

Supplementary material:

Section 1: Research in biodegradable and compostable materials since 1952

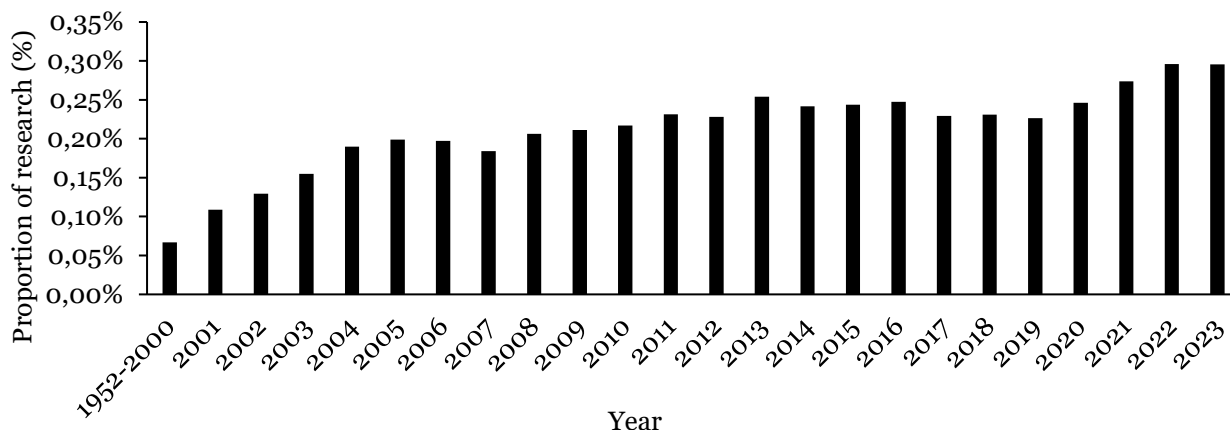


Figure: Proportion of papers published in the research area of compostable and biodegradable plastics extracted from the Engineering Village Navigator (August 2024, using request: ((Biodegradable OR compost) AND (polymer* OR plastic*)) over total number of paper published per year*

Section 2: Molecular weight distribution obtained from GPC results

UV is known to induce cross-linking. For example, using a UVC lamp with an emission peak at 254 nm, Otts et al. have shown that crosslinking could occur when exposing thiol–ene polyurethane dispersions. Cross-linking is typically associated with the formation of higher molecular weight compounds, which should appear in the molecular weight distribution given by GPC. However, as shown in Figure B.2, the molecular weight distribution for the discs does not exhibit such higher-molecular-weight compounds. To verify whether larger molecular weight species were filtered prior to GPC analysis of the UV-exposed material, a dissolution test was performed. A solution was prepared using 30 mg of UV-exposed DDD-treated powder dissolved in THF and chloroform, both known as effective solvents for PLA. The solution was filtered through a 0.4 μm filter, and the residual mass on the filter was measured after evaporation of remaining solvent. For both THF and chloroform, approximately 4 wt.% of the material remained on the filter. This figure is deemed to be low compared to the significant reduction observed in both number and weight average molecular weight. However, molecular

weight values presented in the main body of article may thus be slightly underestimated. As such, the reported values should only be considered as an indication of chain scission occurring under the effect of UV on the surface. This conclusion is strengthened by a greater molecular weight reduction observed when comparing the first 20 μm of the surface with the whole disc exposed on both sides, or the powder as shown in Table 4.3. Molecular weight values for UV-exposed samples should not be interpreted beyond their use as an indication of surface-level chain scission.

