducted 28-month and 30-week soil burial studies [23, 34] and in field studies conducted in Tennessee, Texas, and Washington [35–37]. Although white-colored SB mulch was ineffective for weed control in 2010 at all three locations, black-colored SB mulches demonstrated weed prevention that matched the performance of commercially available biodegradable mulches in 2011 and 2012 [36, 37]. Further, the SB mulches possessed greater strength and puncture resistance compared to commercially available mulch films [36, 37]. The authors have prepared MB nonwovens, materials possessing smaller fiber diameters (4–8 μm), hence lower tensile strength [23], than SB nonwovens, to undergo biodegradation more rapidly than SB materials. MB nonwovens are manufactured by forcing a thermoplastic polymer melt through an extruder dye. First-generation MB-PLA mulch prepared by us underwent an 85 % decrease of tensile strength when buried in compost- and lime-augmented soils for a 10 week

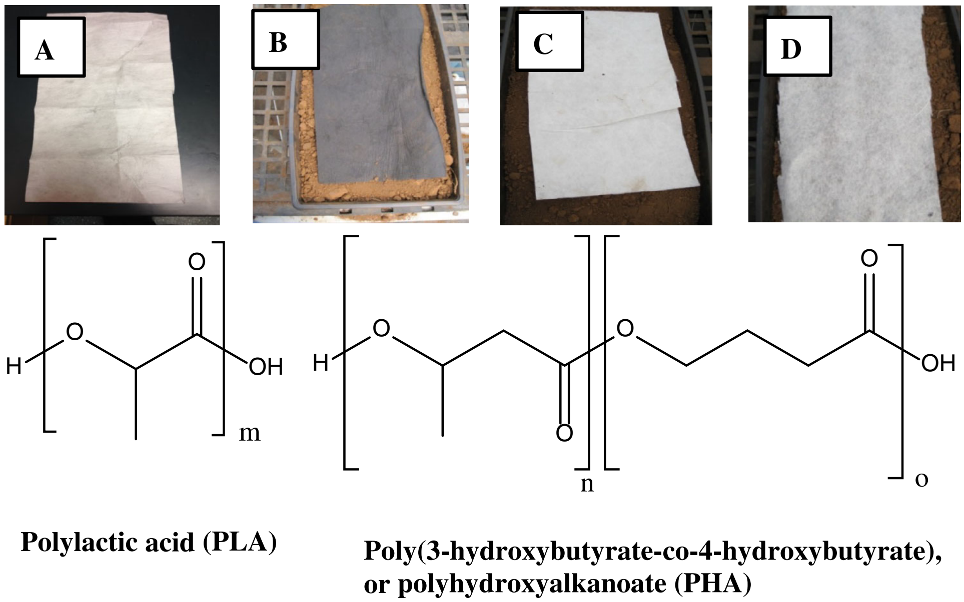

Fig. 1 Photographs of fully biobased agricultural mulches prepared using nonwoven textile technology [**a–d** spunbond (SB)-PLA-black, SB-PLA-white, meltblown (MB)-PLA, and MB-PLA+PHA, respectively], and molecular structure of their biopolymeric constituents

greenhouse incubation period, thereby reflecting the initial stages of biodegradation [23–27]. More recent greenhouse soil burial studies demonstrate that the incorporation of PHA into PLA-based nonwoven mulches enhanced biodegradation (Dharmalingam et al., submitted).

In the present work, the effect of simulated weathering on four different PLA-based nonwoven mulches was evaluated. To mimic the life cycle of mulches [38], the nonwovens were exposed first to simulated laboratory weathering (reviewed in [39]), following the ASTM standard G155 [40], to assess the effect of photodegradation, photooxidation and abiotic hydrolysis, and then subjected to biodegradation via ASTM D5338 [41]. To the best of the authors' knowledge, the biodegradation of fully biobased mulches after exposure weathering under controlled conditions has not been investigated. This investigation is relevant to a new ASTM standard being developed for biodegradation of plastics under ambient soil conditions which requires plastics to undergo 90 % mineralization within 2 years, WK29802 [42]. The standard includes two categories: plastics "as received" (Category I) and plastics subsequent to environmental exposure for a long period of time (Category II). The ultimate goal of this research is to develop a nonwoven mulch material that will fulfil the standard requirements [42] as a Category II material.

Experimental

Materials

The four biobased PLA-based mulches (Fig. 1) were prepared by the authors using nonwoven textile technology. Two SB mulches, one white (naturally white with no titanium dioxide added) and the other black in color (SB-PLA-white and SB-PLA-black, respectively), were made in 2010 from Ingeo^{TM} 6202D and 6252D PLA feedstocks, obtained by Natureworks (Blair, NE USA), respectively, with the latter formulated with Carbon Black (CB) at a nominal concentration of 1.1 % using facilities available at Saxony Textiles (Chemnitz, Germany). A contractor with Saxony prepared a 15 % "master batch" of a proprietary source of CB with Ingeo^{TM} 6252D PLA. During the SB processing at Saxony, 7 wt % of the 15 % CB master batch pellets were added to 6252D PLA in the dry mixing section prior to extrusion. The 6202D feedstock possesses a slightly higher molecular weight than the 6252D PLA source (melt indices of 15–30 and 70–85 g per 10 min, respectively) and a slightly lower fraction of D-lactic acid monomer (2.0 and 1.4 % D-lactic acid, respectively, with the remainder of the monomers being L-lactic acid). The melt temperatures in the SB processing of 6202D and 6252D PLA (with CB) were 239 and 224 °C, respectively, and the dwell time during extrusion was approximately 1 min for both. Ingeo^{TM} 6202 and 6252D PLA possessed weight-averaged molecular weight (M_w) values of 347,000 ± 18,000 and 150,000 ± 5,000, respectively (based on polystyrene standards) and polydispersity index (PDI) values of 1.87 ± 0.01 and 1.56 ± 0.01, respectively, according to gel permeation chromatographic (GPC) analysis.

Two MB nonwoven mulches, both naturally white in color (no titanium dioxide present), were prepared from 100 % Ingeo^{TM} 6252D PLA supplied by NatureWorks and a blend of 6252D PLA and PHA nominally at 75/25 w/w (72.5/77.5 w/w, via ^{1}H-NMR analysis) that was kindly provided by GreenBio (Tianjin, China). The PLA-PHA feedstock was dry mixed and extruded into pellets at Greenbio to ensure

Table 1 Effect of simulated weathering treatment on the dry weight, thickness, average fiber diameter, and inherent biodegradability of PLA- and PLA + PHA-based nonwoven agricultural mulches

Mulch	Weathering time, days	Dry weight per area (g m^{-2})[a,b]	Thickness, µm[b,c]	Fiber diameter, µm[b,d]	% biodegradation[e]
SB-PLA-white	0.0	83.5±6.9	629±26	14.9 ± 0.3	54 ± 3
	21.0	94.8	734	14.8 ± 0.3	72 ± 5
SB-PLA-black	0.0	75.6±5.2	608±45	15.8 ± 0.4	72 ± 3
	21.0	80.3	636	14.7 ± 0.4	68 ± 4
MB-PLA-100 %	0.0	79.6±0.6	687±6	7.5 ± 0.6	83 ± 4
	21.0	85.4	743	7.3 ± 0.4	93 ± 4
MB-PLA+PHA 75/25	0.0	80.1±0.8	570±6	15.3 ± 0.6	63 ± 4
	21.0	79.9	595	13.6 ± 0.8	91 ± 5

