

Oxidative Degradation of Thermoplastic Starch Induced by UV Radiation

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Abstract: Among biopolymers, thermoplastic starch (TPS) is a good candidate to obtain biomaterials because of its natural origin, biodegradable character, and processability. Exposure to ultraviolet (UV) radiation causes significant degradation of starch-based materials, inducing photooxidative reactions which result in breaking of polymer chains, production of free radical, and reduction of molar mass. These changes produce a deterioration of TPS mechanical properties, leading to useless materials after an unpredictable time. In this work, changes induced on TPS by UV radiation, analyzing structural properties and mechanical behavior, are studied. TPS was obtained through thermo-mechanical processing of native corn starch in the presence of water (45 % w/w) and glycerol (30 % w/w) as plasticizers. Films were obtained by thermocompression and, before testing, specimens were conditioned to reduce material fragility. Photodegradation process was performed by exposing TPS to 264 h UV radiation in a weathering test chamber. Specimen's weight loss was determined gravimetrically. Chemical changes were studied by Fourier Transform Infrared Spectroscopy (FTIR) and morphological modifications were analyzed by Scanning Electron Microscopy (SEM). Reduction of weight average molar mass was measured by Static Light Scattering (SLS). Changes in mechanical properties were studied from tensile tests. After 96 h exposure, TPS specimens presented a weight reduction of 4-6%, mainly attributed to plasticizers lost by evaporation. SEM observations showed that UV radiation induced morphological changes on TPS, evidenced by an increment of specimens cracking. By FTIR, it was detected the presence of an additional band located at 1726 cm^{-1} in samples submitted to UV radiation, attributed to the formation of -C=O groups. Weight average molar mass of native starch was in the order of 107 g mol^{-1} . TPS exposure to UV radiation decreased significantly its molar mass, confirming molecular degradation of the biopolymer. When TPS was exposed during 48 h, it was detected a considerable decrease in elongation at break values ($\sim 85\%$), indicating that TPS flexibility was reduced. On the other hand, after 48 h exposure, TPS elastic modulus was 55 times higher than those of the unexposed specimens, evidencing an increase in material rigidity. TPS maximum tensile strength was also increased by UV light, with an increment of $\sim 400\%$ after 48 h exposure. Results revealed that starch-based materials can be degraded by exposure to UV radiation, modifying their microstructure and mechanical performance.

Keywords: Thermoplastic starch; UV radiation; structural properties; mechanical behavior

1 Introduction

Biopolymers constitute a group of naturally occurring polymers such as starch, cellulose, chitosan, pullulan, alginates, and poly(hidroxyalcanoate)s. The use of these renewable natural polymers for bioplastics production offers a good alternative to synthetic materials, therefore environmental pollution by conventional plastics can be minimized. Because of their special characteristics such as ecocompatibility,

biocompatibility, and biodegradability, biopolymers have emerged as a major group of attractive and renewable substitutes for synthetic plastics. Increase in petrochemicals price and major environmental concerns have turned the attention of scientific community, environmentalists, and administrators towards the development of novel technologies for human use and commercialization of products made of biopolymers. Thermoplastic starch (TPS) is a semicrystalline material obtained by starch destructuring in the presence of plasticizers such as water and glycerol, among others. This biopolymer can be processed with conventional technologies used for manufacture of synthetic plastics such as extrusion and injection-molding, among others [1,2]. Aging resistance of polymeric materials, especially to ultraviolet (UV) light, is relevant for outdoor applications since degradation usually shortens their use-life [3].

