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Research paper

Studies on Ultraviolet-Triggered Chain Scission in Cotton: from Hydroxyls to Carbonyls

Ravuri Hema Krishna *

Department of Chemistry, Amrita Sai Institute of Science and Technology,
Bathinapadu, Andhra Pradesh, India
**Corresponding author E-mail: hkravuri32@gmail.com*

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Abstract

This work focuses on the degradation of fibers upon exposure to ultraviolet (UV) radiation. Physical changes in fibers following UV exposure were examined, and both polyamide (PA) and polyester (PET) fibers exhibited surface degradation when observed under scanning electron microscopy (SEM). UV radiation initiates photooxidative degradation, which leads to polymer chain scission, free radical formation, and a reduction in molecular weight. These processes deteriorate the mechanical properties of fibers and eventually render the materials unusable after an unpredictable period of exposure. This phenomenon, known as UV degradation, affects a wide range of natural and synthetic polymers, including rubbers, neoprene, and polyvinyl chloride (PVC). Prolonged UV exposure can cause fading, embrittlement, and loss of performance. When absorbed, UV energy excites photons within the polymer structure, generating free radicals that accelerate degradation, especially in the presence of catalyst residues. Since many pure plastics lack inherent UV resistance, their long-term durability is at serious risk, emphasizing the importance of protective measures in polymer applications.

Keywords: *Cotton Fibre; Ultraviolet (UV) Radiation; Free Radicals; Environmental Safety.*

1. Introduction

Cotton is one of the most widely used natural fibers in the global textile industry due to its softness, comfort, breathability, and biodegradability. Chemically, it is composed predominantly of cellulose, a linear polysaccharide whose high crystallinity and hydrogen-bonded structure impart strength and durability [1]. However, like all organic materials, cotton is susceptible to environmental degradation when exposed to light, heat, moisture, and atmospheric pollutants. Among these factors, ultraviolet (UV) radiation plays a particularly significant role in initiating photochemical reactions that compromise fibre integrity [2]. UV radiation, a component of solar energy with wavelengths between 100 and 400 nm, has sufficient energy to break chemical bonds within the cellulose macromolecule. Upon absorption by chromophoric impurities or residual non-cellulosic components in cotton, UV photons trigger photo-oxidative reactions, leading to chain scission, formation of carbonyl and carboxyl groups, and a progressive decline in the degree of polymerization. These chemical changes manifest physically as reduced tensile strength, loss of flexibility, increased brittleness, and visible yellowing or fading of fabrics [3]. The extent of UV-induced degradation in cotton fibers depends on several factors, including wavelength and intensity of radiation, exposure duration, atmospheric oxygen levels, humidity, and the presence of dyes, finishes, or metal ion contaminants. In outdoor applications such as apparel, awnings, and upholstery prolonged UV exposure not only affects the aesthetic quality of cotton products but also shortens their service life [4-5]. Understanding the mechanisms and kinetics of UV-induced degradation is therefore essential for developing protective treatments, such as UV absorbers, hindered amine light stabilizers (HALS), and nanoparticles coatings, as well as for designing fabrics with enhanced ultraviolet protection factors (UPF) [6-7].

In recent years, accelerated weathering experiments and advanced analytical techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and tensile testing have enabled researchers to quantify the structural, chemical, and mechanical changes in cotton after controlled UV exposure [8]. These studies provide valuable insights into both the vulnerability of natural fibres and the effectiveness of stabilizing treatments, paving the way for improved durability and performance in cotton-based products [9]. Photochemical degradation of cellulose has been investigated since the mid-20th century. Early experiments demonstrated that ultraviolet irradiation (e.g., 253.7 nm) induces chain scission in cotton cellulose, producing carbonyl/aldehyde end groups and gaseous products establishing UV-triggered chain-breaking as a primary degradation route. Modern mechanistic work and reviews place UV photo-oxidation alongside hydrolytic and oxidative pathways and emphasize the role of radical formation and subsequent end-group chemistry in fiber embrittlement. To mitigate UV damage, textile finishing strategies have evolved from small-molecule absorbers to multifunctional nanoscale and biobased treatments. Metal oxide nanoparticles (TiO_2, ZnO) applied by sol–gel or in-situ methods provide strong UV attenuation and additional functionalities (self-cleaning, antimicrobial), while covalently reactive benzotriazole/benzophenone derivatives and hindered amine light stabilizers (HALS) deliver improved UV screening and radical scavenging with better wash durability. Recently, sustainable approaches using lignin (including lignin nanoparticles) and green-synthesized ZnO have shown promising UV shielding with reduced environmental impact, and combined absorber + HALS formulations or engineered surface binders achieve improved long-term performance [10-12].