[a] Via ASTM D3776 (Cleveland et al., 1992; R Development Core Team, 2009)

[b] Uncertainty range given for the reported values reflect standard error

[c] Via ASTM D5729 (R Development Core Team, 2009)

[d] Via scanning electron microscopy (SEM)

[e] Percent mineralization of mulch during testing via ASTM D5338 at 90 days. (See Fig. 6.)

uniformity, then sent to Biax-Fiberfilm (Greenville, WI USA) in 2010 for conversion into a MB mulch. The melt temperatures in MB processing of PLA and PLA+PHA-75/25 were 262 and 231 °C, respectively. (Typically, higher melt temperatures are employed in MB with similar polymers compared to SB due to the need for lower melt viscosity in achieving smaller diameter fibers in MB.) A lower temperature was employed for the nonwoven processing of MB-PLA-PHA since PHA is more thermally unstable than PLA. The dwell time during extrusion for MB processing of both PLA and PLA+PHA-75/25 was approximately 1 min. GreenBio PHA consists of a co-polymer of 3-hydroxybutyrate and 4-hydroxybutyrate (Fig. 1); the latter monomeric unit being present at 17 % (but at 19.2 % within the PHA component of MB-PLA+PHA, NMR analysis), with M_w and PDI equal to 455,000 ± 12,000 and a 1.41 ± 0.01, respectively (GPC analysis, based on polystyrene standards), all of which agree with values reported in the literature [33, 43, 44]. Physical properties of the mulches are given in Table 1. Mulches were stored at room temperature in closed black polyethylene bags prior to use. Cellulose powder DS-0, utilized as a positive control in composting biodegradation tests, was purchased from Fluka (St. Louis, MO USA). Chloroform, HPLC grade, was obtained from Fisher Scientific (Pittsburgh, PA USA).

Methods

Simulated Weathering

Simulated weathering of the mulches (69 × 149 × 3 mm^3) by UV irradiation and water-spray was carried out according to the ASTM standard G155 [40] in an accelerated weathering chamber (Ci4000 Xenon Weather-Ometer, Atlas Material Testing Technology LLC, USA). The films were irradiated with UV rays (Irradiance: 0.35 W/m^2 nm; Wavelength: 340 nm) at a black-panel temperature of 63 °C for 102 min followed by 18 min under UV rays and water spray while the temperature decreased inside the weather-ometer. This cycle was repeated 252 times for a total exposure of 504 h (21 days).

Weight and Thickness

Weight (gm^{-2}) and thickness (µm) of mulches before and after 21 days of simulated weathering were measured according to ASTM D5729 and D3776, respectively [45, 46]. Five-to-ten subsamples measuring 2.54 cm × 15.24 cm in the machine direction were cut per mulch sample. However, MB mulch underwent significant deterioration during simulated weathering, according to visual observation; therefore, smaller, 2.54 cm × 10.16 cm (machine direction), dimensions were employed for preparing subsamples of all MB mulches.

Scanning Electron Microscopy

Samples of mulch films before and after 21 days of simulated weathering were mounted on a 1.2 cm diameter aluminum disk using double-sided adhesive carbon tape, and sputter-coated with a thin layer of gold (<5 nm) in a vacuum chamber using argon gas and an electrical current of approximately 3 mA. Digital photomicrographs were made of the initial mulches and weatherometer-treated mulches at 100×, 500×, and 1,000× with a LEO 1525 field emission scanning electron microscope (Zeiss, Oberkochen, Germany).

Tensile Strength Testing

Tensile strength (i.e., breaking force, or peak load) for the four mulches before and after 8.5, 16.5, and 21.0 days of simulated weathering was measured according to ASTM D5035. The test were carried out with a United Testing Systems (UTS, model SFM-20 load frame, load cell: 10 kN, United Calibration Corporation, Huntington Beach, CA USA), at 25 °C. At each sampling time, each mulch was cut into 4–8 subsamples in the MD, with the subsample sizes being 2.54 cm × 15.24 cm and 2.54 cm × 10.16 cm for SB and MB samples, respectively, employing gauge lengths of 7.62 cm, and 2.54 cm, respectively. The strips were tested by extending the subsamples at a failure rate of 30.48 cm per minute. At least four subsamples were tested for each mulch.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to determine M_w and PDI of the PLA component for all four mulches before and after 8.5, 16.5, and 21.0 days of simulated weathering. At least two 20 g subsamples were analyzed for each sample, and at least two chromatograms obtained for each subsample. Each sample (approximately 20 mg) was dissolved in 5 mL of chloroform. Then the mixtures were stirred for 1 h, centrifuged at 10,000 rpm (6,149 g) for 1 min, and passed through 0.20 μm nylon filters to remove any chloroform-insoluble particles. The filtered solution (300 μL) was injected into a dual-pump HPLC system (Varian, Walnut Grove, CA USA) equipped with model Mark III evaporative light scattering detector (WR Grace, Deerfield, IL USA), and a 300 × 7.5 mm ID PL Gel mixed D column purchased from Agilent (Santa Clara, CA USA). The mobile phase consisted of $CHCl_3$ delivered at 0.8 mL min^{-1}. Molecular weight values are reported as polystyrene molecular weight equivalents, using EasiVial PS-H polystyrene standards from Agilent. Response factors that relate detector signal and concentration were included in the calculations.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed for all four mulches before and after 21 days of simulated weathering using a DSC Q20 (TA Instruments, New Castle, DE USA) under nitrogen flow. To determine the thermal properties profile, a subsample (5–10 mg placed in an aluminium pan) was heated to 200 °C at 10 °C/min, held at the latter temperature for 5 min, then cooled to −50 °C at 10 °C/min, held at this temperature for 5 min, and finally heated again to 220 °C at 10 °C/min. The glass transition temperature (T_g) and the melting temperature (T_m) were determined from the first heating cycle, while the crystallization temperature (T_c) was obtained from the second heating cycle (Fig. 2).

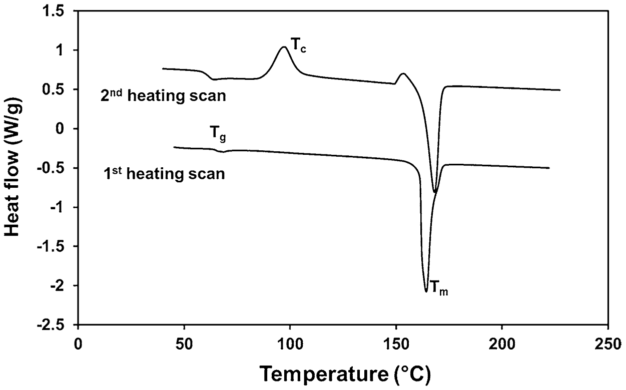

Fig. 2 DSC thermograms of the non-weathered SB-PLA-black mulch for the first second heating cycle. T_c, T_g, and T_m refer to the crystallization temperature, glass transition temperature, and melting temperature, respectively

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra of the four mulches before and after 21 days of simulated weathering were acquired on a FT-IR (IRAffinity-1, Shimadzu Co., Tokyo, Japan) equipped with a single reflection ATR system (MIRacle ATR, PIKE Technologies, Madison, WI USA). A resolution of 4 cm^{-1} and 32 scans were used for measuring of the spectrum.

