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Long-Lasting Hydrophilicity Induced by Ultraviolet Light on Surface Modified Hydrophobic Polylactic Acid

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ABSTRACT

Surface treatments are used to tailor the wettability of compostable polymers for outdoor applications. However, imparting hydrophobicity can have direct and indirect consequences on the polymer's eventual degradation during use. In this research, a solvent-treated hydrophobic (water contact angle of $147.2^\circ \pm 0.6^\circ$) polylactic acid (PLA) substrate could be altered significantly to a wicking sample ($22.5^\circ \pm 3.1^\circ$) with a single 2-h ultraviolet-C (UVC) exposure. Wicking behavior remains consistent even 1 year post-exposure, implying a long-lasting hydrophilic change to the polymer surface. UVC irradiation induced chain scission near the surface, reducing considerably the molecular weight. Reduction in molecular weight impacts properties, including lower glass transition, melting, and degradation temperatures. However, no significant chemical composition changes could be detected with X-ray Photoelectron Spectroscopy (XPS). Infrared spectroscopy has shown a very minor oxidation with an increasing signal of the peak related to carbonyl groups at 1724 cm^{-1} from α -cleavage. Force-distance spectroscopy confirmed the increase in polarity of the UVC-exposed solvent-treated surfaces. The increase in wettability and more precisely surface polarity relates to an orientation of polar oxygen bonds towards the surface made possible by the chain scissions.

1 | Introduction

As of 2022, the world's plastic production had grown to over 400 million metric tons annually, and forecasts suggest that this number could soar to nearly 1 billion metric tons by 2050 [1, 2]. Currently, waste management systems do not have the capacity to handle this quantity of plastic wastes and the ever increasing fraction of mixed polymer products, which results in the landfilling or ocean-dumping of massive quantities of plastic wastes [3, 4]. Since the most used plastics are not biodegradable, they accumulate in the environment, not only in the form of visible products such as macroplastics but also as microplastics. These tiny particles have been found everywhere,

from alpine glaciers [5] to the invertebrates of Antarctica [6], posing significant threats to both fauna and flora [7–9]. To help address this ever-growing issue, biodegradable and compostable materials have been under intensive and increasing research over the last 20 years (Supporting Information Section 1). The idea of using biopolymers or bioplastics is not new. As a matter of fact, bio-based plastics were known well before petroleum-based plastics were discovered [10], but either their cost of production was high or their mechanical properties were insufficient when compared to other options available at an industrial scale. Now that mass production technologies are well-developed and plastic pollution has become a major concern due to the accumulation of plastic in

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the environment, compostable materials are gaining renewed interest as a potential solution to manage residual waste, in parallel with reduction efforts.

Among the conditions required for a plastic to be classified as compostable according to ASTM Standards D6400-21, at least 90% of the remaining polymeric material should reach a size smaller than 2.0 mm after 12 weeks of composting [11]. Compostable plastic bags and straws are examples of ASTM D6400-21 certified products. Polylactic acid (PLA) is a bio-based and, under appropriate conditions, biodegradable polymer that can meet this requirement. It is a polymer derived from renewable resources and biodegradable in industrial composts; the term bioplastic will subsequently be used in the text to describe synthetic polymers that are biobased and/or biodegradable [12]. Drumright et al. have demonstrated the complete degradation of PLA in a 60°C composting environment over a span of 40 days [13]. Concurrently, Karamanlioglu et al.'s review [14] confirms that PLA degradation in composting conditions at 50°C–60°C typically took 45–60 days. These same researchers specified, however, that the rate of PLA decomposition in compost depends on the PLA product geometry: 30 days for bottles, 20 days for sheets, and 40 days for fabrics. This can be explained by the fact that degradation is influenced by material parameters such as molecular weight, crystallinity, thermal behavior, surface/volume ratio, and by environmental factors such as humidity, temperature, and microorganism species present in the compost. This explains why some articles mentioned longer degradation times, sometimes above 6 months [15, 16]. Although industrially compostable polymers such as PLA hold promise for a better waste management system, some applications remain hard to reach for bioplastics.

PLA is generally produced from corn, sugar beet, maize, potato, and sugarcane. PLA has ester functional groups in its polymer-chain backbone, with hydroxyl and carboxyl groups at the end of the chain. These polar groups facilitate intermolecular interactions with water, namely through hydrogen bonding. Retained by the resulting hydrophilicity, water stagnating on a surface can promote bacterial and fungal growth. This might cause a durability issue for outdoor applications; it has been well documented since 1997 [17] that aerobic micro-organisms such as bacteria and fungi can degrade PLA [14, 16].

As such, the susceptibility of PLA towards biodegradation in humid conditions limits its usage in outdoor applications and brings about the requirement for controlled humidity during bulk storage in warehouses. Tuning the surface properties from wetting (hydrophilic) to non-wetting (hydrophobic) could optimize the behavior of PLA for different periods of its life cycle, that is, hydrophobic during use and storage to prevent degradation, hydrophilic at the end of life to promote microbial attachment and thus compostability. The benefits of hydrophobicity can vary significantly depending on the application. For instance, making agricultural nets hydrophobic can reduce humidity levels, which in turn inhibits fungal and bacterial growth. This reduction in microbial growth can lead to a decreased need for fungicide usage [18]. In the case of PLA, several surface engineering methods have been explored, such as photo-initiated chemical vapor deposition (PICVD) [18–20], inductively coupled plasma

with fluorocarbon-based coatings [21], electrospinning [22–24], and one-step spraying methods [25], to impart hydrophobic surface properties. Our research team developed a two-step solvent-induced recrystallization protocol, called dip-dip-dry (DDD), to modify the wettability of lab-scale and commercially available PLA for outdoor applications [18, 20, 26], imparting hydrophobicity. During usage, hydrophobicity is desirable but, as shown earlier, at the end of life, microorganism attachment to the surface depends on surface wettability [27]. Hydrophobicity can be conferred either through surface morphology (roughness) or chemical composition change (non-polar groups)—in both cases, this prevents water from reaching the material surface efficiently or even penetrating inside the material, thus hindering degradation. Thus, surface-treated compostable bioplastics are more likely to last longer in the environment and accumulate, since degradation is hindered by hydrophobicity.

As such, it is necessary to restore a bioplastic's hydrophilicity to allow it to become compostable anew after the intended use in outdoor settings. UV irradiation is a potential path to switch the wettability of a material by photodegradation causing oxidation [28]. Under exposure to radiation, chain scission occurs reducing the molecular weight and leading to formation of oxidized end groups that are polar, which contributes to increasing the wettability. For example, exposing glass substrates to Hg discharge lamps (emitting in the 200–300 nm UVC range) has been shown to increase surface wettability [29]. Hyun Jeong Jeon et al. [30] reported that water contact angle decreased moderately from 84.5° to 73.9° on PLA following a 24 h exposure to UVC lamps emitting at 185 and 254 nm, with irradiance at 6.41×10^{-3} and 3.22 mW/cm^2 , respectively for each wavelength. Similarly, via an energetic dose of 63.6 J/cm^2 , Koo and Jang [31] found an increase in PLA hydrophilicity with the water contact angle decreasing from 61.4° to 39.2° after UVC irradiation. Herein, this research demonstrates that, a solvent-treated hydrophobic PLA substrate can be reverted well below its original wettability, all the way down to capillary wicking behavior, with a very similar UV energetic dose and short treatment time (2 h). The wettability change was tested for 1 year, implying durable change. The reason for this significant change compared to literature is determined by studying surface chemistry and morphology.

