Modifying biodegradable plastics with additives based on condensed tannin esters

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ABSTRACT: Condensed tannins derived from *Pinus radiata* bark have been esterified and added to biodegradable plastics as extrusion compounded functional plastic additives. The presence of longer alkyl chain hexanoate esters promoted tannin miscibility in the commercial polyesters Bionolle[TM] and Biopol[TM] whereas short chain acetate esters tended to remain as discrete domains, acting as fillers in the processed plastics. In the aliphatic polyester Bionolle the presence of tannin esters at typical plastic additive loadings did not alter plastic mechanical properties whereas at 5% content in Biopol the tannin-additives reduced both flexural and tensile properties. Similarly tannin esters do not alter the melt or glass transition temperatures of the polyesters, but tannin hexanoate at 5% can influence the crystallization temperatures. Artificially aging plastics realized the functionality these plant extracts can impart to plastics in acting to reduce ultraviolet (UV)-induced plastic degradation. Results indicate the tannin-additives likely provide a stabilising role through inhibiting UV penetration into the plastic, with color analysis suggesting the tannin moiety itself was sacrificial and preferentially degrading. The imparted UV stability was linked to the dissolution of tannin esters in the plastic with longer chain esters providing greater protection against UV degradation. Tannin esters showed potential as functional additives for biodegradable polymers enhancing the UV stability of the plastic. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41626.

INTRODUCTION

Drivers for sustainable materials and practises are at the forefront of many industrial sectors. Within the plastics industry bioplastics have begun to gain market share due to consumer choice and increasing availability.[1] With this market acceptance is an array of research available on renewable and biodegradable plastic systems for substituting petrochemical synthetics.[2] In the lucrative plastic additives market, sustainable options remain less developed, particularly those additives being both renewable and biodegradable.[3] Plastic additives contribute a range of functionality to plastics and include plasticization, stabilization, flame retardancy, and lubrication.[4] There is a range of bioderived plastic additives in development ranging from fermentation products[5] and modified vegetable oils[6] to those based on plant extracts such as lignin.[7,8] The use of polyphenolic tannins remains relatively unexplored with few examples of these compounds blended with plastics.[9–12] Condensed tannins are polyphenolic oligomers based on a flavanyl repeat unit (Figure 1). Being ubiquitous in leaves, bark, and wood of trees and plants, condensed tannins are potentially available in relatively high

volumes due to use in leather tanning and adhesives.[13] In plants these compounds offer a range of protective roles, inhibiting pathogens, oxidation, and ultraviolet (UV) degradation.[14] The antioxidant and UV absorbing properties relate to the degree of hydroxylation present about the flavonoid unit with B-ring ortho-dihydroxylation known to provide potent antioxidant activity.[15] These functionalities make condensed tannins attractive as plastic additives, where such functionality is often sought from petrochemical derived compounds.

Condensed tannins are inherently intractable and hydrophilic and perhaps unsuited to direct incorporation into plastics. However, their relative ease to chemically modify *via* either etherification or esterification[16] make functionalized tannins potentially compatible with many plastics. In the current study, variously esterified tannins have been evaluated as additives to a range of biodegradable plastics based on polyesters or starch. Tannin ester chemistries have been evaluated for their resulting compatibility and impacts to the physical and polymer properties of the tannin-modified plastics. The tannin esters have also been evaluated for their contribution to the modified bioplastics

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Additional Supporting Information may be found in the online version of this article.
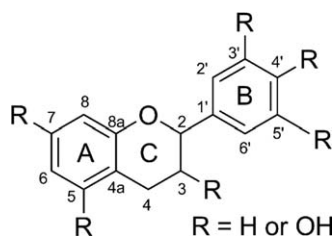
Figure 1. Flavanyl repeat unit, where polymerization typically occurs through C-4 and C-6 or C-8.

UV stability and biodegradability. Ultimately outcomes from this study will contribute to understanding how these polyphenolics may be integrated with plastics as functional additives.

MATERIALS AND METHODS

Materials

Pine bark tannin (PBT) was a spray dried product obtained from hot water (90°C) counter current extraction of air-dried *Pinus radiata* bark (moisture content *ca.* 14%).[17] Acetic, propionic, butyric and hexanoic anhydrides were all laboratory grade reagents sourced from BDH. Pentan-2-one and 1-methylimidazole (Aldrich) were used as received. The plastics were Biopol[TM] D400GN a poly(hydroxybutyrate-co-hydroxyvalerate) obtained from Monsanto, Bionolle[TM] 1020 a poly(butylene succinate adipate) sourced from Showa HighPolymer and Mater-Bi[TM] Y101U a starch-copolymer product from Novamont. All plastics were technical grade and dried according to manufacturer recommendations prior to processing.