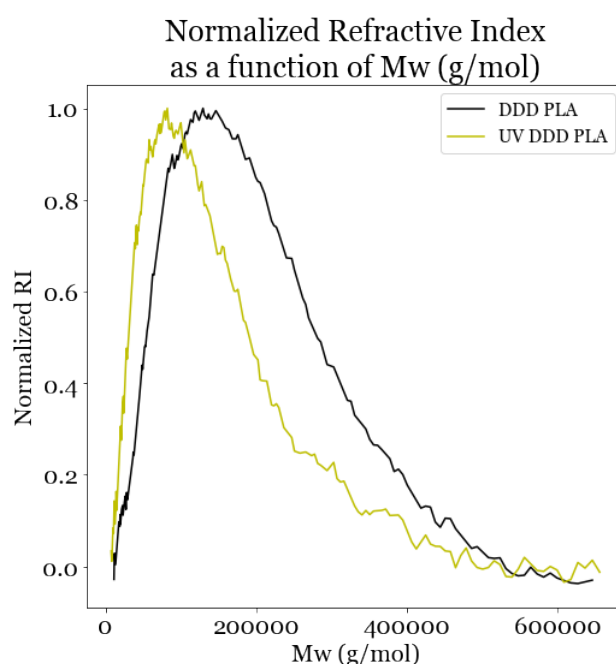


Figure: GPC distribution for DDD-treated and 2h UVC exposed DDD-treated PLA discs

Reference: Otts, D.B., E. Heidenreich, and M.W. Urban, Novel waterborne UV-crosslinkable thiol-ene polyurethane dispersions: Synthesis and film formation. Polymer, 2005. 46(19): p. 8162-8168.

Section 3: Summary of literature review in a table format

Table: Summary of existing literature as a table describing for each article the material, the type of exposure and treatment, the chemical changes and the techniques used to detect them as well as the chain scission mechanisms. Reference numbers are according to the article bibliography.

Article	Material	- Type of treatment, lamp, wavelengths, - Characterization technique	Bond change	Mechanism of degradation
Koo and Jang [31]	PLA	- UV Mercury lamp (184.9 nm and 253.7 nm)/ozone - FTIR, XPS, surface energy measurement	-ester bonds=O, C-O-C, and O-C-C were diminished. -carbonyl groups created and observed at 1724 cm ⁻¹ -decreased bending of C-H group more than the stretching band	α -cleavage of the ester linkage with partial hydrogen abstraction in PLA
Nie et al. [41]	PP	- UV Mercury lamp (184.9 nm and 253.7 nm)/ozone - AFM	formation of carbonyl and hydroxyl groups	Breakage of PP chains by atomic oxygen
Dodiuk et al. [42]	PC, PEI, carbon-reinforced PEEK, Al, Copper with and without fiberglass coating	- ArF excimer laser 193 nm - FTIR, XPS	PC: carbonate bonds get broken to form hydroxyls and carboxyls PEEK + Carbon fibers: carbonate bonds get broken to form hydroxyls and aldehydic groups (crosslinking increases and polarity decreases).	Carbonate bonds scission
Olewnik-Kruszkowska et al. [43]	PLA PLA+PCL PLA+Montmorillonite PLA+Montmorillonite+PCL	- UVC low-pressure mercury vapor lamp (TUV30W, Philips, Netherlands) mainly 253.7 nm - FTIR, NMR	-new peak stretching of alcohol and carboxylic acid groups (3290 cm ⁻¹) -increase in the number of -OH end groups -1753 cm ⁻¹ corresponding to stretching vibration of carbonyl groups - creation of acetic anhydride with C=O (1847 cm ⁻¹)	Chain scission with breaking of C(CH ₃)-O bonds/Norrish I/Norrish II