2 | Experimental

2.1 | Materials

Commercial grade PLA 6202D with an average molecular weight of 140 kDa and a 2 wt% D-isomer content (NatureWorks LLC, USA) was pressed to form amorphous PLA discs as described in our group's earlier publications [20, 32]. Prior to pressing, PLA pellets were dried over 24 h at 80°C under vacuum (19–22 mmHg). PLA pellets were then put in a mold between two PTFE sheets and sandwiched between metal plates. The whole structure was then pressed in a heating press (model 3912, Carver Inc., US) set at 180°C under air atmosphere. During the first 4 min, no pressure was exerted until the desired plate temperature was reached. Then, pressure was increased to 4.45–5.34 MPa and held for 2 min. Finally, the pressure was released, and the samples were quenched in cold water. Discs were then trimmed, washed, and finally dried in the fume hood for

at least 24 h. The same protocol was used for microtomed samples, where PLA rods were pressed instead of PLA discs.

Alternatively, these same PLA pellets were ground with a Daigler-WAR700S mill after dipping in liquid nitrogen to make PLA powder. Acetone (ACS grade 99.5% anhydrous) and diiodomethane (Thermo Scientific Chemicals, 99%, stabilized) were purchased from Fisher Scientific, and deionized water (DIW) with a conductivity of $1 \mu\text{S}\cdot\text{cm}^{-1}$ was provided by the university's infrastructures.

2.2 | DDD-Treating Discs

DDD is a two-step solvent-induced recrystallization protocol [20]. In a solvent bath (acetone), polymer chains at the surface of the amorphous PLA discs are slightly dissolved over 10 min. Mobile chains remaining on the surface will shrivel when dipped in a coagulant bath (DIW) for an additional 10 min. During this phase, recrystallization occurs as the chains contract due to water acting as a nonsolvent for PLA. This causes the formation of a water-repellent microstructured surface. The DDD-treated samples are then dried for 48 h in the fume hood.

2.3 | Exposure to UV

PLA discs (diameter 2.5 cm, thickness 1.0 mm) were placed 3.5 cm below a UVC low-pressure Hg discharge lamp (Cole-Parmer, VL-230.G) with a primary emission peak at 253.7 nm and a secondary emission peak at 184.9 nm. The lamp was preheated for 30 min prior to sample treatment to ensure that irradiance was constant during the experiment time (less than 1% change over 30 min). Average irradiance was $8.7 \text{ mW}/\text{cm}^2$, measured by an ILT1700 Research Radiometer (International Light Technologies). Exposure times varied from 30 min ($15.7 \text{ J}/\text{cm}^2$) to 2 h ($62.6 \text{ J}/\text{cm}^2$). For all UVC exposure times considered, no ozone could be measured in the closed environment containing the UVC lamp (box volume 1.6 m long, 0.5 m wide, and 0.5 m height) using a Draeger 8000 ozone detector with a 0.01 ppm resolution. As such, the presence of the secondary emission peak and ozone should not be considered (the glass material of the lamp is likely filtering out the 184.9 nm radiation capable of O_3 synthesis).

2.4 | Characterization

Wettability change was assessed using the sessile drop method with an OCA-20 optical contact angle measuring and contour analysis system from Dataphysics. Static contact angles were measured 2 s after laying a $5 \mu\text{L}$ water droplet or $1 \mu\text{L}$ diiodomethane droplet on the surface (3 measurements per disc, conducted in triplicate). In the case of UV-exposed DDD-treated discs, the time needed for droplet disappearance on the surface via adsorption and evaporation was also recorded.

Morphology was studied using scanning electron microscopy (SEM). A Hitachi Model TM3030Plus Tabletop microscope was used for low magnification imaging with beam voltage at 5 kV, 5.0 mm working distance, combined with a sputter coater to

apply a conductive 25 nm chromium coating to PLA discs (model SC502, Fisons Instruments, UK, 30 s, 40 mm sample target distance, 16 W). A Low Vacuum Scanning Electron Microscopy (LVSEM), Thermo Fischer Scientific Quattro S, ETD detector, with beam voltage at 2 kV, current at 5.6 pA, working distance 5.6 mm, combined with the same sputter coater model but applying a thin 5 nm conductive gold coating on the PLA discs, was used to observe fine morphology at higher magnification.

Chemical composition was assessed using Fourier Transform Infrared (FTIR) spectroscopy (Spectrum 65, Perkin Elmer, operated in attenuated total reflectance (ATR) mode with a ZnSe crystal, analysis range of $4000\text{--}600 \text{ cm}^{-1}$, 64 scans, 0.5 resolution). Near-surface analysis was also conducted using X-ray Photoelectron Spectroscopy (XPS) with a VG ESCALAB 3 MKII apparatus. Monochromatic Al $K\alpha$ radiation with an energy of 1486.68 eV was used. Residual gas pressure was below 10^{-7} Pa. The survey scan (pass energy 150 eV) was used to confirm atomic composition and high-resolution spectra (pass energy 20 eV) were used to quantify the distribution of chemical bonds. Smart background subtraction was applied using the Advantage software (version 6.6.0) to process the signal. Peak fitting and bond percentage quantification was done with the peak constraint method, allowing 0.1 eV and 0.1% variation in the peak's full width half maximum and Lorentzian/Gaussian (L/G) mix ratio (%) respectively for peaks of same spectrum. Atomic force microscopy (AFM) was used to characterize adhesion force using an NTEGRA II (NT-MDT Spectrum Instruments) laid on an Accurion Halcyonics-i4 table to isolate the system from vibration. Relative humidity was maintained at 30%. Parameters for studying topology in tapping mode were as follows: 500 lines on a $10 \mu\text{m} \times 10 \mu\text{m}$ scan area at a scan rate of $2 \mu\text{m}/\text{s}$ with silicon cantilevers (NSG10, also from NT-MDT Spectrum Instruments). For force-distance curves in contact mode, CSG01 silicon cantilevers (NT-MDT Spectrum Instruments) were used and 10 measurements per sample were conducted on 4 different discs to ensure representative results.

Thermal behavior was assessed using differential scanning calorimetry (DSC) with a DSC Q2000 (TA Instruments). The cooling and heating rates were fixed at $10^\circ\text{C}/\text{min}$ from 25°C to 200°C (2 heating/cooling cycles, 5 mg sample). Thermogravimetric analysis (TGA) was conducted up to 800°C with a Q500 TGA (heating rate at $10^\circ\text{C}/\text{min}$, 15 mg sample). Thinner discs (diameter 3.2 cm, thickness 0.5 mm), prepared with same pressing protocol, were used for DSC and TGA in order to minimize the effect of the bulk on the results. For both TGA and DSC, tests were performed under nitrogen atmosphere. Crystallinity changes were further measured using X-ray diffraction (XRD) with a D8 ADVANCE (Bruker), using a copper source ($K_\alpha = 1.54060 \text{ \AA}$), operated at 40 kV and 40 mA, in angle increments of 0.05° , from 5° to 50° . For XRD, larger discs (diameter 3.8 cm, thickness 2.6 mm) were produced to fit the measurement range. Crystallinity was calculated with the integral method, comparing the area under the baseline for the amorphous percentage and the area between the baseline and the curve for the crystallinity. Gel permeation chromatography (GPC) was used to measure the effects of treatment on polymer chain length with an Agilent PL-GPC 120 when assessing powders or microtomed slices, and with an Agilent HPLC 1260 Infinity II for discs. A Shodex column KF-804 and a refractive index (RI) detector were used. PLA samples were

dissolved in THF at a concentration of 3 mg/mL and polystyrene (PS) standards were used for calibration. Finally, PLA rods (length 13 mm, width 5 mm, thickness 0.3 mm) were cut using a microtome with a Leica RM2165 equipped with an LN21 cooling system to observe morphology and mechanism of rupture a few microns below surface. All experiments were conducted in triplicate except TGA and GPC that were conducted in duplicate.

