Effect of ultraviolet irradiation on the thermal stability of bleached eucalyptus kraft pulp

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ABSTRACT: The changes occurring on cellulosic fibers caused by ultraviolet irradiation at 360 nm for 24 h and 48 h were investigated. A never-dried industrial *Eucalyptus urograndis* elemental chlorine free–bleached kraft pulp sample (O/OD[EP]DP sequence) was used throughout the work. After irradiation, the cellulosic fibers were analyzed for polymerization degree changes, extractive and pentosan content, ultraviolet and visible spectrometric changes of water leachate from the fibers and thermal analysis (TGA/DTA). The ultraviolet treatment had no effect on the degree of cellulose polymerization. The water extracted from ultraviolet-treated fibers revealed cellulose oxidation, with increasing absorbance signals for carbonyl and carboxyl groups. Those oxidations influenced fiber thermal stability.

Application: Mills can benefit from understanding that exposure of bleached paper to ultraviolet rays can cause irreversible damage to properties of the paper.

Cellulose is a linear polysaccharide of α-D-glucose linked by 1, 4-glycosidic bonds [1,2]. It is an important raw material in many applications because of its insolubility in many solvents, low density, biodegradability, and high sustainability [3–7]. Several process and sources may be used for cellulose fiber extraction. According to Belman et al. [8], more than 1000 vegetal species are capable of delivering cellulose fibers in large scale. Nowadays, the most used process is based on alkaline delignification of wood followed by elemental chlorine free (ECF) or total chlorine free (TCF) bleaching sequences [9].

In addition to cellulose, bleached cellulosic fibers derived from wood possess other components such as extractives (resins, sterols, wax, and fatty acids), noncellulosic carbohydrates (hemicelluloses, nonvolatile carbohydrates), and minerals. Those noncellulosic materials may have a role in important after-processing reactions, leading to color formation, depolymerization, and strength and thermal stability reduction [10–16].

The literature has pointed out that cellulose structure can suffer oxidative and/or hydrolytic degradation via mechanisms generally induced by heat and ultraviolet (UV) or bacterial exposure, whether catalyzed or not by transition metals [12,14,17,18–23]. According to Malesic et al. 2005, UV radiation is one of the most significant sources of carbohydrate degradation. Although degradation does not occur directly with UV radiation having wavelengths >340 nm, the energy absorbed may induce free radical formation with consequent degradation reactions. Malesic et al. [22] showed that free radical formation caused by UV radiation reaches its maximum at 360 nm.

The cellulose oxidation by free radicals forms double bonds, including those in carbonyl and carboxyl groups, leading to depolymerization or the ring opening and thus increasing susceptibility of cellulose to degradation. According to Malesic et al. [22], photo-oxidative reactions resulted in the increase of cellulose carbonyl and carboxyl groups. Direct effects of those reactions were observed on optical and mechanical properties, polymerization degree, and stability of cellulosic fibers.

Thermogravimetric analysis (TGA) is a great tool to access the thermobehavior of materials through measurement of mass losses or on its first derivative curve (DTG). Princi et al. [24] highlighted that TGA is the best tool for thermal stability evaluation of cellulosic materials, and Wielage et al. [25] reported that important information on the natural fiber stability may be obtained using TGA analysis. By using the derivative thermal analysis (DTA), physicochemical information such as phase transformation, solid state reactions, polymerization, and combustion behaviors may be monitored. Such monitoring represents another important form of viewing and explaining the changes happening during cellulosic fiber heating.

Our study investigated the changes occurring on bleached eucalyptus cellulosic fibers caused by UV irradiation at 360 nm for 24 h and 48 h. Untreated and UV-treated samples were compared in regard to their polymerization degree, extractive and pentose contents, and UV and visible spectra of water leachate from fibers and TGA/DTA analysis.

EXPERIMENTAL

Materials

A never-dried industrial *Eucalyptus urograndis* ECF bleached (O/OD(EP)DP sequence) kraft pulp sample was used throughout the work. After sampling, the pulp was thoroughly washed and the inorganic matter was removed in acid water (pH 2.5) at 20°C for 5 min. The pulp pH was adjusted to neutral and dried to 90% consistency by centrifugation and air drying.

Pulp characterization

E. urograndis ECF bleached (O/OD(EP)DP pulp was characterized to determine some important data on pulp characterization. The content of hexene uronic acids was determined for untreated pulp, and the glucose percentage and degree of polymerization were determined for the untreated pulp and after treatment. The values were shown in **Table I**. The treatments did not modify the main properties shown in the table.

