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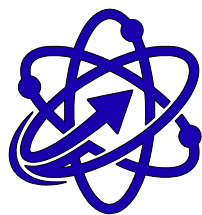
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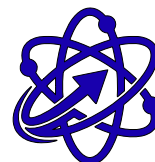
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# STUDY ON THE DEGRADATION OF POLYETHYLENE TEREPHTHALATE WASTE UNDER THE INFLUENCE OF ULTRAVIOLET (UV) RADIATION

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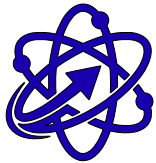
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**Abstract.** The widespread use of polyethylene terephthalate in the production of soft drinks and oil packaging results in a large amount of waste accumulating in landfills. In landfills, waste is exposed to sunlight, heat, and various aggressive 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.*

**Annotatsiya.** Polietilen tereftalatning alkogolsiz ichimliklar va moyli qadoqlash ishlab chiqarishda keng qo'llanilishi poligonlarda ko'p miqdorda chiqindilar to'planishiga olib keladi. Poligonlarda chiqindilar quyosh nuri, issiqlik va turli xil agressiv muhitlarga duchor bo'ladi. Markaziy Osiyo sharoitida ulardan eng zararlisi yuqori quyosh nurlanishi bo'lib, u foto va fotooksidlovchi parchalanishni kuchaytiradi. Ushbu tadqiqotda Markaziy Osiyo ultrabinafsha (UB) nurlanishining



ikkilamchi PET (IPET) ga qanday ta'sir qilishi o'rganilgan. Iste'moldan keyingi PET chiqindilari yarim yilgacha tabiiy quyosh nuri va tezlashtirilgan ultrabinafsha nurlanishiga uchragan. IPET namunalarning tuzilishi va termokimyoviy tahlili o'rganildi. Fotooksidlovchi parchalanishga eng chidamlisi bo'yalmagan (shaffof) IPET ekanligi aniqlandi. Yarim yil ichida uning o'rtacha molekulyar og'irligi 8,8% ga kamaydi. Shuningdek, boshqa rangdagi pigmentlarni o'z ichiga olgan IPET ning parchalanish tezligi ham pasayganligi aniqlandi. Taqdim etilgan ma'lumotlar shuni ko'rsatadiki, ushbu degradatsiya davrida eng yuqori parchalanish darajasi jigarrang namunalar ishlab chiqarish uchun ishlatiladigan IPETda kuzatilgan - 36%. Ko'rinishidan, parchalanish chuqurligiga IPET ning dastlabki molekulyar og'irligi ham ta'sir qiladi. Bundan tashqari, IPET tarkibida bo'yoqlar mavjudligini inkor etib bo'lmaydi. To'q jigarrang pigment ultrabinafsha nurlarining to'liq yutilishiga hissa qo'shadi, bu esa chuqurroq yo'q qilinishiga olib keladi (36%).

**Kalit so'zlar:** turli rangli ikkilamchi polietilen tereftalat namunalari, UV nurlanish apparati, infraqizil (IQ) spektroskopiya tahlili, differensial skanerlash kalorimetriyasi, molekulyar xususiyatlari, kristallanish darajasi.

**Аннотация.** Широкое применение полиэтилентерефталата (ПЭТ) при производстве упаковки для безалкогольных напитков и растительных масел приводит к накоплению большого количества отходов на полигонах. На свалках отходы подвергаются воздействию солнечного света, тепла и различных агрессивных сред. Наиболее вредным фактором в условиях Центральной Азии является высокая солнечная радиация, способствующая фото- и фотоокислительной деградации. В данной работе исследовано влияние интенсивного ультрафиолетового (УФ) излучения Центральной Азии на вторичный ПЭТ (ВПЭТ). Отработанные ПЭТ-листы подвергались воздействию естественного солнечного света и ускоренного ультрафиолетового излучения в течение полугода. Были проведены структурные и термохимические анализы образцов ПЭТ. Наиболее устойчивым к фотоокислительной деградации оказался неокрашенный (прозрачный) ВПЭТ. За полгода его средневзвешенная молекулярная масса снизилась на 8,8%. Также установлено, что скорость деградации ВПЭТ, содержащего пигменты других цветов, также снижается. Представленные данные показывают, что наибольшая степень деградации за данный период старения наблюдалась у ВПЭТ, использованного для производства коричневых бутылок — 36%. Очевидно, что глубина деградации также зависит от исходной молекулярной массы ВПЭТ. Кроме того, нельзя исключить влияние красителей, присутствующих в ВПЭТ. Тёмно-коричневый пигмент способствует полному поглощению ультрафиолетовых лучей, что приводит к более глубокой деструкции (36%).

**Ключевые слова:** образцы вторичного полиэтилентерефталата разных цветов, установка для УФ-старения, инфракрасный (ИК) спектроскопический анализ, дифференциальная сканирующая калориметрия, молекулярные характеристики, степень кристаллизации.