Qi Bao et al. [47]	PLA+PHB	- UV low-pressure mercury-vapor fluorescent lamps, Philips TL-D 18 W × 3, 370 nm - With seawater - With/without air bubbling - FTIR, degradation experiment, DSC	-Variation carbonyl bonds of the esters -OH groups ascribed to the end groups of PLA/PHB polymers located in the range of 3683–3033 cm⁻¹ almost disappeared after aging process	-Hydrolysis degradation effect of seawater and diffusion of water soluble molecules +UV: beta-scission leading to formation of anhydride-groups-based fragments
Bocchini et al. [44]	PLA PLA+nanocomposite (montmorillonite, sipiolite, silica)	- 4 medium-pressure mercury lamps with borosilicate envelope: wavelengths > 300 nm - In air in a SEPAP 12/24 unit at 60 °C - FTIR, WAXS	- formation of a band with a maximum at 1845 cm⁻¹ (Figure 5), formation of anhydride groups. - broader absorption band with a maximum at 3400 cm⁻¹ (hydroperoxides or alcohols)	- most probable one is beta-scission leading to anhydride creation
Janorkar [45]	PLA	- Photografting: 100-W mercury arc lamp (model 8261, Oriel) with a wavelength range of 232–500 nm (25 mW.cm⁻² at 365 nm) - Sterilization : UVC Mercury Lamp Philips TUVG30T8 30-W - GPC	No chemical analysis done	-photolysis reaction leading to breakage of the backbone C-O bond -formation of a hydroperoxide derivative and its subsequent degradation to compounds containing a carboxylic acid and diketone end groups.
Zaidi [46]	PLA PLA/C30B composite	- Sun exposure/ East Coast of Algeria from May to September 2009 - FTIR, TGA	- Neat PLA: new bands 920, 956 and 1654 cm⁻¹ (vinyl unsaturated groups), -1684 cm⁻¹ alpha-beta unsaturated ketones -3500 cm⁻¹ alcohols (free hydroxyl groups) -No production of anhydride - PLA/C30B: peak at 1844 cm⁻¹ production of anhydride	- Neat PLA: photodegradation of PLA proceed via the Norrish II mechanism at ester group and ethylidene group adjacent to the ester oxygen - PLA/C30B: radical abstraction of the tertiary hydrogen of PLA leading to peroxide formation and a b-scission after peroxide decomposition

Tertyshnaya [49]	PLA PLA-LDPE	- VL-6.LC Vilber Lourmat unit (wavelength 254 nm) - FTIR, DSC, EPR	- low-intensity peak at 1654 cm ⁻¹ , which is due to the vibrations of the vinyl group. C=C bond forms	PLA: Norrish II type PE-PLA: Pure LDPE and the samples with more than 50 wt % LDPE exhibited UV resistance
Sato et al. [48]	PLA	- Xenon excimer lamp at 172 nm, 2-3 mW.cm ⁻² , 3, 6, 10, 30, 60, and 100 min - FTIR, XPS, DSC, XRD, permeation properties	new peak at 1650 cm ⁻¹ -peak near 912 cm ⁻¹ slightly appeared for irradiated VUV (represents beta-crystalline structure) -1735 cm ⁻¹ carbonyl increased	Norrish II (chain cleavage and formation of C=C and hydroperoxide O-H)
Copinet et al. [50]	PLA	- UV (315nm)+RH((30%, 50% or 100%)+T°(30, 45 or 60°C) - FTIR, SEC	For 60 °C: - C–C stretch peak decreased (modification of crystallinity) 878 cm ⁻¹ -1095–1270 cm ⁻¹ (C–O stretching ester) and 1759.2 (C=O stretching ester) decreased and shift of these bands towards lower wavenumber in range 1050–1150 cm ⁻¹ corresponding to C–O stretching alcohol and 1730 cm ⁻¹ corresponding to C=O stretch of carboxyl acid	For 60°C: hydrolysis of ester linkage (increased by increasing T° and RH) + signal at 1650 cm ⁻¹ . -no effect of UV light, when PLA plastic films were stored at low RH and low T°
Ikada [36]	PLA PCL	- UV H-400P, Toshiba Litec, range 220 - 580 nm, main peak around 350 nm - FTIR	Increasing absorption at the carboxylic acid OH stretching vibration region (3290 cm ⁻¹) absorption at the C=C double bond region (990 cm ⁻¹) also increases with increasing irradiation time Change in crystallinity due to peak at 932 cm ⁻¹	Norrish II type