Photodegradation of polymer materials is caused by the absorption of photons, particularly at those wavelengths found in sunlight, such as infrared, visible, and UV light. In outdoor applications of plastic materials, UV radiation is responsible for most aging damages because the quantum energy is high enough to cause chain cleavage in the molecules. This phenomenon causes several chemical changes such as depolymerization, crosslinking, formation of double bonds in the polymer chain and other low-molecular compounds [4]. Ozone found in the stratosphere protects from the harmful effects of UV radiation by filtering almost all UV-C (280-100 nm) and nearly 95% of UV-B (315-280 nm) emitted by the sun. However, ozone minimally filters UV-A (400-315 nm), and for this reason, UV-A accounts for more than 95% of UV light reaching the surface of the Earth [5]. Accordingly, it is relevant to analyze the effect of UV-A rays on polymers properties in order to widen their applications. For many experimental studies, it is simply not practicable to use natural sunlight and so artificial sources of UV radiation designed to simulate the UV component of sunlight are employed [6]. Zhou et al. [7] they studied the changes that were generated on the surface crosslinked thermoplastic starch (TPS)/PVA blend films prepared by applying ultra violet (UV-C) irradiation.

Photodegradation includes photodissociation, breakup of molecules into smaller pieces by photons, and irreversible physical and chemical changes. UV light must be absorbed by the substrate (polymeric system), thus existence of chromophore groups in the macromolecules is a prerequisite for the initiation of any photo-chemical reaction [8]. A wide variety of synthetic and naturally occurring high polymers absorb solar UV radiation and undergo photolytic, photooxidative, and thermooxidative reactions that result in the degradation of the material [9]. Nowadays, the employment of polymeric materials has increased considerably but their exposition to natural weather conditions accelerates materials degradation. These drawbacks lead to economic loss and environmental consequences, so several attempts are focused towards comprehension the changes that occur at molecular level in order to find possible alternatives to minimize them. Following different mechanisms, UV radiation induces photooxidative degradation, which results in breaking of the polymer chains, produces radical and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after an unpredictable time [10].

High-energy radiation sources such as gamma irradiation [11] or electron beam [12,13] have been adopted to modify starch materials. Unlike gamma irradiation or electron beam, UV light provides lower energy and has difficulty directly cleaving the C-C or C-H bonds of starch molecules during short periods of exposure time. However, with sufficiently high intensity or long exposure time, the destructive nature of UV can cause photo-reactions in starch, like a decrease of chain length which is often accompanied with yellowing and the formation of carbonyl and carboxyl groups along the polymer chains [14,15]. UV light treatment of starch has been reported to bring about changes in some functional properties, such as an increase in water binding capacity and solubility as well as a decrease in the hot paste viscosity [16,17]. UV irradiation has been reported not to alter the crystallinity of starch or its gelatinization enthalpy [18]. Fiedorowicz et al. [19] found chain scission in the early stage of UV-irradiation, with crosslinking dominant in the later stage (5-15 h) of irradiation in the presence of air.

Even though the effect of UV radiation on starch properties is well studied by several authors, changes on structure and final properties of TPS were less reported. The relevance of evaluating the influence of solar UV radiation on TPS relies on the increasing interest to widen the application field of materials based on this kind of biobased and biodegradable polymer. The knowledge of UV induced changes on TPS allows

to evaluate new possible uses for this biopolymer. In addition, since UV-A rays are almost not filtered by ozone, is an additional variable to take into account in TPS photodegradation studies. Besides, the effect of UV-A radiation on TPS based materials is less studied than the influence of UV-B and UV-C rays. In accordance with this, [20] reported the effect of UV-C irradiation of the TPS and PCL biocomposites with sisal bleached fibers. Besides, Bardi et al. [21] studied the influence of different color inks printed on PBAT/TPS films, cured by UV-B light, and exposed to UV-A degradation followed by an aerobic biodegradation process. On the other hand, Giroto et al. [22] have exposed a composite material of starch/montmorillonite under UV-C radiation, they describe the photoprotective effect of starch/montmorillonite composites on the ultraviolet-induced degradation of ametryne, a commercial herbicide. Also, Zhou et al. [23] they studied the changes that were generated on the surface crosslinked thermoplastic starch (TPS)/PVA blend films prepared by applying UV-C irradiation.

The aim of this work was to evaluate the modifications induced by UV-A radiation under air atmosphere on thermoplastic corn starch (TPS). Structural and morphological changes were monitored by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Besides, reduction of weight average molar mass was determined by Static Light Scattering (SLS) and the effect of UV radiation on TPS mechanical properties was also evaluated by tensile tests.