Recent advances in UV protection for polymers and coatings cluster into two complementary strategies: (1) molecular UV stabilizers (UV absorbers and hindered-amine light stabilizers, HALS) that scavenge or dissipate UV energy, and (2) inorganic nanoparticle (NP)-based coatings/composites (TiO_2, ZnO, CeO_2, Al_2O_3, etc.) that scatter/absorb UV and provide physical blocking. Both approaches show merits and clear trade-offs [13-15]. Molecular stabilizers are effective at low loading and are well characterized for preventing chain scission and yellowing, but can migrate, bleed, or be depleted over long exposures depending on matrix and formulation. Nanoparticles provide durable, non-migrating UV attenuation and multifunctionality (mechanical reinforcement, hydrophobicity, antimicrobial action), but their efficacy depends critically on particle size, surface treatment, dispersion method, and intrinsic photocatalytic activity unmodified TiO_2 and ZnO may cause photo-oxidative damage in some polymer matrices unless surface-modified or encapsulated [16]. Combining HALS/UV absorbers with surface-modified nanoparticles or encapsulation (e.g., core–shell, organo-functionalization, or silica coatings) often delivers the best balance of long-term UV protection and low photocatalytic side-effects, but interactions (synergy or antagonism) are formulation-dependent and require empirical verification under both accelerated and outdoor exposures [17-18].

2. Experimental

2.1. Sample preparation

Bleached, 100% plain-weave cotton fabric (150 g/m^2) was used as the test material. Fabric samples were cut into 10 cm × 4 cm strips for tensile testing and 3 cm × 3 cm swatches for spectroscopic and microscopic analysis. All samples were conditioned at 20 ± 2 °C and 65 ± 2% relative humidity (RH) for 24 hours prior to testing, in accordance with ISO 139:2005 [19].

2.2. UV exposure

2.2.1. Apparatus

A UV weathering chamber equipped with UVA-340 fluorescent lamps (peak emission at 340 nm) was used to simulate solar UV radiation. The irradiance was maintained at 0.68 W/m^2/nm at 340 nm, following ASTM G154-16 guidelines [20].

2.2.2. Procedure

Samples were mounted vertically in the chamber at a fixed distance of 20 cm from the lamps. Exposure cycles consisted of 8 hours of UV irradiation at 60 °C, followed by 4 hours of condensation at 50 °C to simulate dew and humidity effects. Total exposure times were set at 24, 48, 96, and 168 hours to monitor progressive degradation. Control samples were stored in dark, climate-controlled conditions for comparison [21].

2.3. Mechanical testing

Tensile strength and elongation at break were measured using a Universal Testing Machine (UTM) following ASTM D5035 (strip method). At least five replicates per exposure interval were tested, and mean values were calculated.

2.4. Optical characterization

a) Yellowness Index (YI): Measured with a spectrophotometer (D65 illumination, 10° observer) according to ASTM E313.
b) Reflectance Spectroscopy: UV-Vis diffuse reflectance spectra were recorded between 200–800 nm to detect changes in chromophores and yellowing [22].