## 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 expanded



the volume of secondary PET (SPET), which in turn necessitates the adoption of innovative recycling technologies [3]. Recycled polyethylene terephthalate (PET) materials have become one of the most important areas in the plastics industry today to solve environmental problems and effectively manage resources. PET plastic is widely used in bottles and other products, and its recycling allows for environmental protection, waste reduction, and the creation of new products [4].

Degradation of polymers in open landfills is associated with many factors: sunlight (ultraviolet, visible, infrared), oxygen, water (dew, rain, humidity, snow), heat (temperature) and dust, smoke, nitrogen oxides, sulfur dioxide, carbon monoxide and other components. During recycling and subsequent use, as well as storage, PET is exposed to the combined effects of various chemical environments, temperature and oxygen, the effects of which are synergistically enhanced. This leads to degradation, which occurs through the breaking of bonds between atoms. [5]. The results of many studies allow us to develop recommendations for the production of yarns and fibers with reproducible properties. An important factor in this regard is the study of the original color of RPET during photooxidation processes [1].

A number of scientific studies are being conducted to study the changes in the properties of RPET during storage under natural conditions in a natural test site and in a climate chamber. [4].

The region is characterized by high solar irradiance throughout the year, elevated summer UV indices, low relative humidity, and large diurnal temperature fluctuations [6]. These factors can contribute to the deterioration of PET's molecular characteristics. 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 %  $\text{Na}_2\text{CO}_3$  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.

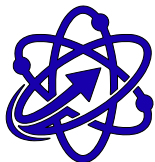
### Exposure Conditions

#### Natural Weathering:

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

**Table 1. Characterization**

Technique	Instrument & Conditions	Measured Property
FTIR	Bruker Alpha II, 4000–400 $\text{cm}^{-1}$ , 4 $\text{cm}^{-1}$ resolution	Chemical groups
DSC	TA Q2000, $\text{N}_2$ atmosphere, 10°C $\text{min}^{-1}$	Glass transition ( $T_g$ ), melting point ( $T_m$ ), crystallinity
Tensile	Instron 3345, ASTM D638	Tensile strength, elongation



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<sup>-2</sup> at 60 °C.

Intervals: 250, 500, 750, 1000 h.

## 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

**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

months outdoors and became brittle after 1000 h in the chamber. Table 2 summarizes mechanical properties.

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<sup>-1</sup>.** A distinct shoulder/peak near **1714 cm<sup>-1</sup>** 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  $1714\text{ cm}^{-1}$  peak has been widely reported for PET exposed to sunlight or accelerated UV [8,10].

2. **Broad O–H Stretch around  $\sim 3400\text{ cm}^{-1}$ .** A broad band near  $3400\text{ cm}^{-1}$  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 ( $\lambda \approx 315\text{--}365\text{ nm}$ ), generating singlet and triplet excited states.
- Homolytic cleavage at the  $\alpha$ -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  $1714\text{ cm}^{-1}$  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  $\text{–COO–}$  linkages produces hydroxyl and carboxyl end groups, responsible for the broad O–H band at  $3400\text{ cm}^{-1}$  [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

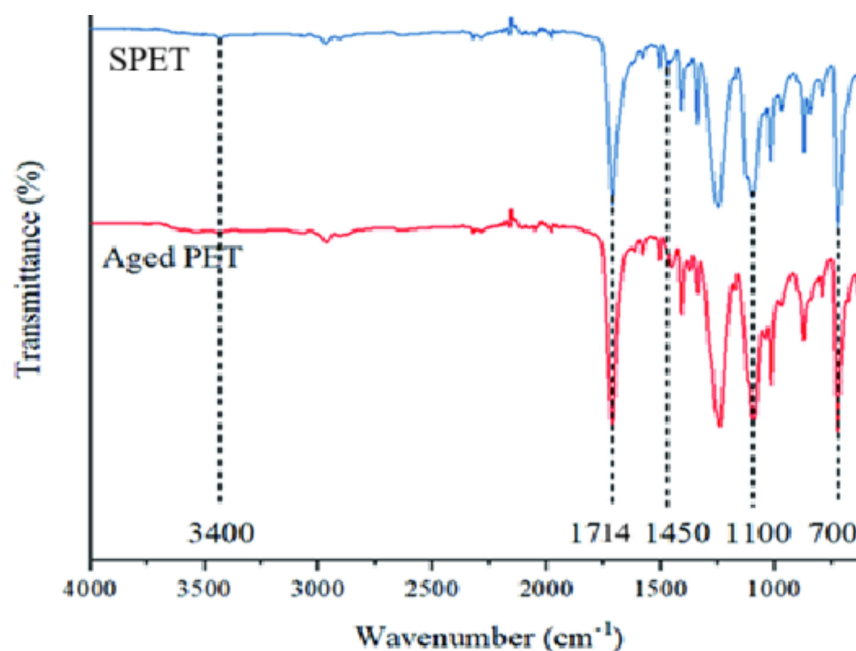
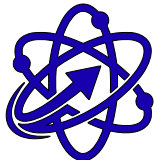


Figure 1. FTIR spectr of rPET films after different UV exposure times (insert your own plot here).

stabilizers (HALS) can reduce formation of these functional groups and slow embrittlement [14].