3 | Results and Discussion

3.1 | Wettability

PLA samples treated by the DDD solvent-based process yielded hydrophobic substrates, as expected; the resulting contact angle of $147.2^\circ \pm 0.6^\circ$ corresponds to the 0 min UVC exposure data in Table 1. The water contact angle on the untreated PLA is approximately 95° . Upon UVC exposure, a switch in wettability was observed: the contact angle dropped from 147.2° to 22.5° after a 2 h exposure. These discs behave as capillary wicking substrates. The water droplet spreading on the surface and its subsequent infiltration are shown in Supporting Information (Video S1a). Two phases are generally observed when studying the wettability of treated substrates using the sessile drop method: (1) the drop attempts to stabilize on the surface; (2) the droplet's contact points no longer move, but the droplet continues spreading as in the capillary wicking regime until it disappears by evaporation and adsorption into the surface [33]. The time needed to reach the contact angle is identified as the stabilization time in Table 1 and is recorded along with the time needed for droplet disappearance by evaporation or both adsorption and evaporation as a function of UVC exposure time. Wettability experiments were conducted on the same day at a constant room temperature of 24.0°C and 10% ambient relative humidity (RH). For 30 min UVC exposure, very little change seems to have occurred. However, upon increasing exposure (45 min and 1 h), a greater decrease to a hydrophilic state occurred and a large time for droplet stabilization is observed. Finally, increasing up to 2 h greatly increased the wicking behavior, reducing droplet stabilization and disappearance time.

The surface energy of the 0 min (unexposed), 30, 60, and 120 min exposure samples was assessed using Wu's harmonic mean method (in the SCA 20 software) [34]. Water was retained as the polar liquid for this test, with a dispersive energy of 22.60 mN/m and a polar component of 50.20 mN/m. The high-dispersive component liquid used for the calculations was diiodomethane, with a dispersive energy of 49.00 mN/m and a polar component of 1.80 mN/m. As illustrated in Videos S2, the

adsorption dynamics of diiodomethane in DDD-treated PLA are rapid for all exposure times tested. Furthermore, diiodomethane fully wets all DDD-treated samples. Consequently, the diiodomethane contact angle on UVC-exposed and unexposed DDD surfaces was set to 0 for all samples studied. From the surface energy measurement data reported in Table 2, the dispersive component of the UVC-exposed discs remains unaffected, whereas there is a significant increase in the polar component of surface energy after 1 and 2 h of UVC exposure.

In agreement with previous literature, UV exposure can mildly affect the wettability of untreated PLA. However, UVC exposure (2 h) on DDD-treated PLA induces a complete switch in wettability. To further explore this, similar UVC exposure was performed on untreated (neat) PLA discs. As shown in Figure 1, no significant change in contact angle was observed between UVC-exposed and unexposed neat PLA discs. Water contact angle (WCA) measurements were repeated over time to assess potential long-term effects. Over a period of 613 days (approx. 1 year and 8 months), no differences were noted between UVC-exposed and unexposed samples. The slight variation observed over time can be attributed to differences in relative humidity, which has been shown to influence WCA measurements and introduce experimental error [35].

These findings lead to two important conclusions. First, when comparing untreated and DDD-treated UV-exposed samples, it is evident that the roughness and porosity introduced by the DDD treatment significantly amplify the effects of UVC on PLA wettability, as forecast by wettability models such as the Wenzel model, showing that surface behavior regarding wettability becomes enhanced when the surface is rough [33]. When rough, hydrophilic surfaces become more hydrophilic; hydrophobic

TABLE 2 | Surface energy (SE) table of DDD-treated PLA as a function of UVC exposure time (0, 30, 60, and 120 min).

Exposure time	0 min	30 min	60 min	120 min
Total SE (mN/m)	44.0 ± 0.1	43.8 ± 0.1	67.7 ± 4.4	78.9 ± 0.9
Dispersive component (mN/m)	44.0 ± 0.1	43.8 ± 0.1	46.1 ± 0.1	45.9 ± 0.1
Polar component (mN/m)	0	0	21.6 ± 4.5	32.4 ± 0.4

TABLE 1 | Water contact angle (WCA), and dynamics of adsorption and evaporation of 5 μL droplet on DDD-treated PLA for different times of UVC exposure (0, 30, 60, and 120 min).

UVC exposure time	0 min	30 min	45 min	60 min	120 min
Average WCA ($^\circ$)	147.2 ± 0.6	140.1 ± 3.0	$104.4^a \pm 22.1$	$46.6^a \pm 9.8$	$22.5^a \pm 3.1$
Time for droplet stabilization (s)	≤ 2	≤ 2	1147 ± 351	642 ± 91	25 ± 5
Time for droplet disappearance (s)	2506 ± 126	2392 ± 41	2588 ± 90	942 ± 30	93 ± 3

Note: 0 min corresponds to unexposed DDD-treated PLA.

^aStabilizing angles.

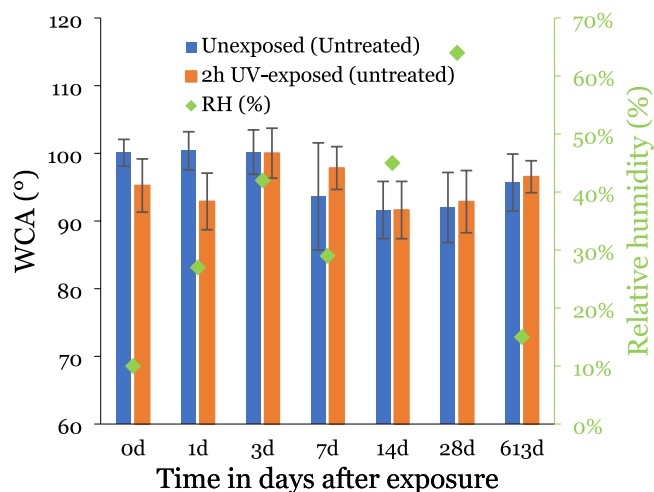


FIGURE 1 | Water contact angles of 2h UVC-exposed and unexposed untreated discs (neat PLA) as a function of time after the UVC exposure. Day 0 being the day of exposure to UVC. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

surfaces become more hydrophobic. Second, when comparing UVC-exposed and unexposed DDD-treated samples, it becomes clear that UVC exposure interacts with or modifies the DDD-treated surface. After 2h of UVC exposure, DDD-treated discs exhibit capillary wicking behavior, a phenomenon that persists even 1 year after UV exposure (see Video S1b). This underscores a long-lasting or potentially permanent change in the surface morphology or chemistry.