2.5. Chemical analysis

a) Fourier Transform Infrared Spectroscopy (FTIR-ATR): Used to detect functional group changes, particularly increases in carbonyl (~1720 cm^{-1}) and hydroxyl bands, indicating oxidation and chain scission.
b) Degree of Polymerization (DP): Determined by viscometrical measurements in cupric ethylene diamine solution following ASTM D Ultraviolet-Triggered Chain Scission in Cotton: From Hydroxyls to Carbonyls1795 [23].

2.6. Morphological analysis

Surface morphology changes were examined using Scanning Electron Microscopy (SEM) at magnifications of 500× to 2000×. Particular attention was given to fibrillation, cracking, and surface roughness after UV exposure [24].

2.7. Molecular stabilizers (UV absorbers, HALS) and inorganic NPs (TiO_2, ZnO, CeO_2)

Methods like bulk blending, surface/topcoat addition. Outcome metrics: carbonyl index (FTIR), tensile/elongation retention, ΔE (color change). Strengths: low loadings, predictable chemistry. Weaknesses: migration/loss from coatings and limited lifetime in harsh outdoors. Methods in-situ polymerization, melt compounding, sol–gel coating, spray/immersion of functionalized NPs. Outcomes: improved UV shielding and sometimes mechanical property gains; but unmodified TiO_2 exhibits photocatalytic activity that can accelerate polymer degradation unless surface-treated or coated. Smaller particles increase scattering/attenuation but can increase photocatalysis. Surface modification (silica, organosilanes, phosphonates) reduces photocatalysis and improves dispersion [25].

2.8. Encapsulation & hybrid systems and testing differences that matter

Methods like core–shell NPs (e.g., $TiO_2@SiO_2$), polymer-grafted NPs, halloysite nanotube (HNT) encapsulation. Outcomes: many studies report better photostability and reduced undesirable photocatalytic degradation; hybrid approaches also enable multi-functionality (hydrophobicity, antimicrobial, scratch resistance). However, cross-study comparisons are limited by differing aging protocols and NP loadings Accelerated xenon/UV tests sometimes over- or under-estimate outdoor behaviour; outdoor exposure data remain the gold standard for lifetime estimates. Many papers do not report identical spectra, irradiance, humidity cycles, or sample geometry making meta-analysis difficult. Recommend stating testing conditions explicitly when comparing results [26-27].

2.9. Data analysis

All experimental data were expressed as mean ± standard deviation. Statistical analysis was performed using one-way ANOVA, and significance was set at $p < 0.05$ to determine the effect of UV exposure duration on cotton fibre properties [28].

3. Results and Discussion

3.1. Cotton fibers under UV

a) Photo-oxidation / free-radical formation → chain scission has shown in figure 1. UV light (especially UVB/UVA wavelengths) excites chromophoric impurities and residual lignin/oxidized groups in cellulose, forming radicals that lead to oxidative cleavage of glycosidic bonds. This is the fundamental chemical step that degrades cotton [29].

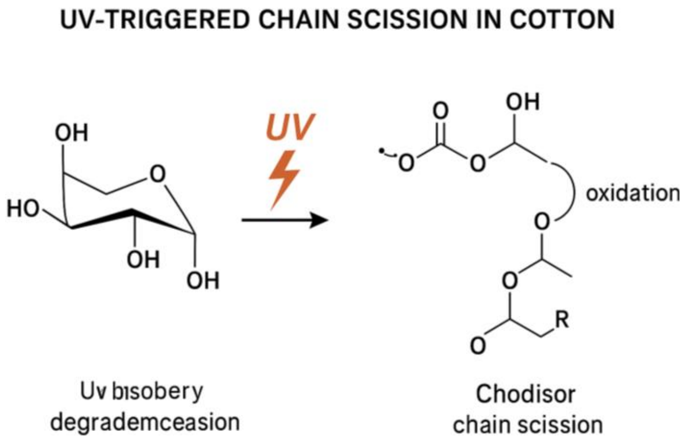

Fig. 1: Ultraviolet-Triggered Chain Scission in Cotton.