Methods

The cellulosic fiber sheets (200 g/cm²) were formed according to the Rapid-Köthen method. The base of the column was formed with an air agitation system, with pressure regulated to mix the pulp solution and ensure homogeneity of the sheets formed. Sheets that were 200 mm diameter, or 315 cm², were produced. The system had a column with a capacity of 10 L; pneumatic vacuum generator at 96 kPa; closed circuit hot water to dryers at 93°C, and closed circuit water cooled to 20°C. The sheets were exposed to UV radiation at 360 nm for 24 h and 48 h at 25°C + 0.2 in air atmosphere. Sheets were irradiated using a Blak-Ray Lamp (Ultra-Violet Products, Upland, CA, USA), model UVL-21, with specifications of long 360 nm wave, 60 Hz, 0.16 Amp, and 115 volts. The sheets were designated as SAI (sample after irradiation) and as SBI (sample before irradiation).

The UV-irradiated and nonirradiated samples were assessed for viscosimetric polymerization degree using the Mark-Houwink-Sakurada equation. Also assessed were acetone extractives in a soxhlet extractor (TAPPI T 280 pm-99, "Acetone extractives of wood and pulp"), UV and visible spectra of water leachate from samples, and pentose content by pentosans (TAPPI T 223 cm-84 "Pentosans in wood and pulp"). Thermogravimetric analyses and differential thermal analyses were performed in a thermogravimetric apparatus SDT 2960 Simultaneous DTA-TGA from TA Instruments (New Castle, DE, USA) with room air temperature heated to 550°C and N_2 atmosphere at 10°C.min^{-1}.

The leaching of samples was made in demineralized water (1.5 mL.g^{-1}) during 24 h at 25°C. The UV spectra were taken on a Varian UV-VIS Cary 50 Probe (Varian, Palo Alto, CA, USA) with double beam from 200 nm to 400 nm, 1-nm and 1-cm optical path step.

The thermal analysis results were used to estimate the carbohydrate decomposition activation energy through the graphic methods of Horowitz-Metzer and Van Krevelen [26]. The expressions used for calculations are shown in **Table II**.

Pulp	Degree of Polymerization	Pentoses (%)	Hexene Uronic Acids (mMol/Kg)
Untreated	638.2	14.61	12.5
Treated 24 h	641.4	14.61	-----
Treated 48 h	641.1	14.61	-----

I. Experimental data of untreated and treated pulps (24 h and 48 h).

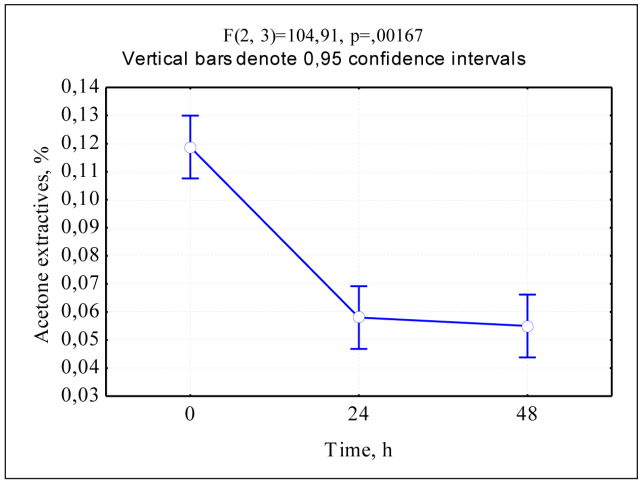
RESULTS

Ultraviolet exposure showed a significant effect on pulp acetone extractive content. The effect was observed at a very low significance level ($p < 0.05$). **Figure 1** shows acetone extractive content as a function of UV irradiation time. A significant pulp extractive reduction (51.1%) was observed for the 24-h irradiation time exposure. According to the Tukey test at 95% of confidence, the averages for 24 h and 48 h were the same.