This permanent change was confirmed by GPC, showing that UVC exposure on DDD-treated PLA discs and powders caused chain scission: the number and weight average molecular weights of the polymer were significantly reduced (Table 3). This is consistent with the UV effect on molecular weight noted in the literature [36–38]. However, the potential effects of cross-linking must be considered and are discussed in detail in Supporting Information Section 2.

UVC radiation has sufficient energy to break bonds and cause chain scission (at 253.7 nm, the photons carry 4.88 eV, sufficient to break C–C and C–O bonds, at 3.7 and 3.5–4.3 eV, respectively [39]). This mechanism is often shown in the literature to be associated with surface oxidation.

3.2 | Surface Chemistry

UV interactions with polymers have been well documented [31, 36, 40–50]. In the case of PLA, the mechanisms identified in the literature are presented in Figure 2. Norrish type II reactions are the most common pathway for PLA under UV exposure, namely at wavelengths below 300 nm [51], such as excimer lasers (172 nm) [48], low-pressure Hg discharge lamps (253.7 and 185 nm) [43, 49], and other lamps emitting some UVC radiation alongside visible radiation [36]. UVB radiation 280–315 nm range in the UV band has also led to Norrish type II reactions under direct sun exposure of PLA [46]. At wavelengths above 300 nm, β -scission leading to anhydride group formation is generally reported [44, 47]. Nevertheless, the degradation

TABLE 3 | Number and weight average molecular weight (respectively m_n and m_w) and polydispersity index (PDI) obtained by GPC of untreated, DDD-treated and UV DDD-treated PLA powders, DDD-treated and UV DDD-treated PLA discs, average of two repetitions. Molecular weight distributions are presented in Supporting Information Section 2.

	M_n (g/mol)	M_w (g/mol)	PDI
Untreated PLA powder	7.30×10^4	1.27×10^5	1.7
DDD-treated PLA powder	6.96×10^4	1.29×10^5	1.8
UV DDD-treated PLA powder	2.54×10^4	6.89×10^4	2.7
Untreated PLA disc	8.69×10^4	1.26×10^5	1.5
DDD-treated PLA disc	8.92×10^4	1.41×10^5	1.6
UV DDD-treated PLA disc	4.18×10^4	8.52×10^4	2.0

mechanisms based on wavelength can change depending on conditions: Zaidi et al. [46] showed that, when adding organo-clay (organically modified clay obtained by replacing natural cations of the clay mineral with cationic organic surfactants) to PLA, the degradation mechanism shifted from Norrish type II to radical abstraction of the tertiary hydrogen of PLA, leading to peroxide formation followed by β -scission. Furthermore, in the case of UVC low-pressure Hg discharge lamps (primary emission at 253.7 nm), α -cleavage of the ester linkage was the degradation mechanism reported when combined with ozone [31].

All degradation mechanisms mentioned above have been identified in most cases using FTIR. A summary of existing literature in a table has been proposed in Supporting Information Section 3. In the present case, no change that could explain this difference in wettability is observed using FTIR analysis (Figure 3a). Specifically, no peaks corresponding to anhydride from β -scission (near 1845 – 1847 cm^{-1}) [43, 44], or no C=C bonds of Norrish type II reactions (near 1654 cm^{-1}) [46, 49] are observed. As shown by Smith [52], the alkene band in the range 1600 – 1680 cm^{-1} is not totally reliable to detect the presence of alkene, as these vibrations can be nonexistent depending on substituents and arrangement around the double bond. To confirm the absence of alkene groups, the C–H stretching vibration bands have to be investigated. As there was no appearance of a new C–H stretching peak between 3100 and 3000 cm^{-1} , Norrish type II reactions can be excluded.

The only change of note is the appearance of a sharp drop in the C–H asymmetrical and symmetrical (2850 and 2921 cm^{-1}) stretching vibrations belonging to CH_2 groups [53]. Less significant changes are observed regarding C–H symmetrical (2945 cm^{-1}) and asymmetrical (2999 cm^{-1}) stretching vibrations belonging to CH_3 groups [31, 43]. This change has been found to only be due to humidity absorption of PLA when comparing these peaks for samples with and without prior vacuum drying before FTIR. There is similarly no change in the 3200 – 3500 cm^{-1}

region, where peaks originating from —OH vibrations forming both inter- and intrachain hydrogen bonds would appear [54] via moisture adsorption. FTIR analyses conducted on samples that have not been dried under vacuum present as a very minor oxidation evidenced by the carbonyl peak. Indeed, when not drying

the polymer, the presence of residual water can affect the intensity and shape of the carbonyl bonds peaks via H bonding. As such, the carbonyl peak is slightly larger for all the UV-exposed samples compared to the unexposed sample (Figure 3b). This matches Koo et al.'s findings, where UV/ozone treatment led to

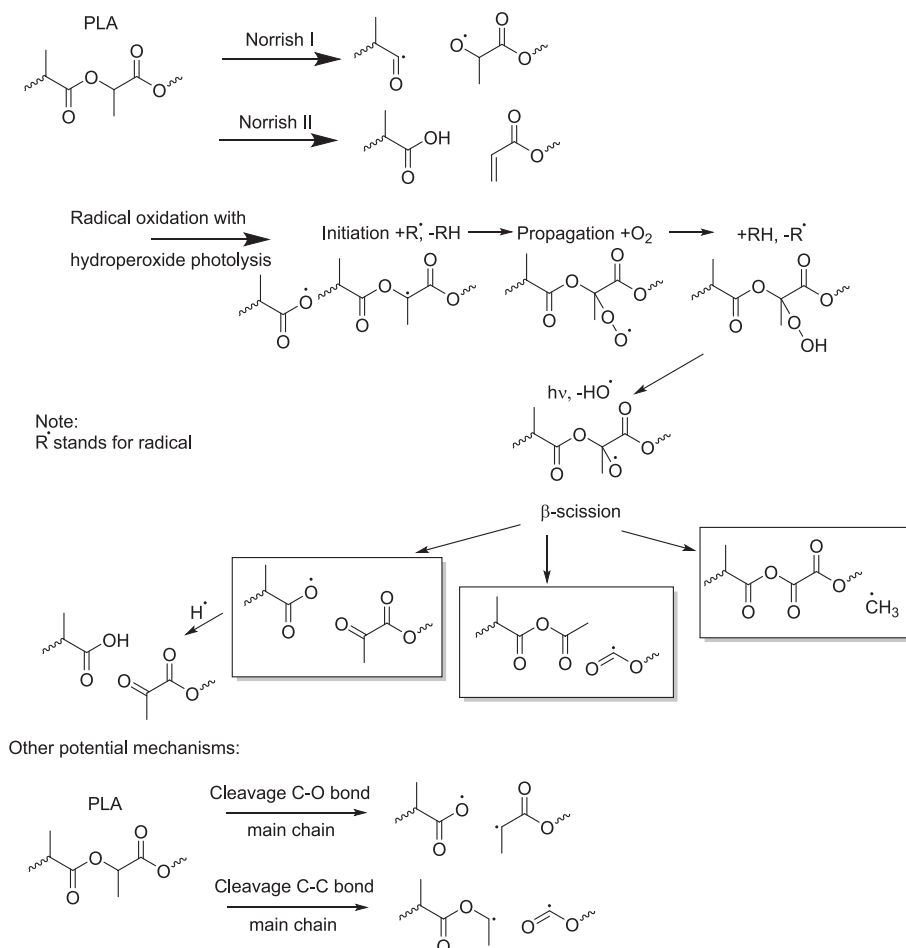


FIGURE 2 | Schema of PLA degradation mechanisms commonly described in the literature resulting from UV exposure.