Section 4: FTIR intensity for all peaks of the different samples and the IR assignment according to Yuniarto et al. [55] and explanation in the article:

Peaks (cm ⁻¹)	Assignment	DDD intensity (a.u.)	30 min UV DDD intensity (a.u.)	1h UV DDD intensity (a.u.)	2h UV DDD intensity (a.u.)
695	C=O	0.0634	0.067	0.0666	0.0669
710		0.0541	0.0572	0.0566	0.0574
737		0.0487	0.0513	0.0509	0.0512
755	s C=O + δ CO	0.0869	0.0932	0.0916	0.09
872	ν C-COO	0.0733	0.0805	0.0808	0.0814
920	Indicator of crystalline phase	0.0267	0.0271	0.0283	0.0316
1044	C-CH ₃	0.247	0.2672	0.2611	0.2528
1086	C-O-C	0.4479	0.5068	0.4932	0.4734
1130	Ras CH ₃	0.288	0.343	0.3512	0.3445
1182	C-O	0.3856	0.4505	0.444	0.429
1268	CH+COC	0.0461	0.0456	0.0434	0.0459
1293	CH+COC	0.0328	0.0364	0.0375	0.0391
1305	CH+COC	0.0313	0.0327	0.0329	0.0345
1359	CH-CH ₃	0.0939	0.1037	0.1032	0.0999
1368	CH + CH ₃ (symmetric bending)	0.0723	0.0777	0.0776	0.0774
1381	CH	0.0733	0.0777	0.0767	0.0771
1386	CH	0.0729	0.0794	0.0794	0.0795
1456	CH ₃ (asymmetric bending)	0.0936	0.1021	0.1014	0.1001
1654	C=C (Norrish II)	None	None	None	None
1724	C=O (indicator of α -cleavage)	0.0402	0.0551	0.0677	0.0833
1748	C=O	0.3954	0.4563	0.4521	0.4313
1756	C=O	0.4287	0.5071	0.5078	0.475
1845	anhydride groups (radical oxidation and photolysis)	None	None	None	None
2850	C-H stretching vibrations	Not applicable due to humidity adsorption as mentioned in the article			
2921	C-H stretching vibrations				
2945	C-H symmetrical stretching vibrations belonging to CH ₃ groups				
2999	C-H asymmetrical stretching vibrations belonging to CH ₃ groups				

Section 5: DTG curves for DDD-treated and UV DDD-treated PLA discs

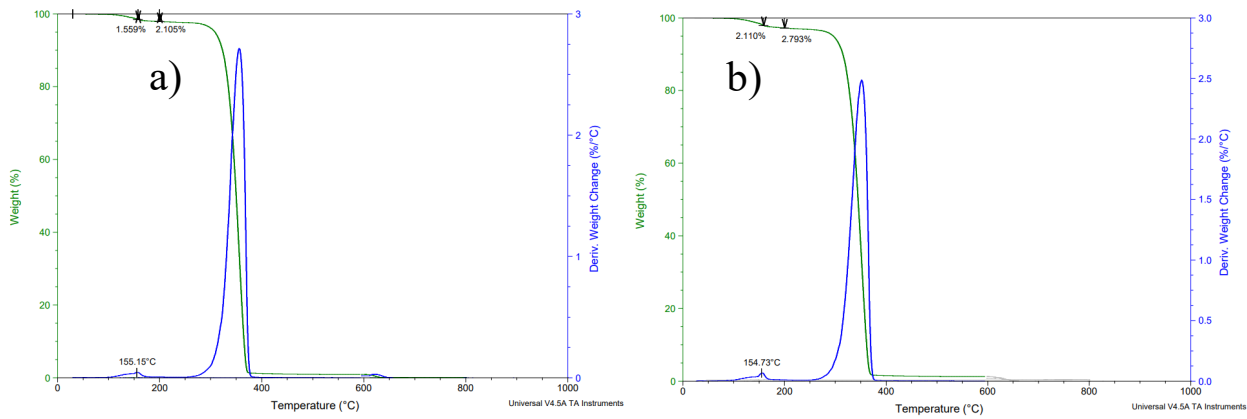


Figure: TGA and DTG curves for a) DDD-treated and b) 2h UVC exposed DDD-treated PLA

