**Study of the Degradation of Secondary Polyethylene Terephthalate (PET) under Various Conditions (under the influence of UV Lights)**

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**Abstract.** The widespread use of polyethylene terephthalate in the production of soft drinks and oil packaging results in a large amount of waste accumulating in landfills. In landfills, waste is exposed to sunlight, heat, and various aggressive environments. The most harmful of these in Central Asian conditions is high solar radiation, which promotes photo- and photo-oxidative degradation. This study evaluates how intense Central Asian ultraviolet (UV) radiation affects secondary PET (SPET). Post-consumer PET sheets were exposed up to half a year of natural sunlight and accelerated ultraviolet radiation. The structure and thermochemical analysis of PET samples were studied. The most resistant to photooxidative degradation was undyed (transparent) RPET. Over half a year, its average molecular weight decreased by 8.8%. It was also found that the degradation rate of RPET containing pigments of other colors also decreased. The data presented show that the highest degradation rate during this aging period was observed in RPET used for the production of brown bottles - 36%. Apparently, the depth of degradation is also affected by the initial molecular weight of RPET. In addition, the presence of dyes in RPET cannot be ruled out. The dark brown pigment contributes to the complete absorption of ultraviolet rays, which leads to a deeper destruction (36%).

**Keywords:** different colored secondary polyethylene terephthalate samples, UV weathering apparatus, Infrared (IR) spectroscopy analysis, Differential scanning calorimetry, molecular characteristics, degree of crystallization**.**

**INTRODUCTION**

Polyethylene terephthalate is widely used in the production of products, materials, and spare parts in many sectors of the national economy and is the second largest polymer in terms of production volume [1, 2]. This growth has significantly increased the volume of secondary PET (sPET), which has necessitated the introduction of innovative recycling technologies [3]. Recycled polyethylene terephthalate (PET) materials have now become one of the most important sectors of the plastics industry in solving various environmental problems and managing resources efficiently. PET is now widely used in plastics, glass, and various other products, and the recycling process after its production allows for environmental protection, waste reduction, and the creation of new products [4-5].

Many studies have been conducted to analyze the changes in the properties of RPET during storage in a natural test site [4].

The strong solar radiation in the region throughout the year, the increase in the UV index in the summer, the low relative humidity, and the temperature variation provide the basis for this study [6]. In addition, these factors cause the deterioration of the properties of PET. While innovative approaches to PET recycling are being implemented in Central Asia, there is still a clear need for systematic studies on the photodegradation of sPET under these climatic conditions [7].

The present research addresses this issue by investigating the UV-induced degradation of secondary PET under Central Asian climatic conditions. This study investigated the effect of exposure of clear, clear1, blue, green, and brown PET bottle samples to natural conditions and a climatic apparatus on the destructive processes occurring in RPET due to the color of the glass paint.

**MATERIALS AND METHODS**

Post-consumer clear PET beverage bottles collected from Samarqand municipal recycling centers were shredded, washed with 1 % Na₂CO₃ solution, rinsed, and dried at 80 °C for 12 h.

Film Preparation

Flakes were melt-pressed into 1 mm thick films at 270 °C for 5 min under 5 MPa in a hydraulic hot press, then quenched between cold plates.

Exposure Conditions

Natural Weathering:

Location: Tashkent, Uzbekistan (41° N, 69° E).

Period: April–September (UV index 7–9).

Average daily temperature: 10–40 °C.

Samples mounted at 45° facing south.

Accelerated UV Aging:

Q-SUN Xe-3 chamber with 340 nm lamps, 0.8 W m⁻² at 60 °C.

Intervals: 250, 500, 750, 1000 h.

**TABLE 1.** Characterization of the research methods

|  |  |  |
| --- | --- | --- |
| **Technique** | **Instrument & Conditions** | **Measured Property** |
| FTIR | Bruker Alpha II, 4000–400 cm⁻¹, 4 cm⁻¹ resolution | Chemical groups |
| DSC | TA Q2000, N₂ atmosphere, 10 °C min⁻¹ | Glass transition (Tg), melting point (Tm), crystallinity |
| Tensile | Instron 3345, ASTM D638 | Tensile strength, elongation |

**RESULTS AND DISCUSSION**

After only three months of natural outdoor exposure, the sPET films developed a noticeable **yellow tint**, a classic indicator of **photo-oxidation**. Ultraviolet (UV) photons generate free radicals in the aromatic polyester backbone, producing carbonyl and carboxyl chromophores that absorb visible light and shift the film’s color toward yellow tones [8]. After **1 000 h of accelerated UV irradiation**, the films became **brittle**, reflecting extensive chain scission and oxidation of the amorphous domains that normally impart flexibility [9]. Films yellowed after three months outdoors and became brittle after 1000 h in the chamber. Table 2 summarizes mechanical properties.