2 Experimental

2.1 Materials

Native corn starch was provided by Misky-Arcor (Tucuman, Argentina) with an amylose content of $23.9 \pm 0.7\%$ [24] Glycerol (Anedra, Argentina) was used as plasticizer.

2.2 Thermoplastic Starch Preparation

Mixtures of native corn starch, glycerol (30 % w/w), and distilled water (45 % w/w) were prepared. Then, they were processed in a batch two-screw mixer Brabender Plastograph (Germany) at 150°C and 50 rpm. After 15 minutes mixing, a thermoplastic material was obtained, which was then submitted to thermo-compression at 10 kg cm^{-2} and 150°C during 5 min. Finally, sheets of variable thickness (1.3-1.5 mm) were obtained. TPS samples were conditioned at 25°C and 60% relative humidity (RH), according to ASTM D618-05. This procedure led to eliminate the material fragile nature. Since TPS is a semi-rigid material, samples were cut according to the probes Type V dimensions, established in ASTM D638-1996.

2.3 Ultraviolet (UV)-A Light Irradiation

TPS specimens were exposed to UV-A radiation in a special chamber QUV/spray Accelerated Weathering Tester (USA). UVA-340 lamps programmed to generate an irradiance of 0.72 W.m^{-2} at 340 nm, according to the ASTM D5208-91 were used. UV chamber was located in an ambient at 25°C and the selected test was Cycle C (24 h irradiation at 50°C). As it was mentioned in ASTM D5208-91, condensation step is excluded from this cycle in order to avoid washing away any possible photochemical degradation by products. TPS samples were numbered and weighted before they were located into UV chamber to facilitate changes tracing of each specimen. At least 10 probes were taken every 48 hours and submitted to complementary analysis.

2.4 Structural and Morphological Characterization of Irradiated Samples

2.4.1 Weight Loss and Residual Water

Weight loss of TPS specimens as consequence of UV-A radiation was determined gravimetrically, using the following equation:

$$\text{Weight loss (\%)} = \frac{w_i - w_t}{w_i} \times 100 \quad (1)$$

where w_i corresponds to the specimen initial weight before located into the chamber and w_t is the specimen

weight at each assayed time.

Residual water content was determined by thermogravimetric analysis (TGA) was determined by mass loss at 180°C. Thermogravimetric analyzer Discovery TA Instrument was used to measure the thermal weight loss of each type of film in duplicate in a temperature range between 25°C and 220°C at a heating speed of 10 °C min⁻¹ under a nitrogen stream of 20 mL min⁻¹.

2.4.2 Microstructural Changes

TPS microstructural changes induced by UV-A radiation were evaluated by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). SEM study was performed in a JEOL JSM-35 CF, with secondary electrons detector. Probes were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and coated with a gold layer using an argon plasma metallizer (sputtercoater PELCO 91000). FTIR spectra were obtained using a Thermo Nicolet Nexus spectrophotometer (USA). Samples were prepared by mixing TPS mixtures as fine powder with KBr (Sigma-Aldrich, 99%) at 3 % w/w. Mixture was pressed and a transparent disc was obtained. Spectra were obtained from 70 accumulated scans at 4 cm⁻¹ resolution in the range 4000-400 cm⁻¹.

2.4.3 Weight Average Molar Mass

Weight average molar mass was measured using Static Light Scattering (SLS). Experiments were carried out at 25°C, employing a DAWN DSP (Wyatt Technologies) photometer with a multiangle laser light scattering detector ($\lambda = 632.8$ nm). Samples were prepared by dissolving TPS in 0.5 M NaOH in order to obtain solutions from 1.10⁻² g. mL⁻¹ to 1.10⁻⁴ g. mL⁻¹. Solutions were subsequently filtered with a Milipore 0.45 μ m filter prior to injection. Absolute molar mass of TPS before and after UV-A exposure was determined using the Astra software (Wyatt Technology). Light scattering (LS) at 18 angles were collected and used to calculate the weight average molar mass (M_w). For these calculations a value of $dn/dc = 0.142$ was used, as it was reported by Sagar et al. [25] for starch samples.