Section 6: XRD and DSC results on powders

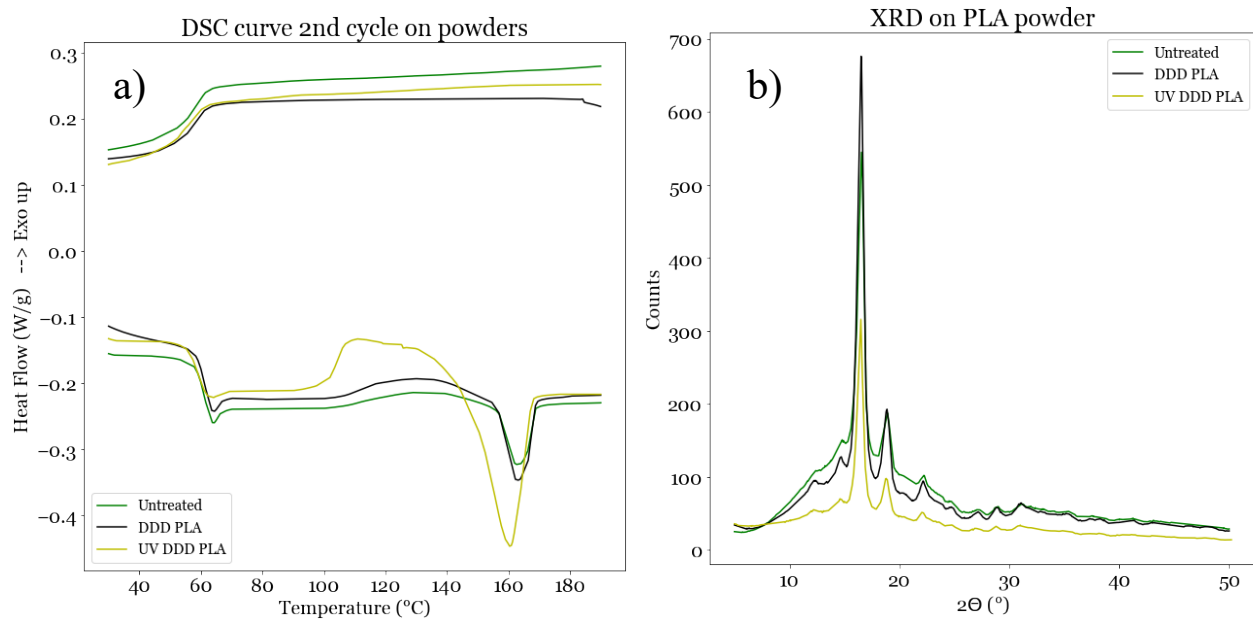


Figure: a) DSC and b) XRD curves for Untreated (neat), DDD-treated and 2h UVC exposed DDD-treated PLA powders

Table: Crystallinity rate χ_c obtained from DSC and XRD for Untreated (neat), DDD-treated and 2h UVC exposed DDD-treated PLA powders

Samples	Neat	DDD	UV DDD
χ_c DSC (%)	30.6 ($\pm$ 0.1)	29.9 ($\pm$ 0.8)	33.2 ($\pm$ 2.5)
χ_c XRD (%)	18.6 ($\pm$ 0.5)	31.5 ($\pm$ 2.1)	34.4 ($\pm$ 5.2)
Melting T° (DSC) (°C)	163.5 ($\pm$ 0.7)	165.4 ($\pm$ 0.1)	162.0 ($\pm$ 0.1)