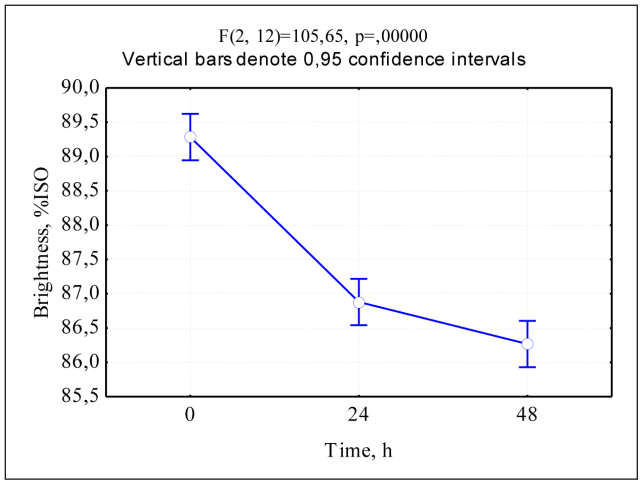
The decrease in extractive content caused by UV radiation does not necessarily mean loss of extractive mass but likely

Method	Expression	Plots
Horowitz-Metzer[26]	$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right]=\left(\frac{E_a.\theta}{R.T_s^2}\right)$	ln[ln(1/1-α)] against θ
Van Krevelen[26]	$\left[\ln\left(\frac{1}{1-\alpha}\right)-1\right]=\ln\left[\frac{A}{\beta}\left(\frac{0.368}{T_m}\right)^{\frac{E_a}{R.T}}.\frac{1}{\frac{E_a}{R.T}+1}\right]+\left(\frac{E_a}{R.T_m}+1\right).\ln T$	ln(1/1-α) against lnT
Ea: activation energy, kJ/mol; R: universal gas constant 8314 J/Kmol; T: temperature, K; A: constant, min^{-1}; β: heating rate; °C/min, α: fractional mass loss.		

II. Activation energy methods and expressions.



1. Effect of ultraviolet irradiation time on pulp acetone extractives.



2. Brightness in time functions of ultraviolet irradiation.

means a decrease in extractive solubility. Reactions occurring during irradiation may have caused changes in the extractive structures with possible introduction of carboxyl groups, thus decreasing their solubility in acetone.

According to Princi et al. [24] UV radiation can penetrate deeply into cellulosic fibers, accessing rich regions of hemicelluloses such as the interface between S_1 and S_2 layers in the fiber wall. The pentosan test is commonly used for measuring pulp xylan content. The statistical variance tests indicated no significant effect of UV irradiation on the pulp pentosan content ($p < 0.20$).

Despite the minimal effect of UV radiation on xylan content, important transformations may have occurred with increase of oxidized structures. Those transformations may be easily observed by the optical property changes, but it is not possible to separate the effect of other oxidized substances such as extractives and cellulose. **Figure 2** shows how brightness was modified by UV exposure.

The variance test for the viscosimetric polymerization degree showed no significant effect of UV irradiation on the pulp degree of polymerization as measured by viscosimetry ($p > 0.05$). These results showed that UV radiation at 360 nm has insufficient energy for glycosidic bond breakage. According to Malesic et al. [22], direct degradation of cellulose fibers by UV radiation does not occur up to 340 nm wavelength, but free radicals may be produced and lead to subsequent degradation.

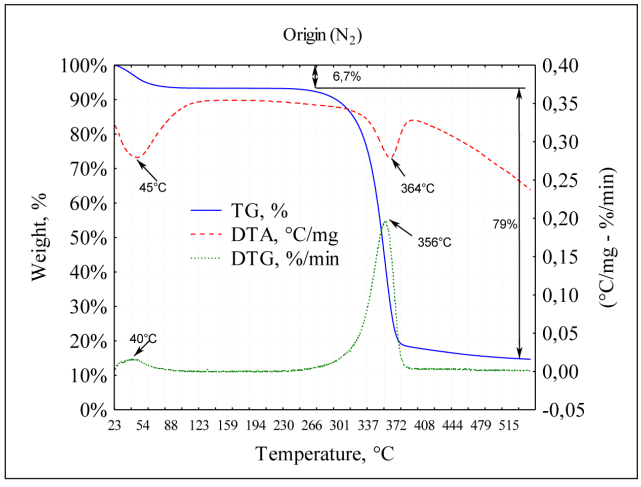
The production of free radicals is usually associated with oxygen and transition metal ions in intermediate oxidation state, especially copper, manganese, and iron. All samples were previously acid treated, leading to cellulose pulp with undetectable levels of metals by atomic absorption spectroscopy. The low pulp transition metal content, and consequent low free radical formation potential, may explain the lack of the UV radiation effect on the pulp degree of polymerization.