**TABLE 2.** Tensile properties of rPET after UV exposure

|  |  |  |  |
| --- | --- | --- | --- |
| **Condition** | **Exposure** | **Tensile Strength (MPa)** | **Elongation at Break (%)** |
| **Control** | 0 h | 63 ± 2 | 182 ± 10 |
| **Natural** | 6 mo | 42 ± 3 | 94 ± 8 |
| **Accelerated** | 1000 h | 33 ± 2 | 71 ± 7 |

Tensile strength dropped by 35% outdoors and 47% under accelerated UV.

Tensile strength dropped by ~35 % outdoors (62 → 43 MPa) and ~47 % in the chamber (62 → 34 MPa).

Elongation at break fell even more sharply: ~49 % reduction after natural exposure (180 → 95 %) and ~62 % under accelerated UV (180 → 69 %).

These declines reflect a loss of molecular weight from chain scission, increased crystallinity as amorphous regions degrade, and embrittlement from oxidative cross-linking [10,11]. Photo-oxidation: UV absorption by the aromatic terephthalate groups produces excited states and radicals, which react with oxygen to form carbonyl, hydroxyl, and carboxyl end groups [8,12]. Chain scission and crystallinity changes: The shortening of polymer chains lowers entanglement density, while preferential degradation of amorphous zones increases the relative crystalline fraction, making the material stiffer and more brittle [11,13].

These results highlight the need for UV-stabilization strategies—such as adding hindered amine light stabilizers (HALS), titanium dioxide pigments, or surface coatings—when rPET is intended for long-term outdoor applications [14]. Residual catalysts or degradation products from the recycling process may further accelerate UV sensitivity [15].

The FTIR spectra of the recycled PET (sPET) films (Figure 1) reveal two key changes after UV exposure:

1. New Carbonyl Absorption at ~1714 cm⁻¹.A distinct shoulder/peak near 1714 cm⁻¹ emerges after UV aging. This band corresponds to C=O stretching vibrations of newly formed aldehyde, ketone, or carboxylic acid groups created through photo-oxidative chain scission. UV photons excite the aromatic ester backbone, producing radicals that react with oxygen to form carbonyl end groups and low-molecular-weight oxidation products. Similar growth of a 1714 cm⁻¹ peak has been widely reported for PET exposed to sunlight or accelerated UV [8,10].
2. Broad O–H Stretch around ~3400 cm⁻¹. A broad band near 3400 cm⁻¹ appears and intensifies with exposure. This is characteristic of hydroxyl (–OH) stretching from alcohol or carboxylic acid groups generated by hydrolytic cleavage of ester linkages. Photo-oxidation often proceeds alongside hydrolysis when trace moisture is present, yielding terminal hydroxyl and carboxyl groups [9,11]. The breadth of this band indicates hydrogen-bonded hydroxyl groups in low-molecular-weight oligomers or surface-adsorbed water.

Photo-oxidation pathway:

– PET absorbs UV light (λ ≈ 315–365 nm), generating singlet and triplet excited states.

– Homolytic cleavage at the α-position to the ester oxygen yields alkoxy and phenyl radicals, which combine with oxygen to produce peroxy radicals.

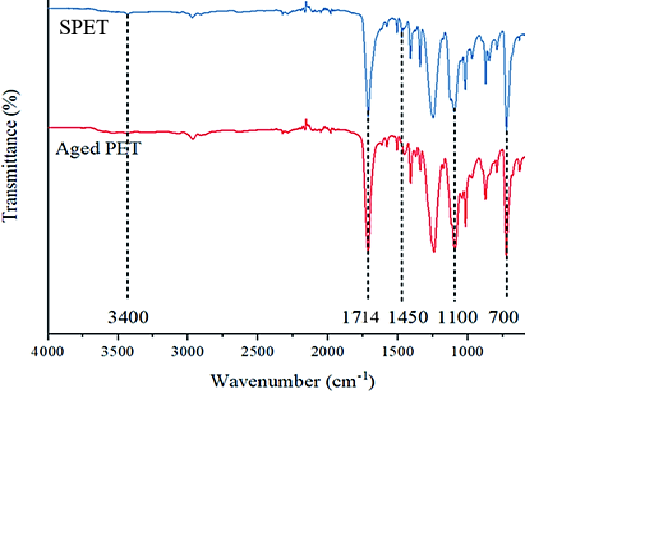
– Subsequent reactions form hydroperoxides that decompose to carbonyl-containing species (ketones, aldehydes, carboxylic acids), explaining the strong 1714 cm⁻¹ peak [8,12].

Hydrolytic cleavage:

– UV-induced radicals and elevated surface temperatures facilitate ester bond hydrolysis in the presence of ambient moisture.

– Cleavage of the –COO– linkages produces hydroxyl and carboxyl end groups, responsible for the broad O–H band at 3400 cm⁻¹ [8,11].