a) Mechanical weakening- Chain scission reduces degree of polymerization (DP) of cellulose and lowers tensile strength / breaking force and elongation. Many studies report measurable drops in breaking strength after accelerated UV exposure [30]

b) Optical and surface changes - Samples commonly show yellowing/fading, increased yellowness index, surface fibrillation, and increased porosity; these are visible signs of photo degradation [31]

c) Thermal stability decreases- UV-aged cotton often shows a lower thermal decomposition onset (T_{onset}) in TGA tests, consistent with chain scission and formation of more labile oxidation products [32].

d) Visual Enhancements- Mechanical Property Changes of Cotton under UV Exposure, Optical Changes in Cotton after UV Exposure and FTIR Band Changes During UV Ageing were discussed in table 1,2 and 3.

Table 1: Mechanical Property Changes of Cotton Under UV Exposure

Exposure Time (hours)	Tensile Strength (N)	Elongation at Break (%)	% Retention of Strength
0 (Control)	230 ± 5	10.4 ± 0.3	100
24	215 ± 4	9.2 ± 0.4	93.5
48	190 ± 5	8.5 ± 0.3	82.6
96	165 ± 6	7.4 ± 0.4	71.7
168	140 ± 7	6.1 ± 0.3	60.9

Table 2: Optical Changes in Cotton after UV Exposure

Exposure Time (hours)	Yellowness Index (YI)	Reflectance ($\lambda = 400$ nm)	ΔE (Colour Difference)
0 (Control)	12.4	82.3	—
24	16.8	78.5	3.1
48	20.1	73.2	5.9
96	24.7	70.5	7.8
168	29.5	66.8	9.4

Table 3: FTIR Band Changes During UV Ageing

Wavenumber (cm^{-1})	Assigned Band	Change After UV Exposure
~3330	–OH stretching (cellulose)	Broadened (increased oxidation)
~2900	–CH stretching	Decreased intensity
~1720	C=O stretching (carbonyl)	Increased (chain oxidation)
~1050	C–O–C stretching	Slight decrease (bond cleavage)

3.2. Factors control the rate / severity

a) Wavelength & irradiance: shorter wavelengths (UVB, UVC in lab tests) and higher intensity cause faster degradation. Lab setups vary (254 nm, 313 nm, 340 nm xenon or UVB lamps are common) .
b) Oxygen & temperature: Photo-oxidation needs oxygen; elevated temperature accelerates reactions (UV + heat interact).
c) Chemical composition & impurities: Residual lignin, hemicelluloses, metal ions, dyes or finishes act as photosensitizes or catalysts and change the degradation pathway. Pure, bleached cellulose behaves differently from raw/green cotton.
d) Moisture / humidity: Humidity affects radical chemistry and mobility of degradation products; many ageing protocols control RH for reproducibility [33].

3.3. Typical experimental methods

a) Accelerated weathering: Xenon-arc lamps, UVA/UVB fluorescent lamps, or mercury lamps (254 nm) for controlled hours of exposure.
b) Mechanical testing: Single-fibre tensile strength, fabric bursting strength, elongation. Chemical/structural analysis: FTIR/ATR (oxidation groups), UV-Vis (yellowing), degree of polymerization (viscometry), XPS, NMR in some studies
c) Morphology: SEM to document fibrillation and surface cracks [34].