Table III presents The UV absorbance of water leachate from untreated and UV-irradiated pulp samples. The UV irradiation caused significant changes in the bands typical of carbonyl (255 nm), conjugated carbonyl (330 nm), and carboxyl (230 nm) groups. These results showed that despite no depolymerization by UV, some oxidation occurred on carbohydrates with acid and carbonyl formation. These oxidized compounds may have derived from cellulose, hemicelluloses, or extractives. Gellerstedt et al. [12], working with water extracts from hardwood fibers subjected to thermal aging, identified 28 distinct compounds, 16 of which were organic acids.

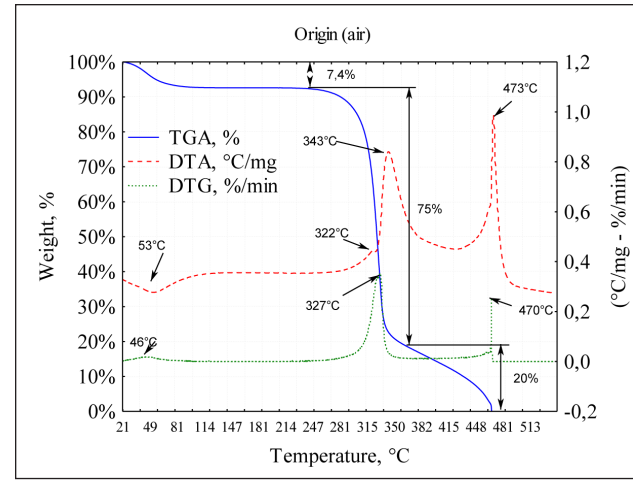
Figures 3 and **4** show the thermal analysis in the N_2 atmosphere of samples before SBI and after SAI UV exposure, respectively. The TGA curve shows mass loss of 6.7% for SBI against 7.0% of SAI up to 250°C, indicating negligible effect of UV irradiation on pulp thermal stability at this temperature range. However, at temperatures above 250°C, the effect of UV irradiation on the pulp thermal stability became visible, with an increase in mass loss from 8.0% (SAI sample) to 14.3%

Functional Group	Wavelength (nm)	Absorbance		Increase in Absorbance (%)
		Before UV Irradiation	After UV Irradiation	
Carboxyl	230	0.2532	0.2954	17
Carbonyl	255	0.2321	0.2700	16
Conjugated Carbonyl	330	0.0949	0.1361	43

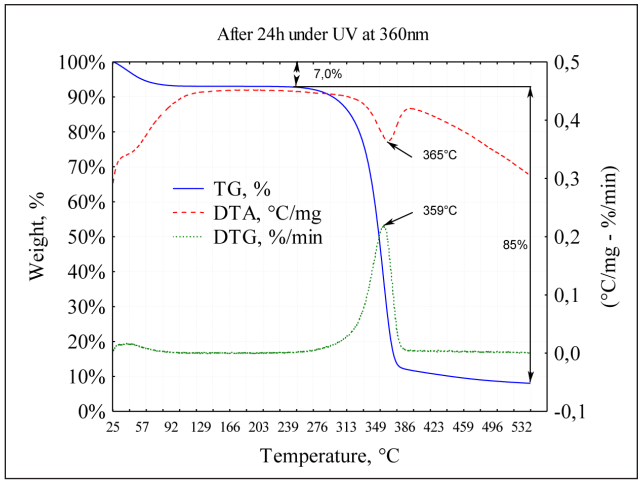
III. Ultraviolet absorbance of water leachate from untreated and ultraviolet-irradiated pulp samples after 24 h.



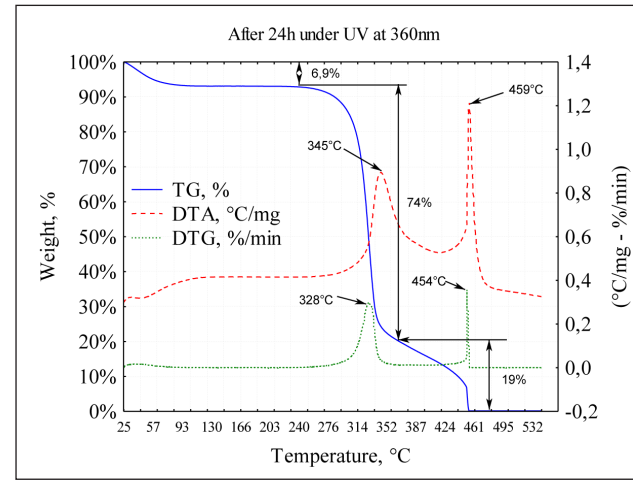
3. Thermal analysis in N_2 atmosphere for untreated sample.