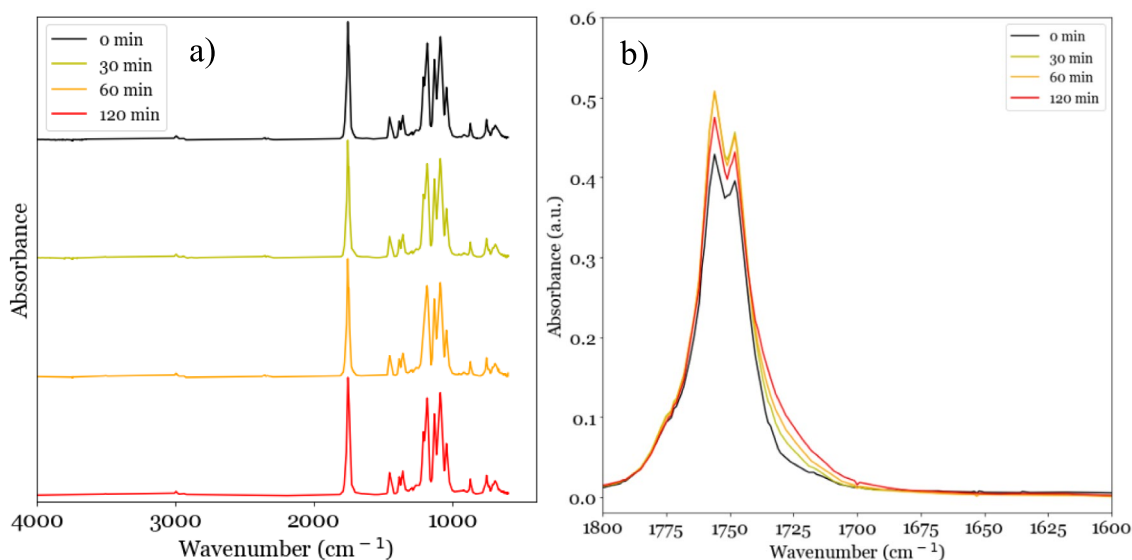


FIGURE 3 | FTIR spectra of DDD-treated PLA discs for different UVC exposure time (0, 30, 60, and 120 min). 0 min exposure referring to unexposed DDD-treated PLA for (a) full 4000–600 cm⁻¹ range and (b) specific 1800–1600 cm⁻¹ range. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.57009)]

the appearance of a new carbonyl group peak at 1724 cm^{-1} when subtracting the two spectra. The identified mechanism was α -cleavage of the ester linkage.

For more complete information regarding FTIR spectra, all the intensity values are given in Supporting Information Section 4. The assignment of the signal to the bonds can be found in the conference proceeding of Yuniarto et al. [55].

Stacking curves together, the only peak that moderately increased as a function of UVC exposure corresponds to carbonyl groups (1724 cm^{-1}) [31, 48], which could be generated through α -cleavage. Further quantification of the different atoms and bonds are needed, with a more surface-sensitive technique. XPS

is better suited at characterizing surface bonds, as it is generally accepted that around 95% of the electrons reaching the detector will come from the first 10 nm of the substrate [56], which makes it a more surface sensitive technique than ATR-FTIR [57], whose depth of penetration is in the order of $1\text{ }\mu\text{m}$ [58]. XPS is thus effective to quantify the increase of oxygen content on a surface due to oxidation. This can be directly correlated with increases in the polar component and wettability changes as shown by Li et al. [59]. They employed O_2 plasma to transform a superhydrophobic coating laid on various surfaces into a hydrophilic, water spreading surface, directly correlated with an increase in the surface oxygen content. Along similar lines, Ren et al. showed a relative increase in oxygen content using XPS on plasma treated PLA to improve wettability and change contact angle from 120°