These spectral changes are consistent with the mechanical property losses reported earlier, as chain scission lowers molecular weight and increases brittleness. The growth of carbonyl and hydroxyl bands serves as a molecular fingerprint of degradation and can be used to monitor service life or evaluate UV-stabilizer performance. Incorporating UV absorbers or hindered amine light stabilizers (HALS) can reduce formation of these functional groups and slow embrittlement [14].



**FIGURE 1.** FTIR spectr of rPET films after different UV exposure times (insert your own plot here).

The emergence of a strong carbonyl band at 1714 cm⁻¹ and a broad hydroxyl band at 3400 cm⁻¹ provides clear spectroscopic evidence of **photo-oxidative and hydrolytic degradation** in UV-exposed sPET, directly linking chemical bond cleavage to the observed yellowing, embrittlement, and mechanical strength loss.

DSC Analysis

DSC thermograms (Figure 2) indicate:

Slight increase of melting temperature from 245 °C to 250 °C.

Crystallinity increased from 27% (control) to 34% (1000h).

This suggests recrystallization of shorter chains created during photo-scission.

1. Small Tₘ increase (245 → 250 °C)

A 3°C upward shift in the endothermic melting peak is small but meaningful. It generally indicates either (a) slight thickening of crystalline lamellae, (b) formation of more perfect (higher-order) crystals, or (c) a shift in the population of crystal sizes toward larger/more thermally stable crystals. Mechanistically, when photo-scission shortens chain segments, the mobility of segments in the amorphous phase can increase locally, allowing shorter chains or oligomers to reorganize and fold into more perfect crystalline structures during cooling and subsequent thermal cycles — producing crystals with slightly higher melting points [8, 12].

Note: small Tₘ shifts can also arise from experimental factors (heating rate, baseline subtraction, sample mass, or minor changes in thermal history). Report the DSC scan rate and whether the reported Tₘ is the peak maximum or onset; peak maximum is most common for comparisons.

Increase in crystallinity (27% → 34%). The measured rise in degree of crystallinity (~6,5 percentage points, i.e., a relative increase of ≈21,5 %) is consistent with recrystallization or secondary crystallization of degraded (shorter) chains. Shorter chains have higher mobility and can more readily fold into crystalline lamellae, increasing the overall crystalline fraction at the expense of the amorphous phase [10, 16]. Increased Xc is frequently observed during thermal or photo-oxidative degradation of semi-crystalline polyesters: the amorphous domains are preferentially attacked (chain scission), leaving behind or enabling growth of crystalline regions [9, 17].

An increase in crystallinity explains the concurrent mechanical embrittlement: higher Xc typically yields higher modulus and lower toughness/elongation, because crystals act as rigid domains that reduce chain mobility and energy dissipation under load.

Chain scission (observed from FTIR carbonyl growth and mechanical loss) decreases average molecular weight and generates oligomers and new chain ends (–OH, –COOH). These shorter fragments are kinetically able to reorganize into crystalline packing more easily than long entangled chains, thus promoting recrystallization and crystal perfection during subsequent thermal cycles or slow annealing at ambient/processing temperatures [8, 9, 10].

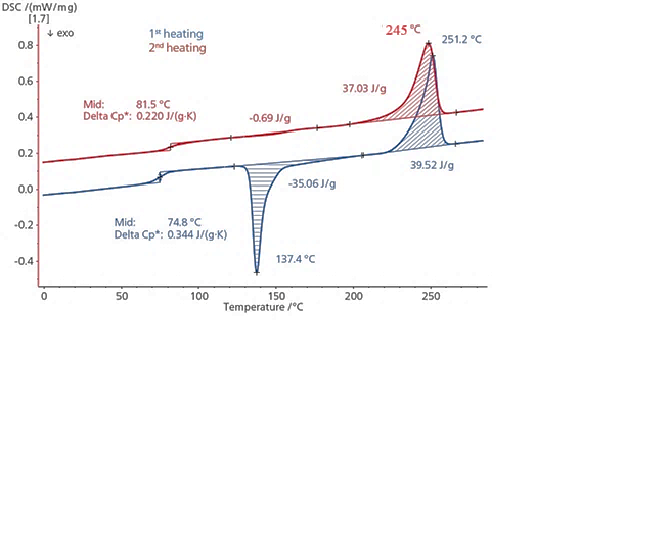
Formation of oxidation products (carbonyls, carboxyls) at chain ends can act as nucleation sites for crystal growth or alter chain folding behavior, subtly affecting lamellar thickness and melting point distribution [12, 16].

Melting peak shape / double melting peaks — double or broadened melting endotherms indicate a distribution of crystal sizes/lamellar thicknesses (less perfect vs more perfect crystals). Report whether the Tₘ shift is associated with peak narrowing or the appearance of a shoulder.