Tannin Ester Synthesis

Tannin esters of varying ester chain length were prepared using an adapted esterification method.[17] In summary, pine bark tannin was reacted with a molar excess of the respective acid anhydride (acetic, propionic, butyric and hexanoic) in the presence of 1-methylimidazole at 65°C for 16 h (Supporting Information, Table S1). The degree of substitution was calculated by ^{1}H-NMR spectroscopy as previously described.[17,18]

Compounding and Injection Molding

An OMC EBVP 19/30 (Italy) high-speed twin-screw extruder was used to produce master-batches of each plastic containing tannin esters. Bionolle, Biopol and Mater-Bi were processed between 125 and 180°C with a screw speed of 100–130 rpm (Supporting Information, Table S2). The compounded plastics were extruded through a strand die, cooled and pelletized to yield master-batches containing 5% (w/w) tannin ester loading.

Injection molding was performed using a BOY 15S injection moulder fitted with a mold to produce both tensile and flexural test specimens. For the three plastics a range of temperatures (nozzle, heating zones, and mold), and injection and cooling times were used (Supporting Information, Table S3). For each plastic system, tensile and flexural test specimens were prepared with 0, 0.5, 1, and 5% (w/w) tannin ester loadings.

Mechanical Testing

Tensile and flexural testing was performed using an Instron 5566 universal testing machine. Prior to testing, samples were conditioned at 23°C and 50% relative humidity according to ASTM D618-00. Tensile properties were evaluated following ASTM D638-01 methodology, with a cross head speed of 5 mm min^{-1} using test specimens of type I dimension. Flexural testing was performed according to ASTM D790-00, with a crosshead speed of 1.37 mm min^{-1} using test specimens with dimensions of 123 mm × 13 mm × 3 mm. For all tests, at least six specimens were tested.

Artificial Aging

Plastic aging was undertaken with a Q-panel lab products QUV tester according to ASTM D4329-99. Specimens were exposed using an adapted cycle A procedure with UV light (UVA-340 lamps at an irradiance of 0.77 W m^{-2} nm^{-1}, 45°C, 8 h), water spray (25°C, 1 h) and condensation (40°C, 4 h; Supporting Information, Table S4). Exposure was undertaken for a total of 500 h, with sample positions periodically rotated to ensure equal exposure. Color measurements were taken prior and after exposure using a Konica Minolta Chroma CR-400 color meter reporting color and color changes (Δ) using the CIE L*a*b* color space protocol.

Polymer Characterization and Analyses

Dynamic mechanical thermal analysis (DMTA) was conducted using a Rheometrics DMTA V instrument operating in three point bending mode. Samples (65 mm × 10 mm × 2 mm) were acquired from flexural specimens. Testing was undertaken using a 3°C min^{-1} heating rate and employed 1 Hz frequency and nominal strain rate of 0.05%.

Differential scanning calorimetry (DSC) experiments were undertaken on a TA Instruments Q1000 DSC. Samples (6–8 mg) were obtained as shavings from original and aged flexural test specimens and transferred to aluminum pans. A heat-cool-heat run between −40 and 200°C was used, utilising a heating rate of 10°C min^{-1} and cooling rate of 5°C min^{-1} under a nitrogen atmosphere.

Biodegradation was characterized using a basic soil exposure test.[19] Samples (60 mm × 12 mm × 3 mm) were conditioned (23°C and 50% relative humidity) to a constant weight before burial in aged compost (40% moisture content) maintained at 27°C and 95% relative humidity. Samples were incubated for 60 days, cleaned by washing with water and then dried at 40°C for 14 days before conditioning (23°C and 50% relative humidity) to constant weight. Evaluations included visual assessment, gravimetric weight change and electron microscopy evaluations.

Fluorescence microscopy was undertaken on a Leica TCS instrument utilising the inherent autofluorescence of tannin compounds.[17] Samples were acquired from flexural test specimens and samples imaged using a 20 × 0.5 dry lens (10–20 images per sample). The images were acquired at a size of 512 × 512 pixels and a total field of view of 500 × 500 μm, yielding a resolution of ~1 pixel μm^{-1}. Scans in the *z*-direction were recorded at 5 μm intervals to a depth of *ca.* 80 μm. Images from the different depths were then combined to produce a 2D projection of a 3D image. Projected 2D images were subjected to image analysis determining the size of any tannin domains in the plastic and employed a custom written macro using V++ software (Digital Optics V.4.0).
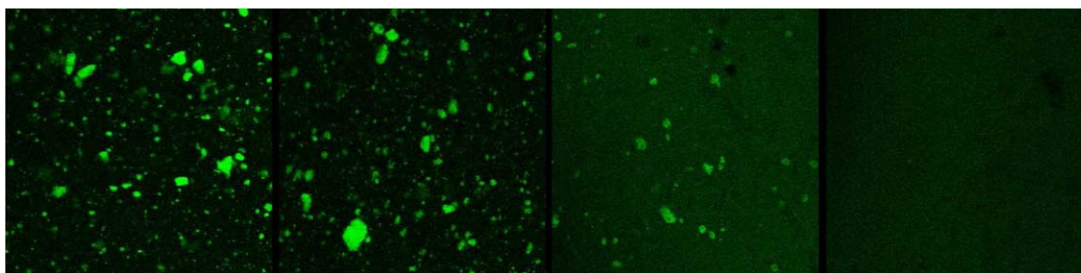
Figure 2. Examples of fluorescence microscopy images for Bionolle plastic containing 5% tannin ester content. Tannin acetate, tannin propionate, tannin butyrate and tannin hexanoate (left to right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Light microscopy was performed using a Leica MZ 125 microscope to examine surface bleaching of aged samples. Samples taken from flexural test specimens were cross-sectioned and images obtained from at least three differing locations for each sample. Images were analyzed using Image J software with results reported as color intensity profiles of sample cross-sections. The depth of color change is reported from the exposed surface to the inflexion of the color profile.