Biodegradability Testing

Biodegradation of the four mulches before and after 21 days of simulated weathering was tested in a controlled experimental environment for a 90 days period. The experimental setup was based on procedures outlined in ASTM D5338 [41]. Three-month-old mature compost (C/N ratio of 16.5) was obtained from the Michigan State University (MSU) composting facility. The compost was size-reduced through a 5 mm sieve and inorganic materials such as glass, stones, and metal were removed. Dry compost (400 g) was mixed with 100 g of dry vermiculite, and the moisture level was adjusted to 60 % of water holding capacity. The vermiculite (grade number 4 soil conditioner; Therm-O-Rock, New Eagle, PA USA) provided aeration and retained moisture. Subsamples of the mulches (9 g) were cut into 1 × 1 cm^2 squares and then added to 275 g of active compost in 2-L glass jars, and incubated at 58 °C for 90 days. No fresh compost was added to the bioreactors during the 90 days biodegradation period. The system consisted of 20 bioreactors: two references (i.e., containing no plastics), two positive controls of cellulose, and two of each of the four mulches before and after weathering.

The average % biodegradation versus time data collected for each mulch was simulated using a loess' function in R [47, 48], a locally weighted polynomial regression model. The smoothness of the loess fit depends on the specific number of observations used in each local fit (neighborhood). Twenty percent of the data were used for each local fit. Residuals are assumed to be distributed identically and described by a Gaussian distribution. The standard error is estimated from the sum of squares for the residuals divided by the degrees of freedom. Confidence intervals (95 %) are computed by adding or subtracting the standard error variance to the estimated value of the % biodegradation.

NMR Analysis

NMR analysis was performed on MB-PLA+PHA mulch and GreenBio PHA feedstock using a 400 MHz spectrometer from Varian, implementing a pulse width of 30° and 90° for ^{1}H and ^{13}C analyses, respectively. ^{1}H-NMR spectral assignments for *poly(3-hydroxybutyrate) monomeric units*, were (in ppm) 5.2 –$\mathrm{OC\mathbf{H}(CH_3)CH_2COO}$– (m), 2.5 and 2.6– $\mathrm{OCH(CH_3)C\mathbf{H_2}COO}$– (m,m), and 1.3 –$\mathrm{OCH(C\mathbf{H_3})}$-$\mathrm{CH_2COO}$– (t); for *poly(4-hydroxybutyrate) monomeric units*: 5.2 –$\mathrm{OC\mathbf{H_2}CH_2CH_2COO}$– (t), 2.3 –$\mathrm{OCH_2CH_2C\mathbf{H_2}COO}$– (t), and 1.9 –$\mathrm{OCH_2C\mathbf{H_2}CH_2COO}$– (m); and for *PLA monomeric units*: 5.1 –$\mathrm{OC\underline{\mathbf{H}}(CH_3)COO}$– (m), 1.6 –$\mathrm{OCH(C\underline{\mathbf{H_3}})COO}$– (d); ^{13}C-NMR spectral assignments for *poly(3-hydroxybutyrate) monomeric units* consisted of (in ppm): 169.1 –$\mathrm{OCH(CH_3)CH_2\mathbf{C}OO}$–, 67.6 –$\mathrm{O\mathbf{C}H(CH_3)CH_2COO}$–, 40.7 –$\mathrm{OCH(CH_3)\mathbf{C}H_2COO}$–, and 19.7 –$\mathrm{OCH(\mathbf{C}H_3)CH_2COO}$–, for *4-hydroxybutyrate monomeric units*: 169.9 –$\mathrm{OCH_2CH_2CH_2}$ COO–, 63.6 –$\mathrm{OCH_2CH_2CH_2COO}$–, 30.8 –$\mathrm{OCH_2CH_2\mathbf{C}H_2}$ COO–, and 24.0 –$\mathrm{OCH_2\mathbf{C}H_2CH_2COO}$–; and for *PLA monomeric units*: 169.6 –$\mathrm{OCH(CH_3)\underline{C}OO}$–, 69.0 –$\mathrm{O\underline{C}H}$ $\mathrm{(CH_3)COO}$–, 16.6 –$\mathrm{OCH(\underline{C}H_3)COO}$–.

Results and Discussion

Effect of Simulated Weathering on Physical Properties of Mulches

Table 1 displays the effect of simulated weathering on the average dry weight per unit area and thickness of mulches. These results demonstrate that SB and MB materials possess similar weights, and that weathering led to a slight increase in weight for all mulches with the exception of MB-PLA+PHA-75/25, perhaps reflecting adsorption of moisture, noting the use of frequent spraying of water within the ASTM G155 protocol, to simulate rain [40]. Also, the thicknesses of the mulches are similar to each other, except that MB-PLA+PHA-75/25 is slightly thinner than the others. The thickness of all mulches increased slightly during simulated weathering. Weight and thickness values for the unweathered mulches reported in Table 1 strongly agree with data published previously for PLA MB and SB prototypes [23]. The average fiber diameter for the two SB mulches (15 μm), determined from SEM micrographs, is significantly larger than the average value for the MB-PLA mulch (7.5 μm), with this trend and the values reported here also consistent with previously published results [23, 27]. The incorporation of PHA into the MB mulches led to a two-fold increase in the fiber diameter, and an increase in the standard error for the average size (Table 1). Simulated weathering slightly decreased the average fiber diameter, by ~1.0 μm, for both the SB-PLA-black and MB-PLA+PHA-75/25 mulches, and increased the standard error for the latter, but had no effect on the average fiber diameter of the SB-PLA-white mulch.

SEM images of the MB mulches before and after weathering treatment are shown in Fig. 3. The random orientation of the fibers observed in the figure is typical of nonwovens. Weathering treatment led to fiber breakage for the MB-PLA+PHA-75/25 mulch, but no fiber breakage observed for MB-PLA (Fig. 3) and SB-PLA mulches (not shown).

In another paper investigating the biodegradation of PLA-based nonwoven mulches in soil via several physical characterization methods: i.e., weight, thickness, air permeability, and tensile strength (loss of breaking load and breaking elongation in the material's machine direction), the tensile strength was the most reflective measurement for the deterioration of the mulches [23]. The report also demonstrated that MB mulches underwent a more rapid loss of tensile strength than SB mulches during soil burial, presumably due to the smaller average fiber size for the former. Similarly, the MB mulches underwent a much larger decrease in the tensile strength than the SB as a result of simulated weathering (Table 2). In particular, the MB-PLA+PHA-75/25 mulch lost 95 % of tensile strength, while the strength loss for MB-PLA was slightly >50 %. The majority of the tensile strength loss occurred during the first 8.5 days of the 21 days weatherometry cycle. The black SB mulch did not encounter statistically significant loss of tensile strength during simulated weathering, while the white SB material lost 14 % of tensile strength (the majority of which occurred within the first 8.5 days of simulated weathering). The underlying reason for the greater tensile strength loss is not clear, but may be related to the smaller fiber diameter for the white versus the black SB mulch. Lastly, SB nonwoven processing provides a much stronger material than either MB nonwoven mulches or commercial mulch films that possess weights twofold to