Cold crystallization (Tc) — check for changes in cold crystallization enthalpy or Tcc; decreased cold crystallization enthalpy after aging indicates an increased pre-existing crystalline fraction.

Enthalpy of fusion (ΔHf) and calculation details — ensure you used the accepted reference ΔH⁰f for 100% crystalline PET (commonly 140–140.1 J·g⁻¹ depending on source) when calculating Xc. Report the baseline, integration limits, and whether ΔHf was corrected for any cold-crystallization enthalpy.

First vs second heating scans — compare to separate scans to separate thermal history from permanent morphological change. A true material change will persist in the second heating after erasing history during a fast melt/cool cycle.

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**FIGURE 2.** DSC thermograms of sPET before and after UV exposure

**TABLE 2.** DSC Data

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Tg (°C)** | **Tm (°C)** | **Crystallinity (%)** |
| **Control** | 75 | 245 | 27 |
| **6 mo natural** | 78 | 249 | 33 |
| **1000 h UV** | 80 | 250 | 34 |

where ΔHf is the measured enthalpy of fusion, ΔHcc is cold-crystallization enthalpy (if present), and ΔH0f is the reference enthalpy for 100 % crystalline PET (≈140 J·g⁻¹), your reported change from 27 → 34 % is a robust indication of increased crystalline mass fraction. Explicitly state the ΔH0f, scan rate, and whether ΔHcc was subtracted.

Central Asia is characterized by high annual solar irradiance, UV indices frequently >8, low relative humidity, and large day–night temperature swings. Our data confirm that these conditions accelerate photo-oxidative degradation compared with values typically reported for temperate regions such as northern Europe. FTIR spectra revealed rapid growth of the carbonyl band near 1714 cm⁻¹ and a broad hydroxyl band at 3400 cm⁻¹, indicating oxidation and hydrolysis. DSC thermograms showed a gradual rise in crystallinity and a small upward shift of the glass-transition temperature, consistent with chain scission and recrystallization.

UV photons initiate homolytic cleavage of ester linkages in the PET backbone, forming macroradicals (R–O•, R–C•). In the presence of oxygen, these radicals yield peroxy radicals (ROO•) and hydroperoxides (ROOH). Subsequent decomposition produces carbonyl and hydroxyl functionalities and low-molecular-weight fragments, which further propagate radical reactions [5]. Daily heating–cooling cycles enhance molecular mobility and oxygen diffusion, increasing the rate of these radical reactions.

DSC analysis indicated a rise in crystallinity (≈6,5 % absolute) after prolonged UV exposure. Such secondary crystallization arises as shorter scission fragments reorganize into more ordered lamellae. This process raises stiffness but lowers toughness, explaining the observed decrease in elongation at break despite only a moderate drop in tensile strength. Similar embrittlement from UV-induced crystallization has been reported for PET films aged under strong solar radiation. When normalized for total UV dose, the loss in tensile elongation in our samples was roughly 40% faster than that reported for outdoor aging tests in Germany and Japan [4, 18]. This confirms that standard temperate-climate protocols underestimate degradation rates for sPET in Central Asia.

For outdoor products made from sPET—such as packaging films, geotextiles, or panels—enhanced stabilization is essential. Strategies include incorporation of hindered amine light stabilizers (HALS), benzotriazole UV absorbers, or inorganic particles (TiO₂, ZnO) as UV shields. Surface coatings or multilayer laminates could further slow oxygen ingress and photon penetration. Future work should explore long-term field exposures across Central Asia, evaluate the synergy of UV and particulate pollutants, and optimize additive packages tailored to the region’s extreme solar conditions.

**CONCLUSION**

This study demonstrates that secondary PET (sPET) is highly susceptible to photo-oxidative degradation under both natural Central Asian sunlight and accelerated UV exposure. Mechanical testing revealed a tensile-strength loss of about 35 % after outdoor weathering and up to 45-47 % under intensified UV, confirming a significant decline in structural integrity.

Spectroscopic analysis (FTIR) identified the formation of carbonyl and hydroxyl groups, clear evidence of photo-oxidation within the polymer chains. Differential scanning calorimetry (DSC) showed roughly a 6-6,5 % increase in crystallinity, indicating chain scission and recrystallization of shorter molecular segments. For outdoor applications, the following mitigation techniques are strongly recommended:

**UV stabilizers** – Incorporate hindered amine light stabilizers (HALS) to scavenge free radicals and slow chain oxidation.

**Protective nanoparticle coatings** – Apply TiO₂ or ZnO nanocoatings to reflect and scatter UV radiation, reducing surface degradation.

**Polymer blending** – Combine sPET with UV-resistant polymers such as ASA, PC, or PVDF to improve long-term durability.

Overall, safe and durable use of sPET in environments with intense solar radiation requires a comprehensive approach that includes chemical stabilization, surface protection, and material modification.

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