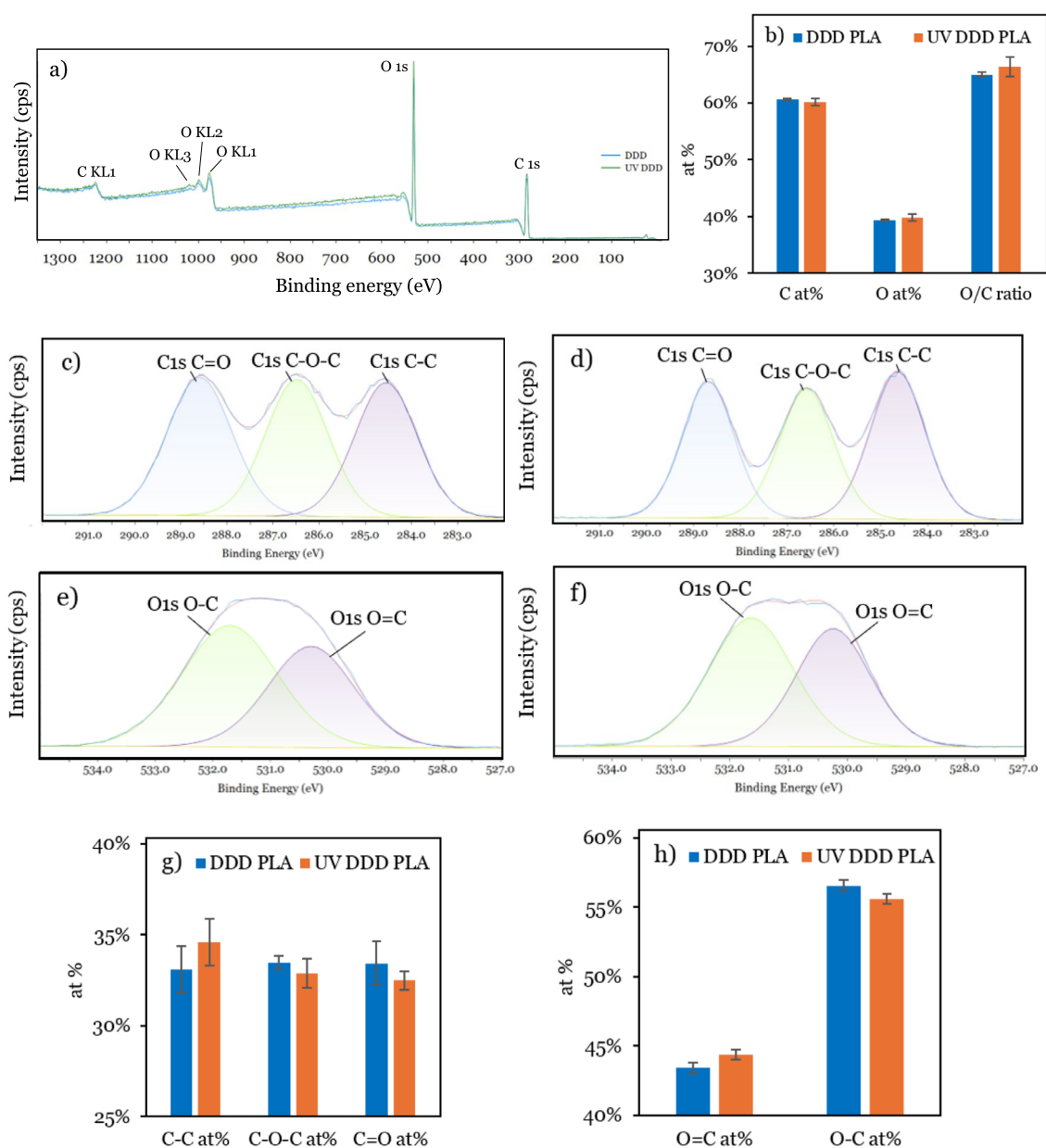


FIGURE 4 | XPS results for comparison of unexposed and UVC-exposed DDD treated discs. (a) XPS survey and (b) quantification of the chemical composition based on surveys. C1s high-resolution spectrum peak fitting on (c) unexposed and (d) UVC-exposed DDD treated discs. O1s high-resolution spectrum peak fitting on (e) unexposed and (f) UVC-exposed DDD treated discs. Quantification of the chemical bonds based on C1s and O1s spectra are presented in (g) and (h). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

to a wicking surface in less than 100s exposure [60]. XPS analysis showed no significant changes in the carbon and oxygen content between unexposed and UVC exposed PLA substrates (Figure 4a,b), nor in the chemical bonds when analyzing the C1s spectra (Figure 4c,d,g).

The only two changes of note are, first when analyzing the O1s spectra (Figure 4e,f), ester groups are hydrolyzed, yielding a carboxylic function impacting the O1s profile. As such, there are proportionally less C—O bonds after UV exposure than there were initially, compared to C=O bonds (Figure 4h). This aligns well with cleavage of the C—O bonds, versus cleavage of the C—C bonds denoted earlier in FTIR. Cleavage of the C—O bonds would lead to a decrease in C—O bonds to proportionally more C—C bonds in the C1s spectra and more O=C bonds when comparing with O—C. The other main significant change is that peaks of the UVC exposed samples are much more defined (Figure 4c,d), which relates to a better ordered surface and a potential change in either surface morphology or crystallinity (Section 3.3), or in the polymer chain's capacity to rearrange due to lower molecular weight which has consequences on thermal properties (Section 3.4).

As such, XPS did not confirm any oxidation and did not support the minor C—C cleavage deduced by FTIR spectroscopy. It shows the minor existence of C—O cleavage. As such, both FTIR and XPS results confirm the fact that the 253.7nm has sufficient energy to break some C—C and C—O bonds. Nevertheless, in both cases, changes were minor, and the main conclusion is that XPS did not show a significant difference in composition after 2h UVC exposure. This means that no significant change in surface chemistry alone can explain the wettability switch occurring with UVC exposure. As exposure to UVC has more effect on recrystallized textured surfaces rather than the untreated PLA, crystallinity and surface morphology of the DDD-treated samples were investigated.

3.3 | Surface Morphology and Crystallinity

As can be seen on SEM micrographs (Figure 5), there are no significant differences in the fine and coarse morphology between unexposed and UVC-exposed samples that could explain the wettability change.

As shown in Figure 6 and Table 4, no significant changes in the crystal types and degree of crystallinity χ_c are observed using XRD. Both 2h UVC exposed and unexposed DDD-treated samples are composed of α -crystals.

As such, one necessarily expects to see changes in the polymer chain's capacity to rearrange at a very small scale with a significant impact on properties such as wettability.

3.4 | Thermal Properties

TGA results showed that for DDD-treated samples and 2h UVC DDD-treated samples, weight change from solvent evaporation appeared at lower temperatures compared to untreated PLA (Figure 7). Following the derivative weight change

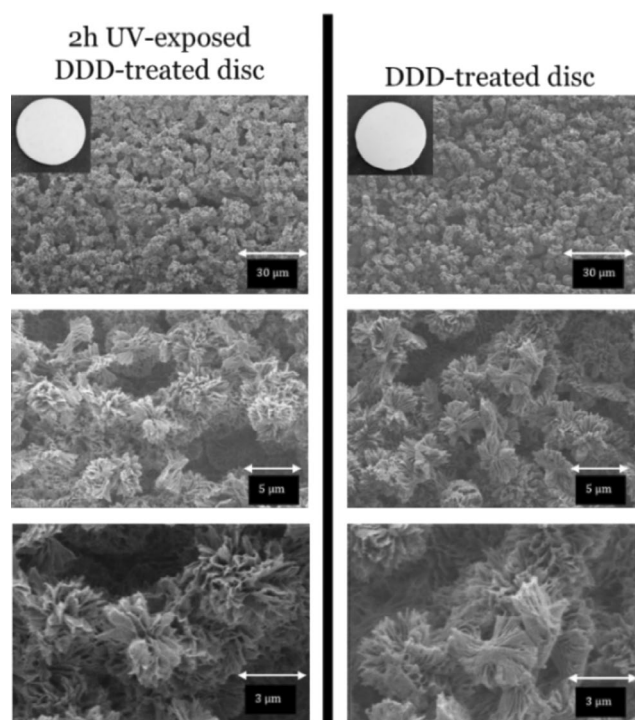


FIGURE 5 | LVSEM pictures of 2h UVC-exposed (left) and unexposed (right) DDD-treated discs.

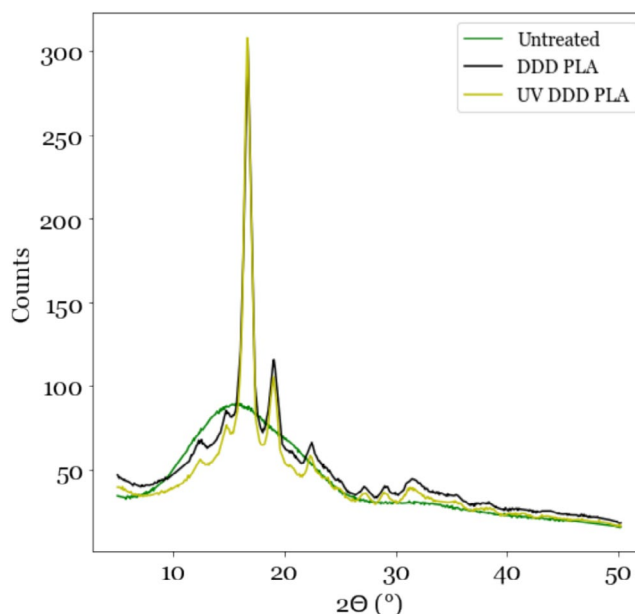


FIGURE 6 | XRD on Untreated, DDD-treated, and 2h UVC-exposed DDD-treated PLA discs. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.57009)]

TABLE 4 | Crystallinity values (obtained by XRD) of DDD-treated and 2UVC-exposed DDD-treated PLA based on the integration method.

Samples	Untreated PLA	DDD PLA	UV DDD PLA
χ_c (%)	7.2 (± 1.2)	34.6 (± 0.9)	34.7 (± 0.6)

(DTG), a degradation peak near 155°C for both unexposed and UV-exposed samples can be seen in Supporting Information Section 5.