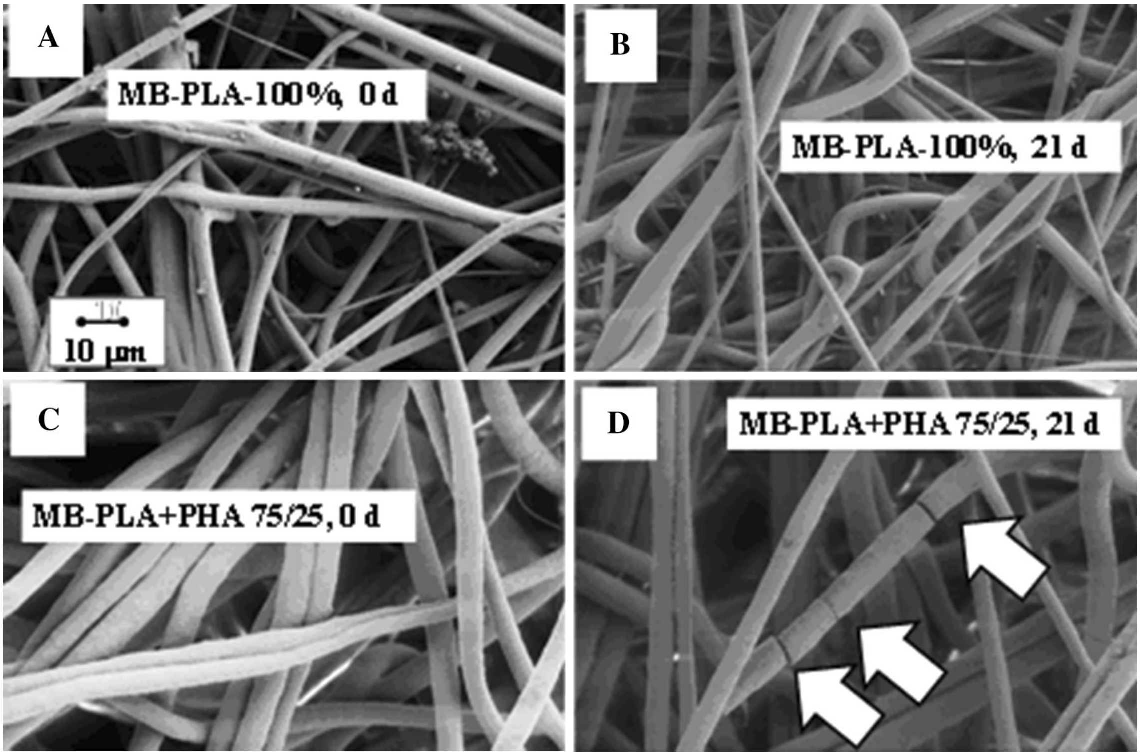

Fig. 3 SEM micrographs of MB-PLA-100 % and MB-PLA+PHA-75/25 w/w mulches before and after simulated weathering for 21 days, 1,000× magnification. *Arrows* show evidence of fiber breakage

Table 2 Effect of simulated weathering duration on the tensile strength of PLA- and PLA+PHA-based nonwoven agricultural mulches

Mulch	Weathering time, days	Tensile strength (N)[a]
SB-PLA-white	0.0	56.21 ± 2.11 a
	8.5	46.02 ± 13.48 abc
	16.5	34.96 ± 1.36 c
	21.0	47.61 ± 8.25 b
SB-PLA-black	0.0	37.12 ± 3.84 c
	8.5	42.52 ± 15.57 abc
	16.5	46.71 ± 6.53 abc
	21.0	39.60 bc
MB-PLA-100 %	0.0	8.96 ± 2.23 d
	8.5	3.68 ± 0.27 de
	16.5	4.66 ± 0.67 de
	21.0	4.12 ± 1.15 de
MB-PLA+PHA 75/25	0.0	3.90 ± 0.09 de
	8.5	0.71 ± 0.11 de
	16.5	0.29 ± 0.09 de
	21.0	0.21 ± 0.27 e

Mean values that posses different lower-case letters reflect a statistically significant difference ($p < 0.05$)

[a] Mean values ± standard error

threefold higher than mulch films, leading to higher processing costs. Whereas the tensile strength for non-weathered SB mulches is near 50 N (with the value for white SB mulch being slightly higher than for SB-black due to the higher molecular weight feedstock employed for the former), the tensile strength of MB-100 % PLA and MB-PLA+PHA-75/25 mulches are 9N and 4N, respectively (Table 2). Commercial polyethylene and biodegradable mulch films possess tensile strength values of 8–12 N [12].

Effect of Simulated Weathering on Chemical Properties of Mulches

Values of M_w and PDI for the mulches initially, and during weathering treatment, are given in Table 3. M_w and PDI are similar for non-weathered SB-PLA-black and MB-PLA, since both share the same PLA feedstock. Moreover, the employment of the two different nonwoven processing methods did not alter the molecular weight distribution of Ingeo™ 6252 PLA feedstock appreciably. The higher M_w value for SB-PLA-white reflects the higher molecular weight PLA feedstock used for its preparation, and agrees with values for the same mulch that were published previously [23]. However, the non-weathered MB-PLA+PHA-75/25 mulch possesses a slight but significant

Table 3 Effect of simulated weathering duration on the weight-averaged molecular weight (M_w) and polydispersity index (PDI) of PLA- and PLA+PHA-based nonwoven agricultural mulches[1]

Mulches	Weathering time, days	M_w, kDa[a]	PDI[a]
SB-PLA-white	0.0	196 ± 1	1.54 ± 0.01
	8.5	191 ± 1	1.53 ± 0.01
	16.5	193 ± 1	1.54 ± 0.01
	21.0	194 ± 1	1.53 ± 0.01
SB-PLA-black	0.0	154 ± 2	1.55 ± 0.01
	8.5	152 ± 1	1.54 ± 0.01
	16.5	150 ± 1	1.54 ± 0.01
	21.0	139 ± 1	1.54 ± 0.01
MB-PLA-100 %	0.0	150 ± 3	1.53 ± 0.01
	8.5	156 ± 7	1.55 ± 0.01
	16.5	137 ± 1	1.53 ± 0.01
	21.0	145 ± 1	1.53 ± 0.01
MB-PLA+PHA 75/25	0.0	95.4 ± 0.4	1.70 ± 0.01
	8.5	99.1 ± 7.0	1.71 ± 0.01
	16.5	70.8 ± 2.0	1.79 ± 0.03
	21.0	70.5 ± 0.1	1.85 ± 0.01

Based on comparison to polystyrene standards

[a] Uncertainty range given for the reported values reflect standard error

decrease of M_w and increase of PDI compared to the PLA+PHA feedstock employed in its preparation (M_w values of 135 ± 3 and 97.1 ± 1.7, and PDI values of 1.65 ± 0.01 and 1.73 ± 0.01 for the feedstock and mulch, respectively), and a lower M_w than for MB-PLA and SB-PLA-black, despite sharing the same original PLA feedstock as the latter two mulches. These results suggest the incorporation of PHA decreased the average molecular weight during the preparation of the nonwoven material.