5. Thermal analysis in air atmosphere for untreated sample.



4. Thermal analysis in N_2 atmosphere for ultraviolet-irradiated sample (24 h at 360 nm).



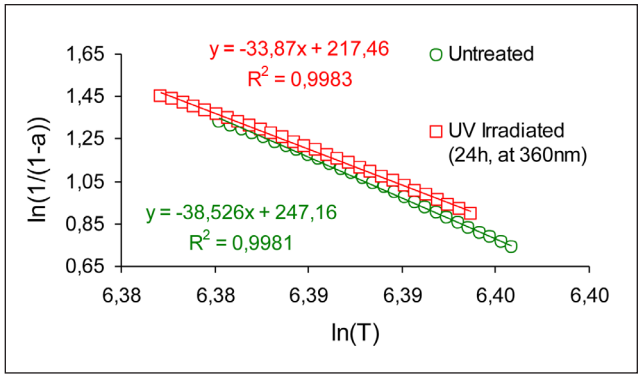
6. Thermal analysis in air atmosphere for ultraviolet-irradiated sample (24 h at 360 nm).

(SBI sample). According to Yldiz et al. [27] and Soares et al. [5], heating until 100°C leads to cellulose dehydration. The decrease in thermal stability at the higher temperature is explained by the carbohydrate oxidation by UV irradiation, which produces new functional groups that facilitate the pyrolysis reactions. Note that the decrease in thermal stability occurred despite the polymerization degree remaining stable during UV irradiation. Yldiz et al. [27] reported that thermal degradation of cellulose rises sharply above 200°C, causing volatile liberation and degradation of crystalline structures beginning at 240°C. Soares et al. [5] showed kraft paper degradation beginning at 250°C and Nada [29] showed viscose grade pulp degradation at 266°C.

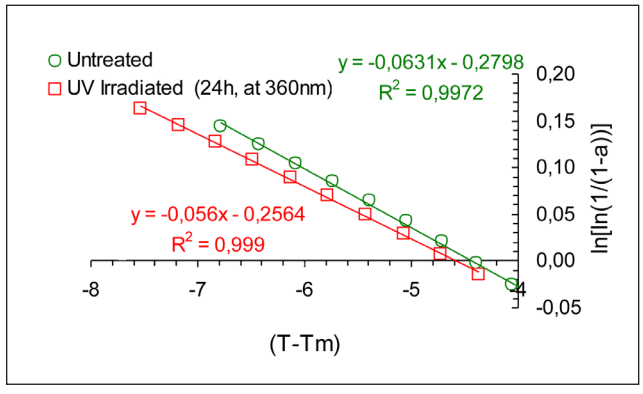
Despite the higher thermal decomposition of the SAI when compared to the SBI sample, the position of decomposition peaks did not change significantly. The DTG curve showed very close peaks for the decomposition of the two samples. Decomposition occurred at 356°C for the reference sample and at 359°C for the sample exposed to UV irradiation. Princi et al. [24] showed peak Whatman paper decomposition at 390°C.

Alvarez et al. [28] showed two peaks for sisal fibers, one at 300°C associated with hemicellulose decomposition and glycosidic bonds breakage and the other at 360°C relative to α-cellulose decomposition. Jandura et al. [29] showed one peak at 337°C for sulfite *Pinus sp.* fiber while Wielage et al. [25] showed a decomposition peak at 323°C for microcrystalline cellulose. Soares et al. 1995 reported a decomposition peak at 350°C for kraft paper, using a heating speed of 10°C.min^{-1}.

The DTA analyses showed endothermic decomposition peaks at 364°C and 365°C for the reference and the UV irradiated samples, which were likely related to carbohydrate decomposition through cleavage of glycosidic bonds. That result showed that the average energy required for pyrolysis is not significantly affected by sample exposure to UV light. Furthermore, the glycosidic bond cleavage is seemingly unaffected by UV irradiation because there were no significant differences in pulp degree of polymerization between the reference and the UV-irradiated pulp samples. By using the



7. Van Krevelen plots for activation energy calculation.



8. Horowitz-Metzer plots for activation energy calculation.

DSC technique, Soares et al. [5] showed the decomposition peak at 362°C for kraft paper, which was associated with depolymerization. Nada et al. [30] showed endothermic peak at 339°C for viscose pulp containing 94.2% of α-cellulose.