Field emission scanning electron microscopy (FESEM) was performed using a JEOL JSM-6700F FESEM. Biodegradation samples were first sectioned, mounted and adhered to stubs with a silver paint and then coated with chromium before analysis.

Fourier transform infrared (FTIR) spectroscopy was performed using a Bruker Vector 33 instrument. Samples were prepared as KBr pellets and spectra acquired in transmission with 32 background and sample scans, at 4 cm^{-1} resolution from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

The various tannin esters were processed into each plastic at loadings of 0.5, 1, and 5% (w/w). This was achieved by first producing master-batches with the tannin esters which were readily processed into Bionolle, Biopol, and Mater-Bi. Injection molding produced an array of colored plastics ranging from pale to dark brown which depended on the tannin ester, its loading and the base plastic opacity. Visually, all samples appeared to be homogeneously dispersed and free of any tannin particle agglomeration.

Tannin Miscibility in Plastics

Tannin ester dispersion within each compounded plastic matrix was investigated by microscopy utilising the autofluorescence inherent to tannin.[17] Fluorescence microscopy revealed the tannin ester domains to be homogenously distributed throughout each plastic with the particle size generally decreasing with greater ester chain length (Supporting Information, Table S5). For Bionolle, the average particle size of the tannin domains was observed to decrease with greater ester chain length for both 1 and 5% tannin ester content (Figure 2) indicating greater dissolution and compatibility of the longer chain tannin esters in Bionolle. This increased miscibility of longer chain tannin esters in this polyester is in accord with a previous finding for tannin esters compounded into poly(lactic acid).[17] For Bionolle containing tannin acetate (TAc) the retention of particle sizes at both 1 and 5% loading may suggest a retarded dissolution of this tannin ester in the plastic matrix, rather than incompatibility with the matrix which may be associated with agglomeration. The particle size distributions of tannin esters in Biopol were similar to Bionolle, with particle size also decreasing with higher tannin ester content. In the case of 1% tannin hexanoate (THex) this sample was marred by a few, relatively large particles which had not completely dispersed.

Combining tannin esters with Mater-Bi, a starch-based copolymer, gave distinct differences in dispersal behaviors compared with the polyesters Bionolle and Biopol (Figure 3). Tannin propionate (TPr) and tannin butyrate (TBu) were more homogenously dispersed within the copolymer matrix, whereas the longer chain ester retained some tannin domains within this
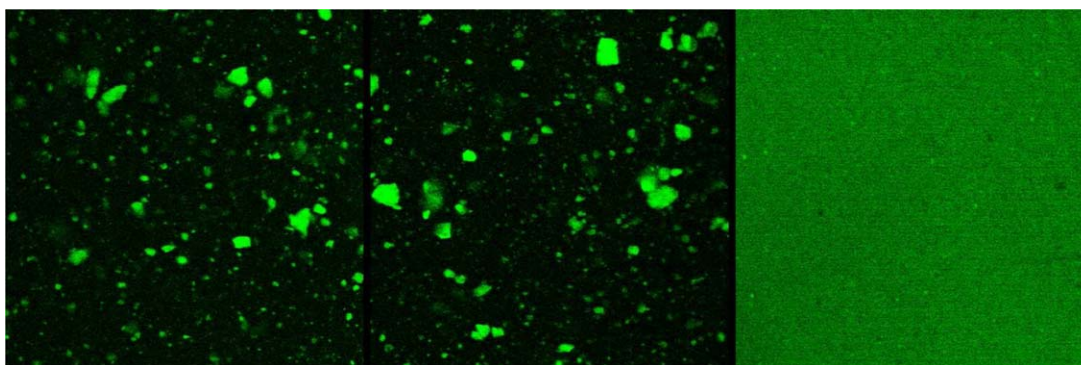
Figure 3. Fluorescence microscopy images of plastics containing 5% tannin acetate. Bionolle, Biopol, and Mater-Bi (left to right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Tensile and Flexural Properties of Bionolle Modified with 0.5–5% Tannin Esters (±95% Confidence Interval)