Simulated weathering led to a 27.4 % decrease of M_w and a 7.1 % increase of PDI for MB-PLA+PHA-75/25 (Table 3). The decrease is believed to be associated with the major loss of tensile strength, the decrease of fiber size, and the occurrence of fiber breakage, the latter two as observed via SEM. Both MB-PLA and SB-PLA-black underwent a slight (<10 %) decrease of M_w; but, SB-PLA-white did not encounter any appreciable change of molecular weight (Table 3), partially attributable to the latter's higher molecular weight. These trends contrast those reported above for tensile strength loss, where SB-PLA-white and MB-PLA underwent a significantly larger loss of tensile strength than SB-PLA-black (Table 2). The result suggests that mechanical weakening of the SB-PLA mulch via weathering is not always coupled with degradation of the individual fibers directly. For all of the mulches (except for SB-PLA-white), the loss of molecular weight occurred gradually over the 21 days simulated weathering period, which contrasts with the more rapid loss of tensile strength, within 8 days (Table 2). The slow decrease of molecular weight versus time reflects a surface erosion mechanism for biodegradation, rather than a bulk erosion mechanism [49]. Presumably, the decrease of tensile strength reflects the opening up of the supramolecular structure, which enables the slow degradation of the individual fibers to occur.

Changes in structural organization after weathering were determined also by differential scanning calorimetry. Table 4 presents the main thermal transitions and Fig. 2 displays the thermogram of SB-PLA-black for the 1st and 2nd heating scans, as an example of thermal transition determination. Before weathering, all mulches were exhibiting similar values of T_g (64 to 67 °C) and T_m (163 to 168 °C), all of which are typical of PLA thermal transitions [50]. Melting enthalpies for non-weathered SB-PLA-black and MB-PLA100 % were found to be similar, certainly due to the use of the same PLA feedstock for their preparation. The incorporation of PHA in MB-PLA+PHA-75/25 was found to decrease the melting enthalpy for PLA. Simulated weathering had the greatest effect on thermal properties of MB-PLA+PHA-75/25 among the mulches investigated, consistent with the larger decrease of molecular weight (Table 3) and occurrence of fiber breakage (Fig. 3). The major change observed during weathering of MB-PLA+PHA-75/25 was a decrease of T_g (from 65 to 57 °C), reflecting the decrease in molecular weight and perhaps the decrease of crystallization enthalpy. An increase of T_g and melting enthalpy were observed for the SB-PLA mulches, indicating that a structural reorganization had taken place for these two materials. This observation was confirmed by an increase of the crystallization enthalpy for these materials.

Furthermore, the chemical structure of the mulches was probed by ATR-FTIR before and after simulated weathering (Fig. 4). FTIR spectra of all mulches exhibit band assignments that correspond to PLA [50], as summarized in Table 5. Most of the same bands also occur for PHA [1]. However, the incorporation of PHA in MB-PLA+PHA-75/25 induced a few differences compared to other spectra: a slightly broader and less intense peak at 1,751 cm^{-1} (–C=O carbonyl stretch, due to the maximum position for PHA' carbonyl stretch reported to be lower, 1,719 cm^{-1} [1]), and a more intense band at 1,300 cm^{-1} (–CH–deformation) and 1,267 cm^{-1} (–C=O bend). Simulated weathering led to several spectral changes for all four mulches. First, a band with a maximum at 1,585 cm^{-1} appeared, corresponding to C=C stretching. A shoulder also appeared at 1,718 cm^{-1}, attributable to carboxylic acid end groups. At the same time, the peak at 1,751 cm^{-1}, representing C=O stretching of ester bonds, decreased slightly. Finally, in the hydroxyl stretching region, a broad

Table 4 Effect of simulated weathering treatment on the supramolecular structure of PLA- and PLA+PHA-based nonwoven agricultural mulches as determined by differential scanning calorimetry (DSC)

Mulch	Weathering time, days	T_m(°C)^a	ΔH_m (J/g)^a	T_g(°C)^a	T_c(°C)^b	ΔH_c (J/g)^b
SB-PLA-white	0.0	163	40	67	113	28
	21.0	163	45	72	115	31
SB-PLA-black	0.0	164	53	64	97	22
	21.0	163	57	74	99	28
MB-PLA-100 %	0.0	168	50	66	101	31
	21.0	167	44	67	98	25
MB-PLA+PHA 75/25 (values for PLA)	0.0	166	38	65	82	17
	21.0	166	33	57	78	10
MB-PLA+PHA 75/25 (values for PHA)	0.0	139	1.2			
	21.0	142	0.7			

Values given are for PLA unless indicated otherwise

T_m = melting temperature, ΔH_m = melting endotherm, T_g = glass transition temperature, T_c = crystallization temperature, ΔH_c = crystallization endotherm

[a] determined from first thermal cycle (cf. Figure 2)

[b] determined from first plus second thermal cycle (cf. Figure 2)

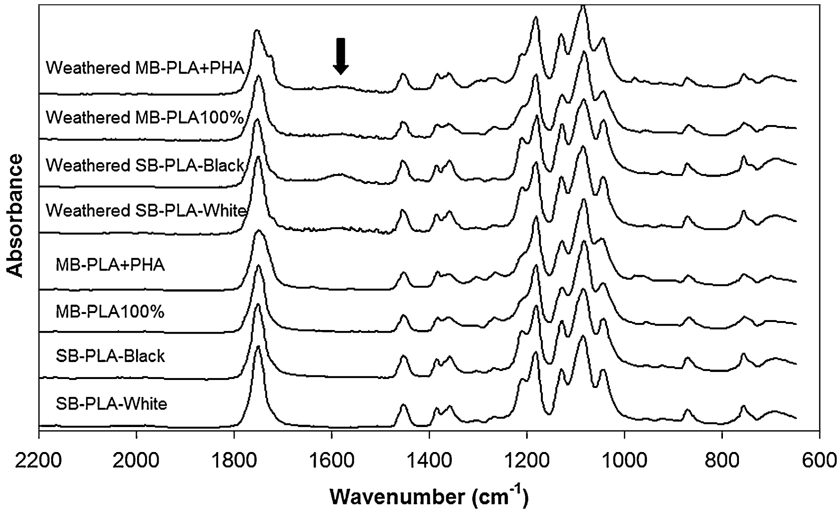

Fig. 4 FTIR-ATR spectra of non-weathered mulches, and after 21 days of simulated weathering. The *arrow* shows the apparition of a peak at 1,585 cm^{-1}, corresponding to C=C bonds and testifying the chemical structure change of mulches

Table 5 FTIR band assignment for the PLA component of the nonwoven agricultural mulches [50]

Wavenumber, cm^{-1}	Band assignment
1,751	–C=O carbonyl stretch
1,460	$-CH_3$ bend
1,382, 1,362	–CH– deformation including symmetric and asymmetric bends
1,267	–C=O bend
1,194, 1,130, 1,093	–C–O– stretch
1,085	–OH bend
926, 868	–C–C– stretch

absorption band with a maximum at 3,370 cm^{-1} formed, which may correspond to –OH end groups, hydroperoxides, and adsorbed water. It appears that ester bonds are cleaved, forming new carboxylic acid, hydroxyl, and C=C end groups. The latter two suggests hydrolysis of ester bonds and Norrish Type II photodegradative cleavage (Fig. 5), The latter was reported previously for PLA [51]. Similarly, PHA is reported to undergo a random scission process to produce double bonds and carboxylic acids [52–56]. But other reports suggest that PHA films are resistant to degradation by sunlight, demonstrated by a constant value of tensile strength [1].