2.4.4 Mechanical Properties

The procedure used to perform tensile tests was in accordance to ASTM D638-98. This standard method specifies test conditions to determine tensile properties of rectangular polymer specimens. Tensile tests were carried out in universal mechanical test equipment Instron 3369 at 25°C and 55% RH, using a speed of 100 mm. min⁻¹. Ten specimens were assayed for each exposure time and stress-strain curves were obtained from load-displacement data. From those curves, Young's modulus (E), maximum tensile strength (σ_m), elongation at break (ϵ_b), and toughness were calculated.

3 Results and Discussion

Materials degradation is defined as a detrimental change in their appearance, mechanical, physical properties, and chemical structure [26]. Appearance of TPS specimens before and after UV exposure at different assayed times is shown in Fig. 1. Visual observation of TPS probes evidenced that UV radiation did not modified their surface color; however, they became more brittle. Similar results were reported by Campos et al. [20] for materials based on thermoplastic corn starch. These authors attributed TPS brittleness increment to surface photo-crosslinking of starch chains during UV exposure. On the other hand, Bertolini et al. [15] found that fluorescence chromophores in cassava starch, which absorb at 290-360 nm, disappear due to the degradation by UV light after irradiation with mercury vapor lamps at 360 nm.

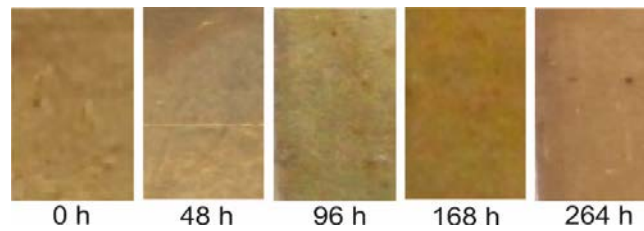


Figure 1: Photographs of TPS probes at different UV exposure times

3.1 Weight loss and Residual Water

Fig. 2 shows the weight of TPS probes as a function of UV exposure time. As it can be observed, specimens weights did not change significantly, reaching a weight loss lower than 6%. This result could be mainly attributed to the loss of plasticizers by evaporation. Similar values of weight loss were reported by Ruiz et al. [2] for thermoplastic yuca starch exposed to solar radiation during 60 days. These authors claimed that reduced weight loss is in accordance with the low microbial charge present during the degradation process. From TGA curves, it was determined that TPS specimens before and after UV exposure during 264 h presented a residual water content of 10.1% and 7.2%, respectively. These results demonstrated that the low weight loss determined gravimetrically could be associated to water evaporation during UV storage. However, it is important to highlight that the plasticizers loss during UV treatment was not significant under the assayed conditions. Reduction in the moisture content could be associated to the crosslinking caused by the UV radiation on the films [4,27].