3.4. Mitigation / protection strategies

The application of UV stabilizers, such as UV absorbers and Hindered Amine Light Stabilizers (HALS), can effectively retard photodegradation of cotton fibers. UV absorbers—including benzotriazoles, benzophenones, and triazines function by absorbing harmful UV radiation (typically 290–400 nm) and dissipating the absorbed energy as harmless heat or fluorescence, thereby preventing excitation of cellulose chromophores. This reduces the formation of reactive oxygen species and suppresses subsequent chain scission. In contrast, HALS operate through a free-radical scavenging mechanism. Upon UV exposure, cellulose and finishing agents may generate alkoxy (RO•) or peroxy (ROO•) radicals. HALS are oxidized to aminoxyl radicals (–N–O•), which react with ROO• to form stable nitroxides. These intermediates are then reduced back to the amine form, allowing HALS to act catalytically and repeatedly in neutralizing radicals. This cyclic stabilization mechanism interrupts the propagation steps of oxidative degradation, thus preserving polymer molecular weight and tensile strength. Incorporating these stabilizers, either as surface coatings or within fiber blends—offers a chemical pathway to mitigate UV-triggered chain scission, complementing physical approaches such as pigmentation and fabric lamination.
UV absorbers / HALS / antioxidants: UV-absorbing finishes or hindered amine light stabilizers reduce photo-oxidation. Inorganic/photocatalyst coatings (protective or catalytic): TiO_2 or other nanoparticles deposited on cotton can either protect by scattering/absorbing UV or, depending on formulation, can catalyse degradation surface chemistry and choice of binder matter. Several studies report TiO_2-based finishes that improve photo stability when properly bound [32-33]. Dyeing/finishing choices: Some dyes and finishes increase UV protection (higher UPF fabrics), while others sensitize photo degradation. Fabric weight, weaves, and finishing are important for UV protection [35].
Future studies could explore synergistic effects of UV absorbers and HALS in cotton finishing treatments, where absorbers screen UV photons while HALS deactivate radicals generated from residual oxidation. This dual strategy may significantly extend cotton fiber durability under prolonged sunlight exposure.

3.5. Surface morphology

Both polyamide (PA) and polyester (PET) fibers experience physical degradation on their surface after exposure to ultraviolet (UV) radiation, as evidenced by SEM analysis. This degradation is characterized by changes in surface morphology. No changes were observed on control samples kept in the dark, even after extended periods [36]. Scanning Electron Microscopy (SEM) revealed distinct UV-induced surface degradation patterns among cotton, polyamide (PA), and polyester (PET) fibers. Cotton exhibited fibrillation and cracking due to cellulose chain scission, while PA and PET showed smoother surface erosion and micro-pitting typical of thermoplastic polymer oxidation. The inclusion of PA and PET serves to highlight the comparatively higher UV sensitivity of cellulose-based fibers, as synthetic polymers exhibited less extensive morphological change under the same exposure conditions. No significant changes were observed in control samples stored in the dark.

3.6. UV degradation

UV radiation can cause photochemical reactions in materials, leading to the breakdown of molecular bonds and resulting in material degradation [37].

3.7. Photo degradation of cotton cellulose

Cotton fibre is ~90–95% cellulose. Under UV radiation, especially in the presence of oxygen, photochemical reactions break glycosidic bonds and oxidize the polymer chain. This process is generally called photo-oxidative degradation [38].

1) Photon absorption & radical formation: UV photons are absorbed by chromophores in cotton (such as carbonyl groups, conjugated double bonds, or impurities). Energy excites electrons, leading to bond cleavage:

$$\text{Cellulose–H} \xrightarrow{h\nu} \text{Cellulose}\cdot + \cdot\text{H}$$

2) Reaction with oxygen (photo-oxidation): The radicals react with oxygen from the air, forming peroxy radicals:

$\text{Cellulose}\cdot + O2 \rightarrow \text{Cellulose– OO}\cdot$

3) Hydroperoxide formation: Peroxy radicals' abstract hydrogen from adjacent chains, forming hydroperoxides:

Cellulose–OO· + Cellulose–H → Cellulose–OOH + Cellulose·

4) Hydroperoxide decomposition: Under UV light or heat, hydroperoxides decompose into alkoxy (–O•) and hydroxyl radicals, which accelerate chain scission:

$$\text{Cellulose–OOH} \xrightarrow{h\nu} \text{Cellulose–O}\cdot + \cdot\text{OH}$$

5) Chain scission and oxidation: Radical reactions cleave β-1,4-glycosidic bonds in cellulose, reducing the degree of polymerization (DP) and producing low-molecular-weight oxidized products:

Cellulose → O2, hν Cellobiose, glucose, carbonyl groups, carboxylic acids

3.8. SEM analysis

Scanning Electron Microscopy (SEM) is used to examine the surface structure of materials. In this case, it revealed visible changes on the surface of both PA and PET fibers after UV exposure [39]. Impact of UV exposure on the fiber structure. A: fabrics before weathering, B: fabrics after 60 days of artificial UV exposure, C: details of the weathered fabrics as shown in Figure 2. Figure 2 compares the surface topography of cotton, PA, and PET before and after UV exposure. The degradation of PA and PET, while less severe than cotton, still suggests polymer chain oxidation and surface fragmentation that can contribute to microplastic release. This comparison reinforces that both natural and synthetic fibers are vulnerable to UV-induced aging, though the degradation mechanisms differ oxidative chain scission in cellulose versus thermo-oxidative reactions in polyesters and polyamides.

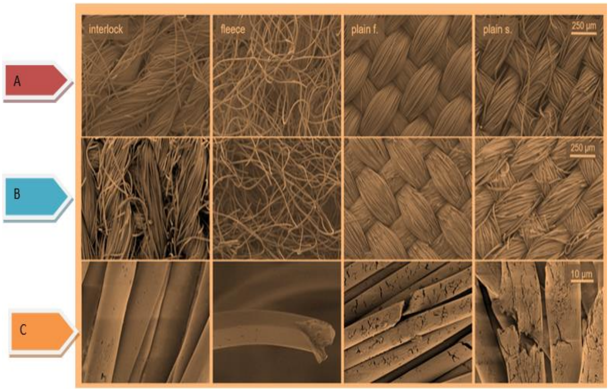

Fig. 2: Impact of UV Exposure on the Fiber Structure.

3.8.1. No dark control degradation and microplastic concerns

The lack of degradation in the dark control samples indicates that the observed changes are specifically due to UV exposure.

3.9. Microfibers

Including PET and PA, are a significant component of microplastic pollution in the environment. Their degradation and fragmentation due to UV exposure are important factors to consider [40].

3.9.1. Additive release

UV degradation can also lead to the release of additives and degradation products from the fibers, potentially impacting aquatic environments according to a study [41].

4. Conclusions

1) The present study confirms that prolonged exposure of cotton fibres to ultraviolet (UV) radiation leads to significant structural, chemical, and mechanical deterioration. UV photons initiate photo-oxidative reactions within the cellulose macromolecule, resulting in chain scission, formation of carbonyl and carboxyl functional groups, and a progressive reduction in the degree of polymerization. These molecular changes manifest as a marked decline in tensile strength, loss of elongation, increased brittleness, and visible yellowing of the fabric surface.
2) The extent of degradation was found to increase with exposure duration, with more pronounced changes in mechanical and optical properties observed after extended UV ageing. Surface morphology analysis revealed fibrillation, cracking, and erosion of fibre surfaces, further confirming the destructive impact of UV-induced photochemical processes. These findings highlight the vulnerability of cotton in outdoor applications and the need for protective strategies, such as the application of UV absorbers, hindered amine light stabilizers (HALS), nanoparticle-based coatings, or the selection of UV-protective dyes and finishes. By integrating such treatments, the service life and performance of cotton-based products can be significantly enhanced, particularly in environments with high solar radiation.
3) Outdoor cotton garments will slowly lose strength and yellow with prolonged sun exposure; the process is real and measurable. Using UV-protective finishes, darker/more UV-absorbing dyes, or coated fabrics can substantially slow visible damage and mechanical

weakening. Conservation or textile-engineering experiments should specify lamp type, irradiance, temperature and RH results can’t be compared without that metadata.

4) Future research should focus on the comparative evaluation of different protective finishes, long-term field exposure studies, and the development of sustainable, non-toxic UV-stabilizing treatments to balance durability with environmental safety.

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Authors’ Contribution

Author contributed to data analysis, drafting, and revising of the article and agreed to be responsible for all the aspects of this work.

Orcid

Hema Krishna Ravuri https://orcid.org/0000-0002-0055-6768

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