Sample	Flexural properties		Tensile properties	
	Modulus (MPa)	Strength (MPa)	Modulus (MPa)	Strength (MPa)
Bionolle	749 ± 2.7	34.5 ± 0.11	715 ± 13	37.8 ± 0.37
0.5% TAc	759 ± 4.3	34.6 ± 0.26	700 ± 27	37.7 ± 0.15
1% TAc	741 ± 6.1	34.0 ± 0.19	702 ± 42	37.6 ± 0.31
5% TAc	773 ± 8.1	34.9 ± 0.25	698 ± 11	34.1 ± 0.28
0.5% TPr	749 ± 6.5	34.1 ± 0.31	696 ± 13	37.7 ± 0.14
1% TPr	748 ± 3.4	34.4 ± 0.13	684 ± 14	37.7 ± 0.17
5% TPr	759 ± 9.8	34.2 ± 0.24	684 ± 9	34.6 ± 0.18
0.5% TBu	762 ± 8.2	34.8 ± 0.20	680 ± 14	37.8 ± 0.43
1% TBu	765 ± 3.1	34.8 ± 0.11	683 ± 9	37.9 ± 0.29
5% TBu	725 ± 6.7	32.8 ± 0.19	642 ± 11	33.8 ± 0.27
0.5% THex	787 ± 5.9	35.3 ± 0.13	670 ± 12	36.2 ± 0.29
1% THex	769 ± 8.2	34.6 ± 0.26	658 ± 8	36.7 ± 0.13
5% THex	731 ± 7.4	32.9 ± 0.16	645 ± 6	34.7 ± 0.18

material. The average particle size of tannin domains generally decreased from tannin acetate to propionate (Supporting Information, Table S5), but was higher with the longer chain esters. However, a comparison of Mater-Bi with the two polyesters suggests these particle sizes were, overall, substantially smaller. Only a few particles were observed and this greater dissolution may also relate to the compatibility provided by the starch and plasticizer present in Mater-Bi.

Plastic Mechanical Properties

Tensile and flexural properties of samples were assessed to understand the influence of each tannin ester on the mechanical properties of plastics. Adding TAc or TPr to Bionolle at low levels had minimal effect on the flexural properties (Table I). At 5% loading, TAc and TPr appear to act as fillers, increasing the flexural modulus. There was also a decrease in tensile strength with higher loadings (5%) of both TAc and TPr, con-

sistent with their behavior as a filler. Both TBu and THex addition gave a modest (3%) decrease in flexural modulus and a greater reduction (up to 10%) in tensile modulus at higher tannin ester loading. Accordingly, the strain at break also increased (up to 5%, Supporting Information, Figures S1–S3), with specimens exhibiting ductile-shear failure, indicative of plasticization. In contrast to unmodified Bionolle, an absence of crazing or crack formation[20] suggests THex modified Bionolle was homogenous, consistent with microscopy analysis (Figure 2).

Flexural properties of Biopol were also observed to show a dependence on tannin ester chain length and loading (Table II). Adding each tannin ester to Biopol generally decreased the flexural modulus. This flexural modulus decrease was most evident for TPr where addition of 5% tannin ester lowered the flexural modulus by *ca.* 10%. Interestingly, testing revealed the 5%

Table II. Tensile and Flexural Properties of Biopol Modified with 0.5, 1 and 5% Tannin Esters (±95% Confidence Interval)

Sample	Flexural properties		Tensile properties	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
Biopol	2.19 ± 0.02	55.7 ± 0.20	2.07 ± 0.04	30.9 ± 0.16
0.5% TAc	2.13 ± 0.02	54.8 ± 0.38	2.12 ± 0.03	31.1 ± 0.2
1% TAc	2.09 ± 0.02	56.2 ± 0.76	2.13 ± 0.05	30.8 ± 0.26
5% TAc	2.07 ± 0.01	53.2 ± 0.30	2.12 ± 0.03	29.6 ± 0.18
0.5% TPr	2.11 ± 0.02	54.4 ± 0.53	2.11 ± 0.05	31.5 ± 0.17
1% TPr	2.04 ± 0.01	53.0 ± 0.20	2.13 ± 0.06	31.5 ± 0.22
5% TPr	1.96 ± 0.01	52.1 ± 0.27	2.06 ± 0.04	31.4 ± 0.08
0.5% TBu	2.14 ± 0.02	55.5 ± 0.33	2.19 ± 0.03	31.8 ± 0.24
1% TBu	2.11 ± 0.01	54.8 ± 0.26	2.13 ± 0.04	31.5 ± 0.10
5% TBu	2.07 ± 0.01	53.5 ± 0.31	2.09 ± 0.07	31.7 ± 0.16
0.5% THex	2.10 ± 0.01	54.4 ± 0.33	2.04 ± 0.04	31.0 ± 0.15
1% THex	2.07 ± 0.02	53.4 ± 0.49	2.05 ± 0.03	31.0 ± 0.17
5% THex	2.17 ± 0.01	51.9 ± 0.26	1.91 ± 0.08	31.0 ± 0.16

Table III. Glass Transition Temperatures of Plastics Modified with Tannin Esters as Determined by DMTA

Additive	Glass transition temperature (°C)		
	Bionolle	Biopol	Mater-Bi
Control	−22	16	111
5% TAc	−19	17	113
5% TPr	−20	18	118
5% TBu	−18	17	110
5% THex	−18	16	116

THex sample was stiffer, compared to the sample with 1% THex addition. The 5% THex sample performance is likely an anomaly as related work reveals THex materials to be beneficial to polyester plastics.[17] Furthermore, in the current work, microscopy revealed the THex to be relatively poorly dispersed in this Biopol sample with respect to the other tannin esters and Bionolle.