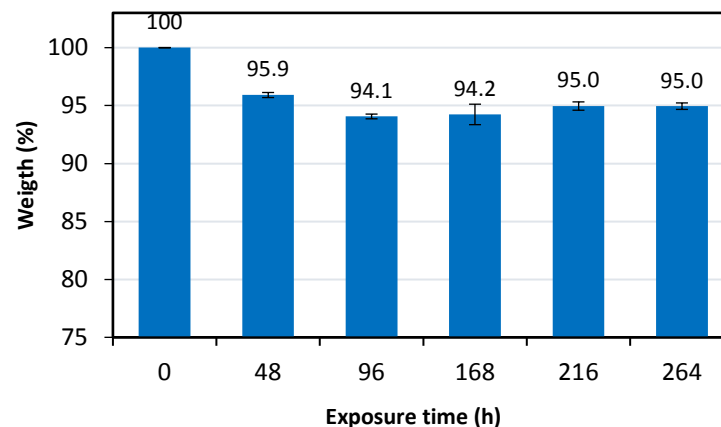


Figure 2: Weight of TPS probes at different UV exposure times

3.2 Microstructural Changes

SEM micrographs of unexposed and exposed surfaces of TPS probes are presented in Fig. 3. Before being submitted to UV radiation, TPS specimens evidenced a homogeneous appearance without the presence of unmolten starch granules (Fig. 3(a)). After exposition to UV light, even though a smoother surface was observed, the presence of several cracks and pores were detected (Figs. 3(b) and 3(c)). In the same way, Campos et al. [20] showed that UV-C radiation induced the occurrence of smoother surfaces with holes and cracks for TPS and TPS/PCL blends-based materials. These authors attributed the observations to the degradation of material surface. On the other hand, cracking of yuca starch materials was also reported, stressing that this observation is the consequence of both plasticizer migration and photodegradation processes [2]. In addition, Cui et al. [4] stressed that is the accelerated weathering test, the cycling changes in moisture and temperature were additional important factors that caused the formation

of surface cracks.

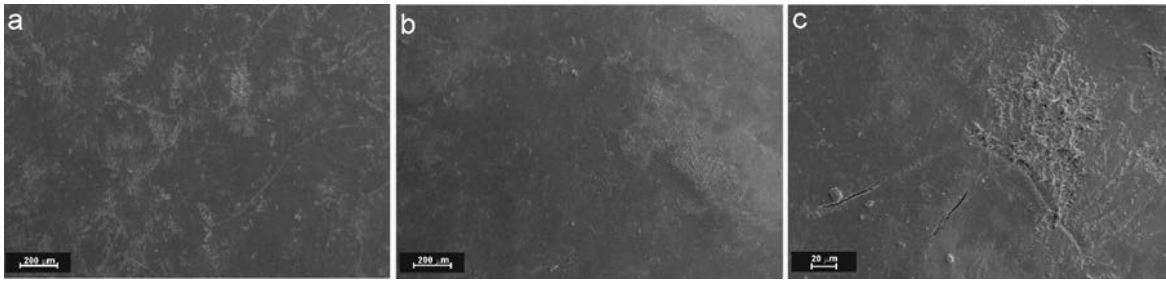


Figure 3: SEM micrographs of probes surfaces: a) unexposed TPS (150x), b) irradiated TPS after 264 h (150x), and c) irradiated TPS after 264 h (1000x)

Fourier Transform Infrared (FTIR) can be used as a powerful tool to detect structural changes such as an oxidation level of TPS due to the UV radiation. Fig. 4 shows the comparison of FTIR spectra of TPS samples before and after being subjected to UV radiation during 48 and 264 h. Spectrum of unexposed TPS presented bands corresponding to the distinctive functional groups of starch and glycerol. Bands at 920, 985, 1026, 1074 and 1148 cm^{-1} (C-O stretching), 1648 cm^{-1} (bound water), 2929 cm^{-1} (C-H stretching), 3385 cm^{-1} (-OH groups), and 1457 cm^{-1} (glycerol) were detected [28]. Besides, several bands at low wavenumbers (627, 581, 560 and 400 cm^{-1}), attributed to complex vibrations modes due to skeletal mode vibrations of the glucose ring were also observed [29]. Spectra of samples exposed to UV radiation were similar to the corresponding to unexposed TPS. Thus, all characteristic signals of starch and glycerol functional groups were detected in FTIR spectra of irradiated TPS. However, the presence of an additional band located at 1726 cm^{-1} in samples submitted to UV radiation, indicate the formation of a new functional group (-C=O). Bertolini et al. [15] studied starch irradiated with a mercury vapor lamp and suggested that photo-oxidation induces the breakage of C₂-C₃ bond in glucopyranose units, producing a starch dialdehyde. Besides, a decrease in the intensity of bands attributed to hydroxyl groups and water flexion was observed. This result is in accordance with samples dehydration during UV exposure. Similar observations were reported for yuca thermoplastic starch submitted to degradation under different media (water, saltwater, landfill, and solar radiation) [2].