As shown in previous works developing the DDD technique [20], there is residual solvent trapped in the material even after drying in vacuum for extended periods. After 48 h, Knoch et al. showed that around 1.5% of residual solvent was trapped in the material—this corresponds to the peak seen here at 155°C, also corresponding to a roughly 1.5% weight change. In the case of UV-exposed samples, a slightly larger weight change is observed for each temperature below the main degradation temperature. This may point to the fact that UV has already degraded the low molecular weight compounds and caused some changes. This

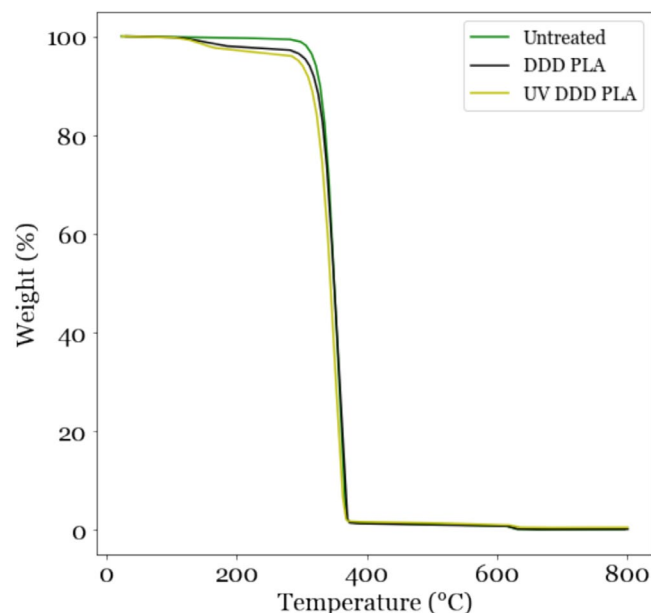


FIGURE 7 | TGA curves for untreated, DDD-treated, and 2h UVC-treated PLA. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

effect is a consequence of lower molecular weight rather than thermal degradation, as the temperature of the exposed surface reaches 45°C after 2 h exposure. Thermal properties were further assessed using DSC. The first cycle of heating during DSC was deeply influenced by the presence of residual solvent trapped in crystals from the solvent-induced recrystallization process. As such, PLA thermal properties were extracted from the second cycle of the DSC tests. 2 h UVC-exposed DDD-treated discs held significant recrystallization ability and a lower melting temperature, as can be seen in Figure 8 and Table 5, due to their reduced molecular weight [62]. This was also confirmed to be true for powder as shown in Supporting Information Section 6.

An increase in chain mobility can be inferred from the observed decrease in both glass transition temperature and melting temperature, due to the reduction in molecular weight. This increase in chain mobility is deemed to be sufficient to allow a change in polar bonds orientation on a textured surface and increase interaction with water. This increase in polarity has been characterized by plotting force–distance curves using AFM. As shown by Nie et al. [41], the use of UVC tends to increase the adhesion force calculated on the surface. This concurs well with our AFM results, showing that UVC-exposed substrates exhibit a higher adhesion force and are, as such, more polar (Figure 9).

TABLE 5 | Melting temperature (T_m), glass transition temperature (T_g), and percentage of recrystallization (%) during second heating cycle of DDD and 2h UVC exposed DDD-treated PLA. Heat of fusion of 100% crystalline PLA was considered to be 93 J/g [61].

Samples	DDD	UV DDD PLA
T_m DSC (°C)	164.1 ± 0.6	160.1 ± 0.3
T_g DSC (°C)	61.4 ± 0.5	58.9 ± 0.2
Recrystallization (%)	0.7 ± 0.2	7.5 ± 1.0

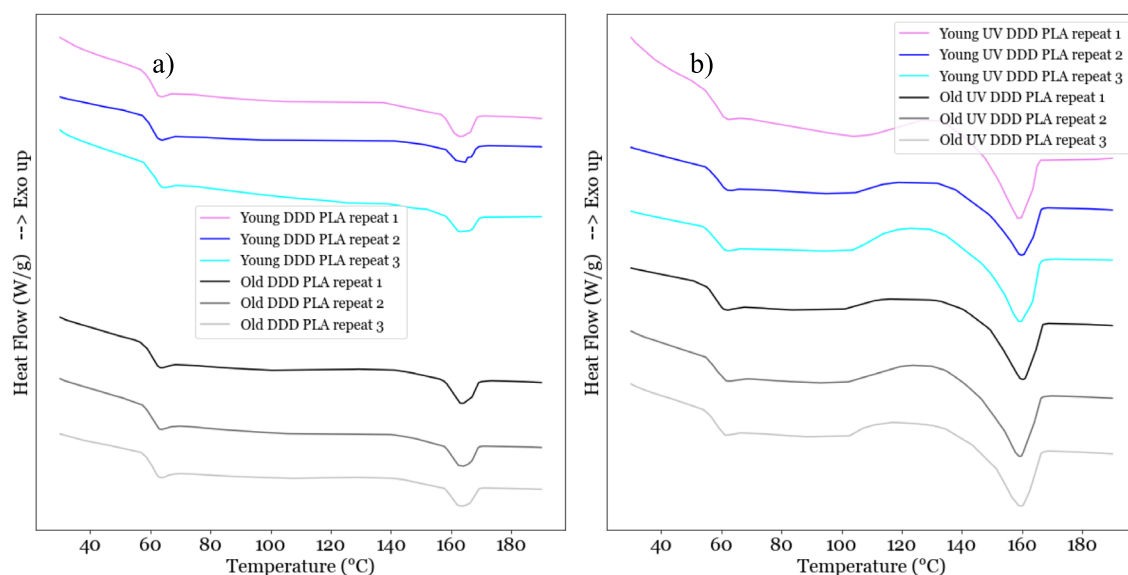


FIGURE 8 | DSC results comparing young (2 days after DDD-treatment) and old (3 months after DDD-treatment) (a) DDD-treated discs (b) 2h UVC exposed DDD-treated discs. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

3.5 | Discussion

Given the various characterizations conducted, the increase in wettability transfers to an increase in surface polarity, which has been confirmed with surface free energy calculation and AFM measurement of the adhesion force. A minor oxidation could be seen in FTIR when intensifying the bonds susceptible to H-bond linkage by not drying the samples under vacuum. As this minor oxidation does not correlate into an increase in oxygen content of the UV-exposed surface, an orientation of the polar oxygen bonds towards the surface is responsible for this wettability change. This change in orientation has been deemed possible with chain scission occurring during UVC exposure. The reduction in molecular weight has been confirmed using GPC and the following effects on thermal properties using DSC and TGA, such as the peaks profile in the XPS spectrum.

Furthermore, the height of the microstructure created by the DDD treatment might be affected by the reduction in molecular weight. Previous works by Kamegawa et al. [63] have shown that pillar height in patterned substrates can have a significant impact on wettability. Specifically, they found that in substrates such as the lotus leaf, the pillars impacting wettability are on the order of 10 μm . As such, studying the subsurface might hold important information.