For modified Mater-Bi samples, both the flexural modulus and strength of samples remained relatively unchanged upon tannin ester addition (Supporting Information, Table S6). Only the 5% TAc sample had a significant reduction in flexural modulus (27%) which may be due to the homogeneity revealed by microscopy (Figure 3). Tensile modulus values were observed to increase by up to 30% on tannin ester addition with 5% TPr showing the greatest increase (1359 MPa). Tensile strength values were also greater with the 5% TPr sample giving a 50% increase in tensile strength (24.7 MPa). Accordingly, strain at break for most samples was greater than pure Mater-Bi indicating more elastic behavior.

Plastic Thermal Properties

Dynamic mechanical thermal analysis (DMTA) together with differential scanning calorimetry (DSC) were used to characterize any differences in polymer properties arising from tannin ester addition. Using DMTA, only relatively small changes to the glass transition (T_g) of each plastic were observed upon 5% tannin ester addition (Table III, Supporting Information, Figures S4 and S5). Evaluation of the tan δ maxima revealed the Bionolle T_g (−22°C) to increase by 2–4°C, perhaps reflective of

the small differences in Bionolle flexural modulus values on tannin ester addition (Table I). For Biopol, which has an ambient temperature T_g, this also was observed to have relatively small changes to T_g values on tannin addition. These results, together with poly(lactic acid) T_g similarly being unaffected[17] by tannin esters[17] suggests the addition of tannin esters do not act to plasticize polyester polymers. This observation was consistent with the minor differences observed in mechanical properties of the modified Bionolle and Biopol samples (Tables I and II). In the case of Mater-Bi, the T_g (111°C) was modified by *ca.* 7°C on adding 5% TPr. However, as above, there was no trend between this copolymer's T_g values and any differences in mechanical performance.

Differential scanning calorimetry (DSC) revealed the addition of 5% THex does not significantly impact the Bionolle melt or crystallization temperatures (Supporting Information, Figures S6–S9). Cyclic heat/cool/heat testing to remove any sample thermal history revealed the onset of melting and degree of crystallization to be relatively similar with no discernible T_g observed by DSC. For Biopol, the presence of 5% THex did not impact the melt temperature nor influence T_g (16°C) as confirmed by DMTA. However, modification with THex led to a significant decrease (13°C) in the crystallization onset temperature. This change in crystallization onset and contribution to sample thermal history may be a contributor to the greater flexural modulus observed in mechanical properties (Table II).

Artificial Aging

To assess whether the presence of tannin esters offered any potential ultraviolet (UV) light stabilising effects, modified plastics were exposed to artificial aging using accelerated weathering conditions. An initial evaluation by infrared spectroscopy confirmed Bionolle and Biopol had evidence of both UV degradation and hydrolysis.[21] These artificially aged polyester samples have increased proportions of hydroxyl groups (3150–3400 cm^{-1}) as well as greater contributions of acid carbonyl groups (1650 cm^{-1}) and C–O stretching (1200–950 cm^{-1}; Supporting Information, Figures S10–S12). This is consistent with the expected hydrolysis of the ester linkages in the plastic during exposure. Furthermore, with the aliphatic ester Bionolle there were also changes about the asymmetric C–H stretch (2900–

Table IV. Mechanical and Colorimetric Analysis of Bionolle Modified with Various Tannin Esters After Artificial Aging Treatment

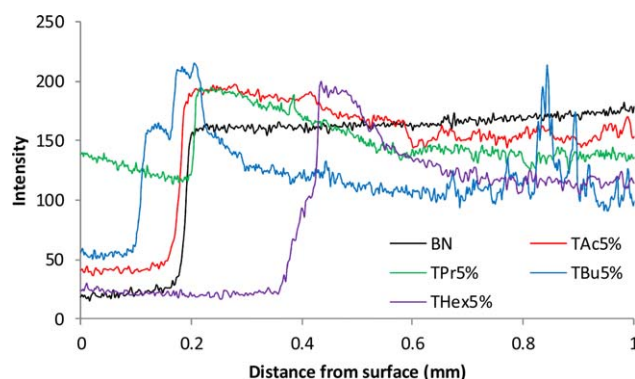| Sample	Flexural properties after aging		Color change after aging			
	Modulus (MPa)	Strength (MPa)	ΔE	ΔL	Δa	Δb
Bionolle	845 ± 12.0	37.7 ± 0.44	4.23	1.93	0.65	3.71
1% TAc	838 ± 2.8	37.2 ± 0.10	6.12	4.15	1.24	4.33
5% TAc	849 ± 9.0	37.1 ± 0.30	12.75	12.48	1.47	2.17
1% TPr	837 ± 7.1	37.2 ± 0.33	8.22	6.48	0.49	5.03
5% TPr	819 ± 8.7	36.2 ± 0.39	16.23	16.00	2.07	1.74
1% TBu	829 ± 6.8	36.9 ± 0.20	10.48	9.77	1.38	3.54
5% TBu	808 ± 6.1	35.8 ± 0.19	11.74	11.22	0.58	3.40
1% THex	831 ± 7.0	37.0 ± 0.27	9.92	7.00	0.45	7.01
5% THex	791 ± 6.9	35.1 ± 0.16	34.03	31.78	6.79	10.11