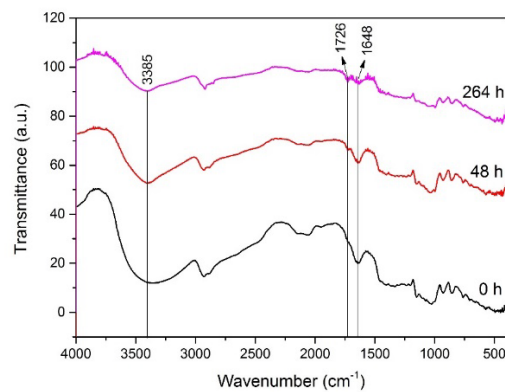


Figure 4: FTIR spectra of TPS at different UV exposure times

3.3 Weight Average Molar Mass

It was determined that UV-A radiation induced a significantly decrease in the TPS average molar mass from $1.76 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ to $6.24 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$ after 264 hours exposure. The value of the unexposed TPS has

the same order of magnitude than other thermoplastic materials obtained from native starches with similar amylose and amylopectin content [30]. Employed UV-A light is known to produce starch photodegradation, resulting in the cleavage of glycosidic bonds, accompanied by the shortening of amylose chains, and debranching of amylopectin chains due to the formation of free radicals [31]. Moreover, thermoplastic starch exposure to UV radiation leads to oxidative depolymerization. Ma et al. [31] stressed that natural molecules such as starch suffer degradation to low molar mass molecules when they are submitted to photodegradation processes.

3.4 Mechanical Properties

Tab. 1 summarizes the mechanical properties of TPS probes before and after being irradiated by UV-A light.

Table 1: Mechanical properties of TPS before and after photodegradation at different exposure times

t (h)	E (MPa)	σ_m (MPa)	Toughness (mN/tex)	ϵ_b (%)
0	2.3 ± 0.2	4.6 ± 0.3	307.8 ± 5.2	22.0 ± 2.1
24	16.5 ± 3.6	15.3 ± 5.0	966.8 ± 30.9	1.2 ± 0.3
48	31.5 ± 3.3	21.8 ± 4.7	1018.0 ± 203.7	1.0 ± 0.2
72	42.3 ± 5.6	20.5 ± 2.7	1269.4 ± 186.1	0.9 ± 0.2
96	31.0 ± 4.8	18.7 ± 2.6	901.5 ± 146.1	0.7 ± 0.1
168	27.0 ± 4.1	18.8 ± 3.8	948.8 ± 148.4	0.9 ± 0.2
216	26.9 ± 1.5	19.5 ± 2.2	972.1 ± 111.3	1.0 ± 0.2
264	25.1 ± 3.0	20.9 ± 1.4	964.9 ± 161.6	0.6 ± 0.1

As it can be observed, after 24 h irradiation elongation at break decreased significantly, reaching a reduction of around 95%. Ferreira et al. [32] stressed that the reduction of elongation at break is a typical behavior of semi-crystalline polymer exposed to radiation that induces reactions with chains breakage, resulting in a more fragile material. Fragility of irradiated samples is in accordance with defects observed by SEM (Figs. 3(b) and 3(c)). According to Subburaj et al. [33], after photo-degradation a decrease in chain length is observed and specimens become brittle. Regarding Young's modulus, maximum tensile strength and toughness values reached a maximum at 48-72 h and then decrease. This behavior could be attributed to the prevalence of crosslinking reactions at short exposure times and chains cleavage at long irradiation times [34,35]. Different authors stressed that a competition between crosslinking and scission reactions may occur along photochemical degradation, which may have promoted some stability in the mechanical properties.

4 Conclusions

The effect of ultraviolet radiation on thermoplastic corn starch was analyzed using several characterization techniques. UV-A light exposure during 264 h produce samples dehydration along with crosslinking and photo-degradation reactions. Thus, a slight weight decrease and a significant reduction of the weight average molar mass were observed. TPS microstructure was affected by UV radiation through the occurrence of cracks and pores onto surface material. Besides, it was demonstrated that this kind of radiation modified starch chemical structure by the formation of new functional groups. Regarding mechanical behavior, TPS exposure under UV radiation led to a less flexible and more brittle and fragile material. The knowledge about the effect of UV light on TPS microstructure and final properties is relevant in order to find feasible alternatives to minimize this undesirable phenomenon.

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