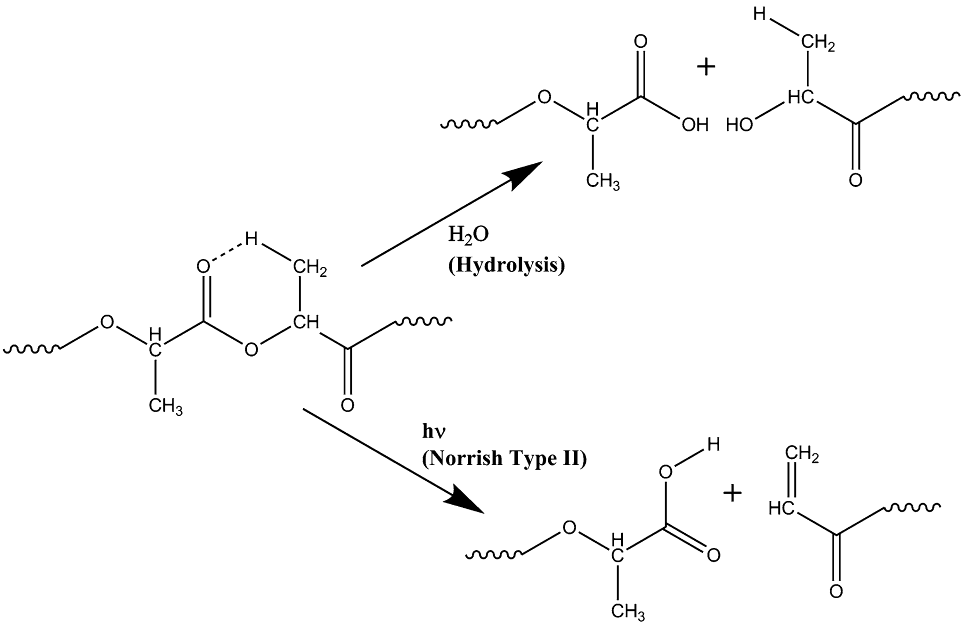

Fig. 5 Depolymerization reactions for PLA during simulated weathering: hydrolysis and Norrish Type II reaction mechanism (photolysis)

Effect of Simulated Weathering on Biodegradability

Figure 6 present the biodegradation of cellulose powder, used as a reference, and weathered and non-weathered specimens of the four nonwoven agricultural mulches, following ASTM D5338 [41]. Only the cellulosic material underwent a significant lag phase during the initial period. The subpar rate and extent of microbial assimilation achieved by SB-PLA-white may reflect this mulch's relatively high molecular weight. All four nonwoven mulches exhibited a lower rate and extent of biodegradation than cellulose, the positive control. At the end of the experiment [41] (90 days), among the non-weathered mulches, MB-PLA-100 % achieved the highest level of biodegradation (83 %), and underwent a higher rate and extent of biodegradation than SB-PLA-black, despite the two mulches being prepared from the same PLA feedstock. The difference may be due to the smaller fiber diameter of the former. Among the nonwoven mulches, MB-PLA+PHA-75/25 underwent the highest rate of biodegradation, but reached a plateau of only 67 %. The lower biodegradation for the MB-PLA+PHA-75/25 mulch relative to MB-PLA may be related to its PHA biopolymeric component. The literature demonstrates that at 60 °C, PHA undergoes a lower extent of biodegradation than at room temperature, presumably due to a lower amount of microorganisms at 60 °C and a high crystallinity for PHA [57, 58].

Simulated weathering greatly enhanced the rate and extent of biodegradation for the nonwoven mulches. The most significant increase was for SB-PLA-white, where the rate increased by over 40 % (approximately 35 and 50 days to reach 50 % biodegradation for non-weathered and weathered mulches, respectively) and the extent increased from 57 to 72 %, respectively. For the weathered mulches, in contrast to non-weathered mulches, the SB-PLA-white mulch was degraded more rapidly and fully than SB-PLA-black. This result reflects the increased degradation of the SB-white mulch relative to SB-black due to weathering, observed by the larger tensile strength loss for the former (Table 2). Weathering greatly enhanced the biodegradation of the MB mulches, with the rates and extents of mineralization being similar to that of the positive control, cellulose. MB weathered mulches may ultimately be compliant with the biodegradability criterion of the compostability standard [59]. The final biodegradation percentage achieved for the weathered mulches (90 days, Table 1) can be classified as followed: SB-PLA-black (68 %) <SB-PLA-white (72 %) <MB-PLA+PHA 75/25 (91 %) <MB-PLA-100 % (93 %). Of the nonwoven mulches studied thus far under ambient soil conditions via greenhouse soil burial studies, MB-PLA+PHA-75/25 underwent the greatest extent of biodegradation (Dharmalingam et al., submitted), that certainly is due to having the lowest percentage of crystallinity observed among the samples (Table 4), thereby facilitating the breakdown of molecules present in the blend. Special interaction between PLA and PHA and surface effects may enhance the subsequent biodegradability. The results of this study demonstrate that weathering greatly enhances the rate and extent of biodegradability for MB-PLA+PHA-75/25, suggesting further that MB-PLA+PHA-75/25 may be a viable candidate for compliance with ASTM WK29802 [42], a new standard under review for biodegradability of plastics