Table V. Mechanical and Colorimetric Analysis of Biopol Modified with Various Tannin Esters After Artificial Aging Treatment

Sample	Flexural properties after aging		Color change after aging			
	Modulus (MPa)	Strength (MPa)	ΔE	ΔL	Δa	Δb
Biopol	2406 ± 29	54.2 ± 0.55	5.57	0.99	1.02	5.39
1% TAc	2245 ± 26	55.7 ± 0.27	5.85	0.43	1.53	5.63
5% TAc	2262 ± 32	54.7 ± 0.40	6.90	4.23	0.31	5.44
1% TPr	2264 ± 13	56.0 ± 0.31	7.74	1.66	0.29	7.55
5% TPr	2194 ± 19	54.3 ± 0.24	13.30	10.17	2.53	8.19
1% TBu	2377 ± 15	57.9 ± 0.26	7.51	3.08	0.80	6.80
5% TBu	2329 ± 32	54.8 ± 0.38	11.48	10.09	2.64	4.80
1% THex	2169 ± 25	54.3 ± 0.33	10.92	3.66	1.30	10.21
5% THex	2454 ± 47	51.4 ± 0.30	20.76	15.18	4.87	13.30

3000 cm^{-1}) with this peak increasing. This indicated carbon-carbon cleavage due to the formation of UV-promoted radicals.[22] In the case of Mater-Bi, while aging was undertaken for this copolymer, this material is not suitable for a wet environment.

After accelerated aging the surfaces of all samples appeared whitened (bleached). This surface whitening was common across all plastics, but most evident for the tannin-modified plastics (Tables IV and V). Typically, higher loadings of tannin esters resulted in greater bleaching, with ΔL values of up to 32 measured after aging of tannin ester modified plastics. Plastics with highly dispersed, longer chain esters appeared to show greater surface bleaching. This was manifested in high ΔL values indicative of whitening, but also Δb values where significant yellowing of surfaces was evident.
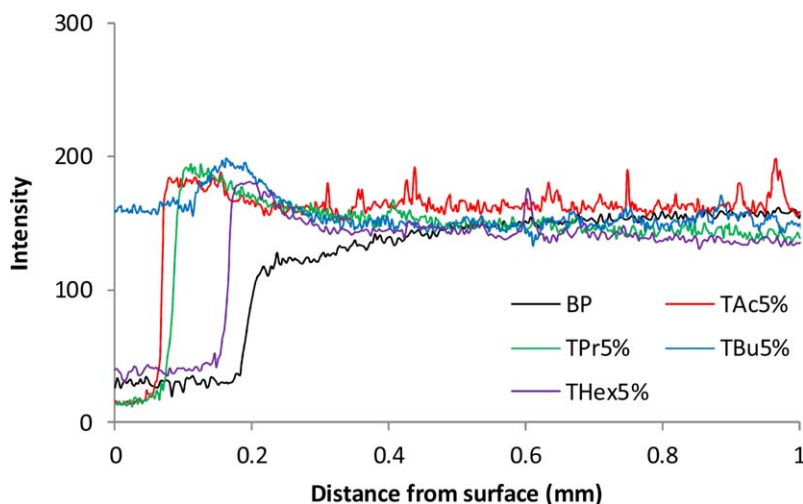
The extent of surface bleaching appeared variable across samples and this was further analyzed by microscopy (Figures 4 and 5). Sample cross-sections were profiled with light microscopy and the depth of bleaching determined by color intensity change. This revealed the bleached layer of samples to be highly variable compared to visual assessments noted above, being dependent on both the plastic and tannin ester. For both Biopol and Bionolle a decrease in the thickness of the bleached layer was observed with greater tannin ester chain length and loading. For Bionolle, the depth of the bleached layer was ca. 0.47 mm of the 3 mm plastic cross-sectional profile with 5% TAc, whereas with 5% THex surface bleaching was reduced by half (0.25 mm). Similar reductions in the depth of bleaching between 5% TAc (0.24 mm) and 5% THex (0.13 mm) were also achieved with Biopol. These findings suggest the tannin component in the plastic was likely inhibiting UV light penetration into the sample and sacrificially degrading. Condensed tannins are known to bleach and degrade on UV light exposure, with the rate of degradation dependant on the flavanyl substitution pattern.[23,24] The variations observed in surface bleaching likely arise from the differences achieved with tannin ester dissolution within each plastic, being consistent with fluorescence microscopy observations.