Figures 5 and **6** show, respectively, the thermal analysis in air atmosphere for SBI and SAI. In both instances, thermal decomposition occurred in three steps. The first step took place up to 250°C and was associated with pulp dehydration and volatile liberation. In the second step, significant mass loss occurrence was associated with the decomposition of carbohydrates through glycosidic bond breakage. The third step was associated with the oxidation of carbonized materials. The three steps showed close mass loss for both instances, basically indicating no impact of UV irradiation on thermal stability at the oxygen atmosphere.

The thermal analysis in air atmosphere showed two decomposition peaks on DTG curves against just one in N_2 atmosphere. The UV irradiation caused a significant shift (-16°C) of the end peak showing significant reduction on activation energy for final material oxidation, which made combustion much easier when compared to the reference sample. The formation of acid groups during UV exposure may have contributed to the facile oxidative hydrolysis process. The cellulose chains were seemingly broken down to smaller fractions, thus becoming easily oxidized by heating in air atmosphere. Soares et al. 1995 [5] also showed two decomposition peaks in air atmosphere for kraft paper at 324°C and 403°C and Whatman paper at 317°C and 329°C.

The DTA curves in air atmosphere showed two exothermic peaks for both irradiated and nonirradiated samples, which is contrary to the endothermic peak observed in N_2 atmosphere. This behavior may be explained by the presence of oxygen in air, which favors oxidation and combustion reactions, whereas pyrolysis reactions are predominant in N_2 atmosphere. The UV irradiation treatment reduced pulp thermal stability, as demonstrated by a 14°C decrease in the decomposition temperature. Soares et al. 1995 [5] showed two exothermic peaks in air atmosphere for Whatman paper, 345°C and 489°C, and for kraft paper, 343°C and 430°C.

Figures 7 and **8** show Van Krevelen and Horowitz-Metzer plots for activation energy estimation at the first peak (~345°C), where a lower slope for SAI was seen when compared to SBI curves, which indicated lower activation energy for the former sample.

The results presented in **Table IV** confirm the reduction of activation energy for the carbohydrates decomposition (first peak of thermal analyses in air atmosphere, Figs. 5 and 6).

CONCLUSIONS

Ultraviolet irradiation at 360 nm was shown to have no effect on the cellulose degree of depolymerization but it promotes pulp oxidation leading to the formation of carbonyl and carboxyl groups. The irradiation decreases the amount of pulp extractable in acetone but has no effect on the pulp pentosan content.

On the basis of all thermal results, the exposure to UV caused a reduction in the thermal stability of cellulose pulp. The oxidized structures produced during UV irradiation reduced thermal stability by the down shift of activation energy and final decomposition peak, which made combustion easy, but not pyrolysis.

Kinetics analysis based on viscosity or mass loss was not sufficient for evaluating the impact of UV irradiation on the cellulose quality. Such treatment may have no effect on those parameters while significantly affecting the pulp stability, as seen by derivative thermal analyses. **TJ**

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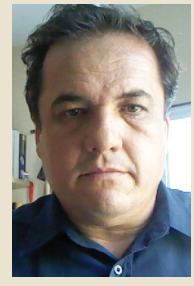
ABOUT THE AUTHORS

The team involved in this work is comprised of experts on natural polymers who have been engaged in the characterization and analysis of the properties of these materials. We focused on the specific interests related to production, because Brazil is a major producer of pulp and paper. The groundbreaking work we conducted serves as a basis for future studies to understand the degradative processes in pulp caused by heat or by the action of incident radiation.



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The main difficulties we encountered were related to understanding the changes provoked in the structure of cellulose after incidence of ultraviolet radiation. The changes occur on the surface and the techniques chosen had to be sensitive enough to ensure the verification of possible modifications. We consider that we were successful in these choices.

On the basis of the thermal results, we concluded that exposure to ultraviolet irradiation causes a reduction in the thermal stability of cellulose pulp. The pulp and paper sector may benefit directly from this work, which showed that exposure of bleached paper to ultraviolet rays can cause irreversible damage to the properties of the product.

We plan to use other radiation sources to study the stability of cellulose fibers. Other exposure times will also be studied because the time factor can be critical for understanding the degradative processes caused by radiation exposure.

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