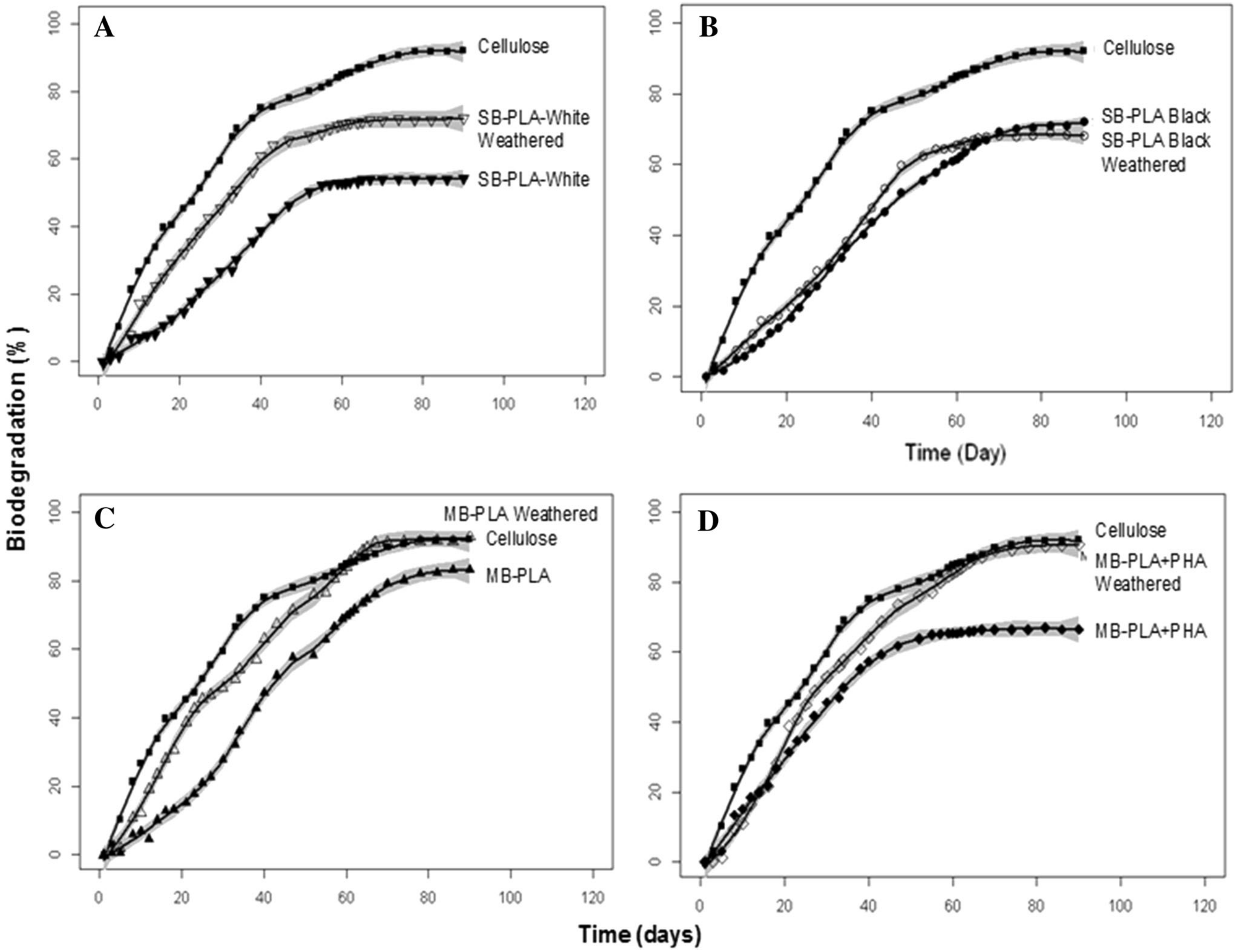

Fig. 6 Biodegradation of cellulose powder compared to non-weathered and weathered **a** SB-PLA-White, **b** SB-PLA-Black, **c** MB-PLA-100 %, and **d** MB-PLA+PHA-75/25 mulches

under ambient soil environments, as a "Category II" material and one that meets specifications (e.g., 90 % biodegradation within 2 years) through previous exposure to environmental factors simulated by weathering.

Conclusions

Simulated weathering greatly enhanced the inherent biodegradability of two fully biobased agricultural mulches, prepared from PLA to a PLA/PHA 75/25 w/w blend via meltblown (MB) nonwoven textile technology, through the weakening of mechanical strength, which promoted breakage of microfibers, and by a slight decrease of molecular weight. Such trends were evident for MB-PLA+PHA-75/25 particularly, and to a lesser extent for MB-PLA-100 %. Based on these results, the former mulch is a viable candidate for a biodegradable agricultural mulch that will meet specifications as a Category II material compliant with the new standard being developed for biodegradation of plastics under ambient soil conditions, ASTM WK29802 [42]. In contrast, weathering affected the physicochemical properties of two spunbond nonwoven mulches (SB-PLA-white and SB-PLA-black) to a small extent (although SB-PLA-white underwent a slightly greater decrease of tensile strength perhaps due to its smaller average fiber diameter). Both SB mulches after weathering achieved 68–72 % biodegradability in 90 days under composting conditions (ASTM D5338 [60]), suggesting the materials will meet the inherent biodegradability specification of the ASTM D6400 and D6868 compostability standards [61, 62], which specify 90 % biodegradation in 180 days. Therefore, SB nonwovens may be useful as durable and compostable materials for long-term agricultural applications, such as row covers and landscape fabric.

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References

1. Rudnik E, Briassoulis D (2011) Comparative biodegradation in soil behaviour of two biodegradable polymers based on renewable resources. J Polym Environ 19:18–39
2. Shogren RL, Hochmuth RC (2004) Field evaluation of watermelon grown on paper-polymerized vegetable oil mulches. HortScience 39:1588–1591
3. Kasirajan S, Ngouajio M (2012) Polyethylene and biodegradable mulches for agricultural applications: a review. Agron. Sustain. Dev. 32:501–529
4. Espi E, Salmeron A, Garcia Y, Real AIJ (2006) Plast. Film Sheeting 22:85–102
5. Lamont WJ Jr (2005) Plastics: modifying the microclimate for the production of vegetable crops. Hort Technol 15:477–481
6. Levitan L (2005) Reducing dioxin emissions by recycling agricultural plastics: Creating a viable alternative to open burning. In Great Lakes Regional Pollution Prevention Roundtable New York
7. Lemieux PM (1997) Evaluation of emissions from the open burning of household waste in barrels US Environmental Protection Agency Report 600/R-97-134a Washington, DC:70
8. Corbin AT, Miles C, Cowan J, Hayes DG, Moore-Kucera J, Inglis DA (2013) Current and Future Prospects For Biodegradable Plastic Mulch in Certified Organic Production Systems, eXtension Foundation,eOrganic Community of Practice:67951
9. Shogren RL (2000) Biodegradable Mulches from renewable resources. J. Sustain. Agric. 16:33–47
10. Gregory MR, Andrady AL (2005) Plastics in the marine environment. In: Andrady AL (ed) Plastics and the environment. Wiley, New York, pp 379–401
11. Martin-Closas L, Pelacho AM (2011) Agronomic potential of biopolymer films. in Plackett D (ed) Biopolymers—New Materials for Sustainable Films and Coatings John Wiley and Sons, Chichester, UK., pp. 277-299
12. Hayes DG, Dharmalingam S, Wadsworth LC, Leonas KK, Miles C, Inglis DA (2012) Biodegradable agricultural mulches derived from biopolymers. in Khemani K, Scholz C (eds) Degradable polymers and materials: principles and practice (2nd Edition), ACS Symposium Series, Vol.1114. American Chemical Society, Washington, DC, pp. 201–223
13. Briassoulis D (2006) Mechanical behavior of biodegradable agricultural films under real field conditions. Polym Degrad Stab 91:1256–1272
14. Briassoulis D (2007) Analysis of the mechanical and degradation performances of optimized agricultural biodegradable films. Polym Degrad Stab 92:1115–1132
15. Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT (2008) Assessment of aliphatic–aromatic copolyester biodegradable mulch films. Part I: Field study. Chemosphere 71:942–953
16. Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT (2008) Assessment of aliphatic–aromatic copolyester biodegradable mulch films. Part II: laboratory simulated conditions. Chemosphere 71:1607–1616
17. Mostafa H, Sourell H, Bockisch F (2010) Mechanical properties of some bioplastics under different soil types used as biodegradable drip tubes. CIGR J, Ag.Eng. Int., p 12
18. Siegenthaler KO, Künkel A, Skupin G, Yamamoto M (2012) Ecoflex® and Ecovio®: Biodegradable, Performance-Enabling Plastics. in Rieger B, Künkel A, Coates GW, Reichardt R, Dinjus E, Zevaco TA (eds) Synthetic Biodegradable Polymers (Advances in Polymer Science, Vol.245). Springer, Berlin, pp. 91–136
19. Tullo AH (2012) Old plastics, fresh dirt. Chem Eng News 90:12–18
20. Goldberger JR, Jones RE, Miles CA, Wallace RW, Inglis DA (2013) Barriers and bridges to the adoption of biodegradable plastic mulches for US specialty crop production. Renewable Agric. Food Sys., 1–11
21. Olsen JK, Gounder RK (2001) Alternatives to polyethylene mulch film—a field assessment of transported materials in capsicum (*Capsicum annuum L.*). Aust J Exp Agric 41:93–103
22. US Department of Agriculture (Agricultural marketing service) (2013) National organic program; proposed amendments to the national list of allowed and prohibited substances (crops and processing) (7 CFR part 205, document number AMS-NOP-13-011; NOP-13-01PR, RIN 0581-AD33). Fed Reg 78(163):52100–52107
23. Wadsworth LC, Hayes DG, Wszelaki AL, Washington TL, Martin J, Lee J, Raley R, Pannell CT, Dharmalingam S, Miles C, Inglis DA, Saxton AM (2012) Evaluation of degradable spunmelt 100% polylactic acid nonwovens mulch materials in a greenhouse envrionment. J. Eng. Fiber. Fabr. 8:50–59
24. Dugan JS (2001) Novel properties of PLA fibers. Int Nonwovens J 10:29–33
25. Feng S, Jiao X (2011) The application of PLA resin on nonwovens production, Adv. Mater. Res. (Durnten-Zurich, Switz.) 332–334:1239–1242
26. Li L, Zhang J, Li S, Qian X (2011) Research progress of elastic nonwovens with meltblown technology, Adv. Mater. Res. (Durnten-Zurich, Switz.) 332–334:1247–1252
27. Khan AYA, Wadsworth LC, Ryan CM (1995) Polymer-laid nonwovens from poly(lactide) resin. Int Nonwovens J 7:69–73
28. Endres H-J, Siebert-Raths A (2011) Engineering Biopolymers-Markets, Manufacturing. Hanser Publishers, Munich, Properties and Applications
29. Sodergard A, Stolt M (2010) Industrial production of high molecular weight poly(lactic acid). In: Auras R, Lim LT, Selke SEM, Tsuji H (eds) Poly(Lactic Acid): synthesis, structures, properties, processing, and applications. Wiley, Hoboken, pp 27–41
30. Tokiwa Y, Calabia BP, Ugwu CU, Aiba S (2009) Biodegradability of plastics. Int J Mol Sci 10:3722–3742
31. Hakkarainen M, Karlsson S, Albertsson AC (1999) Rapid (bio)degradation of polylactide by mixed culture of compost microorganisms-low molecular weight products and matrix changes. Polymer 41:2331–2338
32. Kawai F (2010) Polylactic Acid (PLA)-Degrading Microorganisms and PLA Depolymerases. in Cheng HN, Gross Richard A (eds) Green Polymer Chemistry: Biocatalysis and Biomaterials, ACS Symposium Series,Vol. 1043. American Chemical Society, Washington, DC, pp. 405–414
33. Weng Y-X, Wang L, Zhang M, Wang X-L, Wang Y-Z (2012) Biodegradation behavior of P (3HB, 4HB)/PLA blends in real soil environments. Polym. Test. 32:60–70
34. Ji XM, C.A., Martin, J.T., Wallace, R.W., Wszelaki, A.L., Moore-Kucera, J., Inglis, D.A., and Lee, J. (2013) Effect of biodegradable mulch on high tunnel and open field environments, J. Am.Soc.Hortic.Sci.:in press