Mechanical properties of aged plastics show varying effects of each tannin ester. All Bionolle samples were found to have increased flexural modulus on aging (Table IV). Samples with 5% TPr, TBu, or THex only had an 8% increase in flexural modulus compared to 13% for pure Bionolle. Lower loadings of these esters had >10% increase in flexural modulus as did using TAc at either 1 or 5% loading. Sample flexural strength was also found to increase (6–9%) on aging, however the presence of long chain esters at 5% loading proved to give relatively lower strength increases. On aging Biopol samples, all samples show similar increases in flexural modulus. However, samples containing longer chain tannin esters still maintain relatively lower flexural modulus than pure Biopol (Table V). Biopol was found to have decreased flexural strength (97% retention of flexural strength) whereas those samples containing tannin esters maintain or increase in flexural strength (99–106% retention of flexural strength). Mater-Bi samples did not tolerate artificial aging with samples variously deforming and changing color. Flexural testing showed all aged Mater-Bi samples became significantly stiffer (>50%) with this being most pronounced for the 5% TAc sample (174%; Supporting Information, Table S7). It is possible loss of the polyvinyl alcohol plasticizers on exposure to water for extended periods likely contributed to these significant increases in sample stiffness. Flexural strength also increased for all Mater-Bi samples on aging.


Figure 4. Cross section color intensity profiling of Bionolle modified with 5% tannin acetate, propionate, butyrate, and hexanoate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Cross section color intensity profiling of Biopol modified with 5% tannin acetate, propionate, butyrate, and hexanoate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Using DSC analysis, aged plastics were assessed for any change in polymer properties. Bionolle samples show changes in the melt onset and an increase in the amorphous polymer content of samples on aging (Figure 6). Pure Bionolle also exhibited a decreased crystallization temperature after aging, that may be related to photodegradation via a Norrish type II pathway.[22] Adding THex appeared to mediate this change, with no differences in crystallization observed on UV exposure. In the case of Biopol, Figure 7 shows aged samples have a lower melt onset for both the pure polymer and that containing 5% THex. In the THex sample there was a small increase (*ca.* 4°C) in the crystallization temperature toward that of unmodified Biopol.

Biodegradation

Tannins are well-known antimicrobial agents and enzyme inhibitors,[14] therefore the impact of tannin presence on polymer bio-

degradation was assessed. Sample biodegradation was screened using a soil burial test to evaluate the potential impacts of tannin esters on each plastic. Analysis revealed the polyester samples lose minimal weight, whereas Mater-Bi samples have up to 25% weight losses (Supporting Information). Bionolle samples lose <1% weight after 60 days with little distinction between the tannin ester-modified samples. Scanning electron microscopy (SEM) revealed any Bionolle degradation to be localized, pin-hole degradation on sample surfaces (Figure 8). Similarly, Biopol samples also show <1% weight loss on soil exposure and minimal surface-only degradation (Supporting Information, Table S8 and Figures S13 and S14). In contrast to the polyesters, Mater-Bi samples were considerably more degraded losing some 17–27% weight after 60 days soil exposure with degradation also observed visually (Supporting Information, Figure S13). With Mater-Bi generally, the addition of tannin esters increased
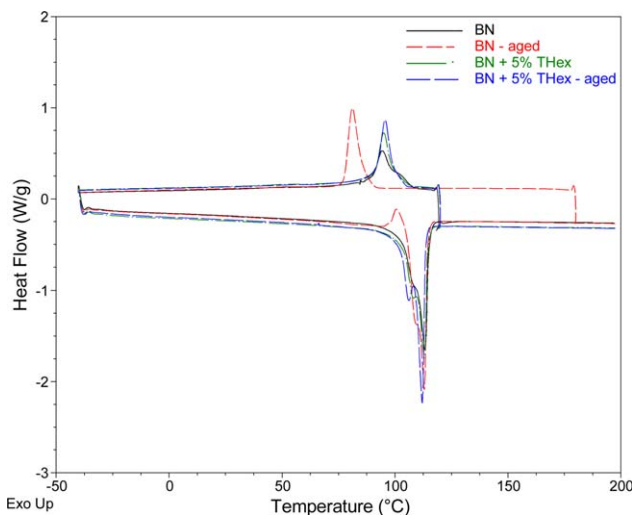
Figure 6. DSC thermograms of Bionolle (BN) and Bionolle + 5%THex before and after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
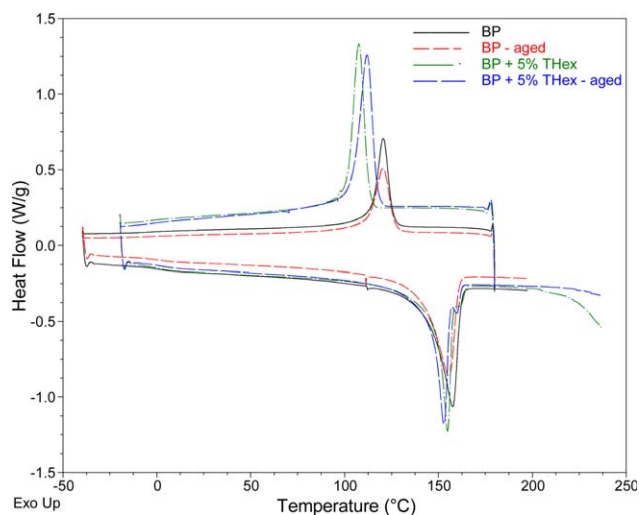
Figure 7. DSC thermograms of Biopol (BP) and Biopol + 5% THex before and after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
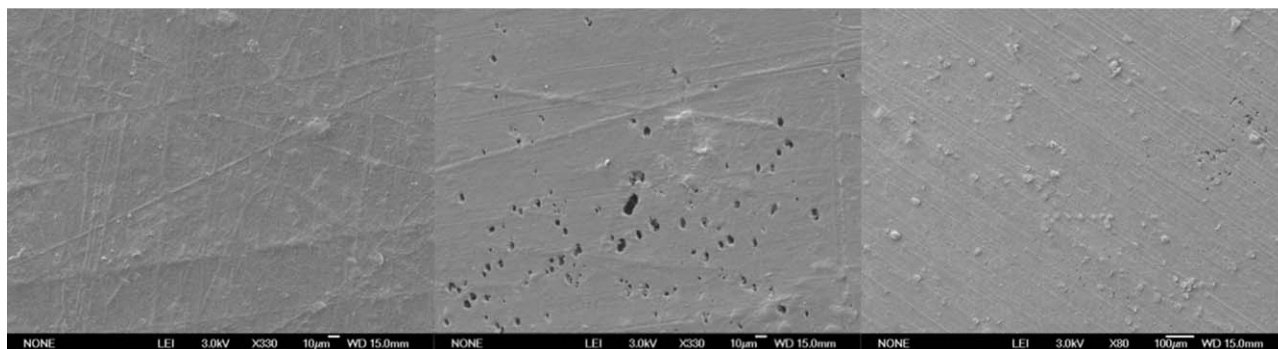
Figure 8. SEM images of sample surfaces of Bionolle samples before and after soil exposure (left = Bionolle, middle = Bionolle after soil exposure, and right = Bionolle + 5% TAc after soil exposure).