As shown in Video S3a where a droplet was laid on the cross-section, wettability behavior change is mainly near the surface as the droplet is climbing up and spreading as it would be the

case in a capillary wicking surface (Video S3b). As such, penetration depths between 1 and 20 μm were studied by shaving off corresponding amount of matter from the top surface using microtome. From SEM observations on 20 μm microtomed rods (Figure 10), some unstable cracks [64] were seen due to the brittleness of the UVC exposed material compared to the unexposed DDD-treated PLA. Brittleness and potential effects of UVC exposure down to 20 μm were confirmed with GPC experiments where it was found that in the range 0–20 μm , the molecular weight was significantly lower than values given in Table 3 for discs and closer to powder due to surface specific effects. For 0–20 μm , number and weight average molecular weight were respectively 2.20×10^4 and 6.06×10^4 g/mol as an average of two repetitions (including 12 samples for each repetition). In other words, UVC exposure did not only change the wettability of the surface, but also the mechanical failure mechanism of the subsurface from ductile to fragile. However regarding the contribution to wettability of the subsurface, AFM experiments to elucidate the topology of the UVC-exposed and unexposed surfaces have shown that the different samples had similar roughness and similar microstructure height. This reinforces the conclusion of a surface chemistry change responsible for the wettability switch, rather than a morphology or topology change.

4 | Conclusions

This study introduced a complete wettability switch triggered by 2 h exposure to UVC light. The wettability of the

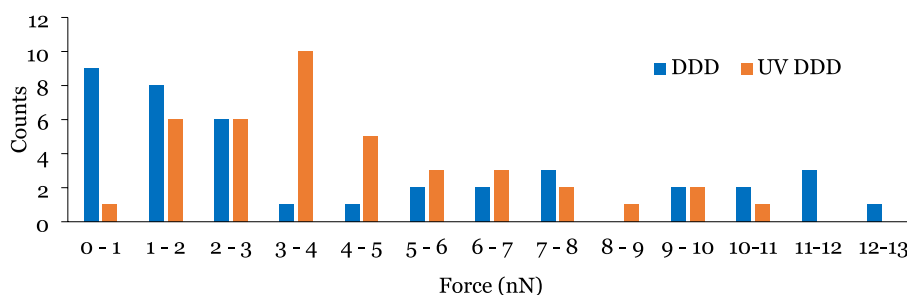


FIGURE 9 | Histogram for the distribution of adhesion forces on unexposed and UVC-exposed DDD-treated surfaces. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

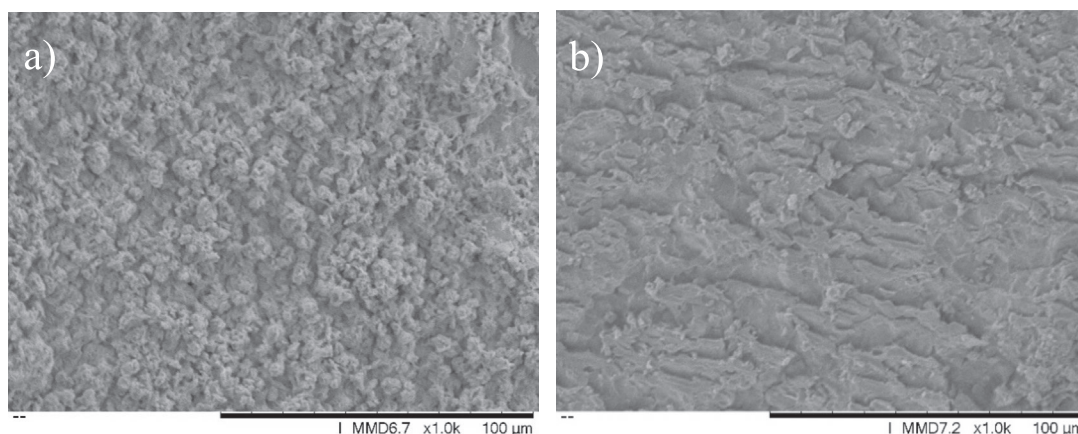


FIGURE 10 | Image of 20 μm microtomed (a) unexposed DDD-treated and (b) 2 h UVC DDD treated PLA rods at $\times 1000$ magnification. Image (b) represents specific zones in the microtomed UV samples which were interesting to identify the rupture mechanism.

solvent-treated PLA samples shifted from almost superhydrophobic to capillary wicking. Exposure to UVC caused chain scission, as confirmed by GPC. Despite this, no alterations in chemical composition were detected by XPS, and no significant morphological changes were observed through SEM. Since UVC exposure had a pronounced effect on the solvent-induced recrystallized surface but not on the untreated amorphous PLA surface, it is inferred that the reduction in molecular weight involved the fragmentation of larger crystals into smaller ones. This is further suggested by changes in peak shape in XPS and decreased polymer characteristic temperatures (glass transition temperature and melting temperature decreased respectively by 2.5°C and 4°C) observed in DSC, as well as a lower degradation temperature in TGA.

This molecular rearrangement likely enhanced the mobility of the polymer chains, allowing the reorientation of polar oxygen bonds towards the surface and thus impacting wettability. This was confirmed using FTIR, where a very minor oxidation with an increasing signal of the peak related to carbonyl groups at 1724 cm⁻¹ from α -cleavage could be seen. This change could be detected only when samples were not dried under vacuum prior to the test. Force distance spectroscopy (in AFM) confirmed the increase in polarity of the UVC exposed DDD treated surfaces with an average increase of 2 nN in the adhesion force after 2 h of UVC exposure. The increase in wettability and more precisely surface polarity without being associated with a composition change relates to a change in the orientation of polar oxygen bonds towards the surface, made possible by chain scission. The impact on the wettability behavior is more important compared to existing literature discussing UV exposure of polymers, likely due to the roughness of the solvent-treated samples.

It was also shown that the mechanical failure mechanism changed from ductile to fragile, as demonstrated by the formation of unstable cracks. UVC exposure also resulted in surface brittleness. This UVC post-treatment approach paves the way toward facilitating biodegradation or composting of surface-treated polymer substrates. Future work will tackle the contribution of the decrease in molecular weight to the wettability switch occurring due to the reorientation of polar bonds to the surface after UVC exposure.

Author Contributions

William Simon: conceptualization (supporting), formal analysis (lead), investigation (lead), methodology (lead), writing – original draft (lead). **Darius Klassen:** formal analysis (supporting), investigation (supporting), methodology (supporting), writing – review and editing (supporting). **Marie Mottoul:** investigation (supporting), methodology (supporting), writing – review and editing (supporting). **Simon Ponton:** conceptualization (supporting), formal analysis (supporting), investigation (supporting), methodology (supporting), writing – review and editing (supporting). **David Brassard:** conceptualization (supporting), formal analysis (supporting), investigation (supporting), methodology (supporting), writing – review and editing (supporting). **Jean-Marie Raquez:** validation (supporting). **Adya Karthikeyan:** conceptualization (supporting), formal analysis (supporting), investigation (supporting), supervision (supporting), validation (supporting), writing – review and editing (supporting). **Marie-Josée Dumont:** conceptualization (supporting), funding acquisition (equal), project administration (equal), supervision (equal), writing – review and editing (equal). **Jason Robert Tavares:** conceptualization

(equal), funding acquisition (lead), project administration (lead), resources (lead), supervision (lead), writing – review and editing (lead).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that supports the results of this study are available from the corresponding author upon a reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.