35. Miles C, Wallace R, Wszelaki A, Martin J, Cowan J, Walters T, Inglis DA (2012) Deterioration of potentially biodegradable alternative to black plastic mulch in three tomato production regions. HortScience 47:1270–1277
36. Cowan JS (2013) The use of biodegradable mulch for tomato and broccoli production: Crop yield and quality, mulch deterioration, and growers' perceptions. Washington State University, Pullman, p 225
37. Martin JT (2013) The Influence of organically managed high tunnel and open field production systems on strawberry (*Fragaria x ananassa*) quality and yield, tomato (*Solanum lycopersicum*) Yield, and evaluation of plastic mulch alternatives. Plant Science. Univesity of Tennessee, Knoxville, p. 128
38. Hussain I, Hamid H (2003) Plastics in Agriculture. In: Andrady AL (ed) Plastics and the environment. Wiley, New York, pp 185–209
39. Searle ND (2003) Environmental effects on polymeric materials. Wiley, New York
40. ASTM International (2013) standard practice for operating xenon arc light apparatus for exposure of non-metallic materials (ASTM G155). West Conshohocken, PA
41. ASTM International (2011) Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions. Incorporating thermophilic temperatures (ASTM D5338). West Conshohocken, PA
42. ASTM International (2012) Standard specification for aerobically biodegradable plastics in soil environment (ASTM WK29802). West Conshohocken, PA
43. Saito Y, Doi Y (1994) Microbial synthesis and properties of poly (3-hydroxybutyrate-co-4-hydroxybutyrate) in Comamonas acidovorans. Int J Biol Macromol 16:99–104
44. Weng Y-X, Jin Y-J, Meng Q-Y, Wang L, Zhang M, Wang Y-Z (2013) Biodegradation behavior of poly(butylene adipate-co-terephthalate)(PBAT), poly(lactic acid) (PLA), and their blend under soil conditions. Polym. Test. 32:918–926
45. ASTM International (2004) Standard test method for thickness of nonwoven fabrics (ASTM D5729). West Conshohocken, PA
46. ASTM International (2009) Standard test methods for mass per unit area (weight) of fabric (ASTM D3776/D3776M-09a$^{E2)}$. West Conshohocken, PA
47. Cleveland WS, Grosse E, Shyu WM (1992) Local regression models. In: Chambers JM, Hastie TJ (eds) Statistical models in S. Wadsworth & Brooks, Cole, pp 309–376
48. R Development Core Team (2009) R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria
49. Kijchavengkul T, Auras R (2008) Compostability of polymers. Polym Int 57:793–804
50. Garlotta D (2001) A literature review of poly(lactic acid). J Polym Environ 9:63–84
51. Ikada E (1997) Photodegradation behaviors of aliphatic polyesters. Photo-and bio-degradable polyesters. J. Photopolym. Sci. Technol 10:265Ā270
52. Grassie N, Murray E, Holmes P (1984) The thermal degradation of poly (-(D)-β-hydroxybutyric acid): part 1—identification and quantitative analysis of products. Polym Degrad Stab 6:47–61
53. Grassie N, Murray E, Holmes P (1984) The thermal degradation of poly (-(D)-β-hydroxybutyric acid): part 2—changes in molecular weight. Polym Degrad Stab 6:95–103
54. Grassie N, Murray E, Holmes P (1984) The thermal degradation of poly(-(D)-β-hydroxybutyric acid): part 3—The reaction mechanism. Polym Degrad Stab 6:127–134
55. Reddy CSK, Ghai R, Kalia VC (2003) Polyhydroxyalkanoates: an overview. Bioresour Technol 87:137–146
56. Lemoigne M (1926) Products of dehydration and of polymerization of β-hydroxybutyric acid. Bull. Soc. Chem. Biol. 8:770–782
57. Kim M-N, Lee A-R, Yoon J-S, Chin I-J (2000) Biodegradation of poly(3-hydroxybutyrate), Sky-Green and Mater-Bi by fungi isolated from soils. Eur. Polym. J. 36:1677–1685
58. Maiti P, Batt CA, Giannelis EP (2007) New biodegradable polyhydroxybutyrate/layered silicate nanocomposites. Biomacromolecules 8:3393–3400
59. ASTM International (2004) Standard specification for compostable plastics (ASTM D6400). West Conshohocken, PA
60. ASTM International (2011) Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions (ASTM D5338). West Conshohocken, PA
61. ASTM International (2012) Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities (ASTM D6400). West Conshohocken, PA
62. ASTM International (2011) Standard specification for labeling of end items that incorporate plastics and polymers as coatings or additives with paper and other substrates designed to be aerobically composted in municipal of industrial facilities (ASTM D6868). West Conshohocken, PA