the level of degradation with little distinction between sample tannin contents or ester chain length.

In summary, an evaluation of plastic compatibility of each tannin ester by microscopy revealed the hexanoate chains of THex were more favored for dissolution in the polyesters compared to short acetate chains. While tannin esters were similarly compounded into each plastic and injection molded, it was the ester chain length which determined the extent of dissolution of each tannin ester. Unsurprisingly, the longer alkyl chains of THex aided the dissolution of THex in both Bionolle and Biopol (Figure 2). This suggests as an inherently compatible plastic additive, tannin-based materials will necessitate C6 or higher alkyl ester chain lengths for these matrices studied. However, the requirement for higher alkyl ester chain length would likely add cost and complexity to the synthesis of tannin esters as anhydrides are unlikely to be used. Regardless of compatibility, as additives to Bionolle the various tannin esters did not detrimentally impact mechanical properties at loadings up to 5% (w/w). In Biopol, only at 5% loading were the tannin esters observed to reduce both flexural and tensile properties. Evaluating polymer properties revealed tannin esters do not influence polyester melt or glass transition temperatures. However, in this study the Biopol crystallization temperature was decreased which has been similarly observed for THex-modified poly(lactic acid).[17] Tannin addition noticeably changed the color of the plastics, imparting a brown color, which would be undesirable in some applications. Apart from contributing color, tannin esters do not significantly affect plastic properties at typical plastic additive loadings (<5%).

In assessing tannin esters as potential functional plastic additives, artificially aging the polyesters led to polymer hydrolysis and photodegradation with the plastics becoming brittle and stiffer (Tables IV and V). Tannin esters acted to reduce UV-induced degradation resulting in smaller changes to mechanical properties of aged plastics. It is likely the tannin additives provide a stabilising role through inhibiting UV penetration into the plastic, with color analysis suggesting the tannin moiety itself was sacrificial and preferentially degrading. This manifested as surface bleaching where the depth of bleaching was determined by the quantity and dissolution of the tannin additive. TAc had relatively poor dissolution in the polyesters compared with the greater affinity of THex (Figure 2). This enhanced dissolution of THex led to increased UV inhibition, lessening the degradation. Furthermore, initial biodegradation testing in soil has revealed the tannin additives do not impact Mater-Bi degradation. However, any biodegradability efficacy in the polyester plastics was not resolved as both Bionolle and Biopol showed <1% weight losses after 60 days soil burial testing.

CONCLUSIONS

As functional additives to biodegradable plastics, the use of tannin esters at typical additive loadings (<5%) did not significantly impact the polymer and mechanical properties of polyester bioplastics. However, longer alkyl ester chain lengths were desirable for compatibility of the tannin additives with polyester plastics. The tannin esters were revealed to be sacrificial UV inhibitors, providing a stabilising role to reduce UV-induced degradation of the plastics on artificial aging, realising a potential functionality these plant extracts can impart to plastics.

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