The emergence of a strong carbonyl band at  $1714\text{ cm}^{-1}$  and a broad hydroxyl band at  $3400\text{ cm}^{-1}$  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  $245\text{ }^{\circ}\text{C}$  to  $250\text{ }^{\circ}\text{C}$ .

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

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

#### 1. Small $T_m$ increase ( $245 \rightarrow 250\text{ }^{\circ}\text{C}$ )

A  $3^{\circ}\text{C}$  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  $T_m$  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  $T_m$  is the peak maximum or onset; peak maximum is most common for comparisons.

**Increase in crystallinity (27%  $\rightarrow$  34%).** The measured rise in degree of crystallinity ( $\sim 6.5$  percentage points, i.e., a relative increase of  $\approx 21.5\%$ ) 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  $X_c$  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].

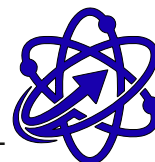
An increase in crystallinity explains the concurrent mechanical embrittlement: higher  $X_c$  typically yields higher modulus and lower toughness/elongation, because crystals act as rigid domains that reduce chain mobility and energy dissipation under load.

**Chain scission** (observed from FTIR carbonyl growth and mechanical loss) decreases average molecular weight and generates oligomers and new chain ends ( $-\text{OH}$ ,  $-\text{COOH}$ ). 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  $T_m$  shift is associated with peak narrowing or the appearance of a shoulder.

**Cold crystallization ( $T_c$ )** — check for changes in cold crystallization enthalpy or



$T_{cc}$ ; decreased cold crystallization enthalpy after aging indicates an increased pre-existing crystalline fraction.

**Enthalpy of fusion ( $\Delta H_f$ )** and calculation details — ensure you used the accepted reference  $\Delta H_f^0$  for 100% crystalline PET (commonly 140–140.1 J·g<sup>-1</sup> depending on source) when calculating  $X_c$ . Report the baseline, integration limits, and whether  $\Delta H_f$  was corrected for any cold-crystallization enthalpy.

**First vs second heating scans** — compare to separate scans to separate thermal

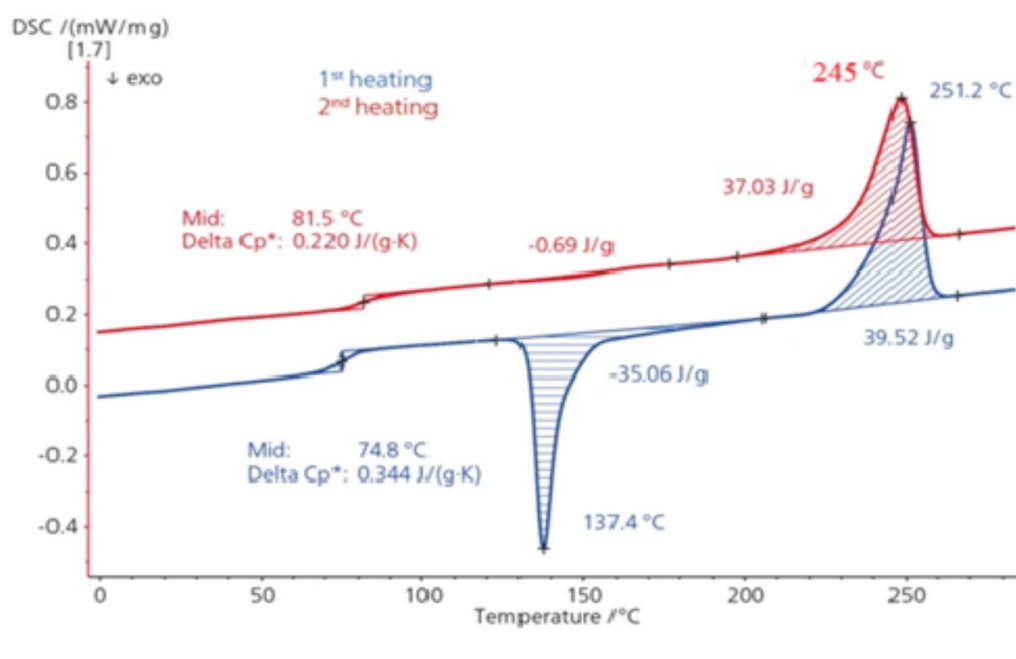


Figure 2. DSC thermograms of sPET before and after UV exposure

Table 3. DSC Data

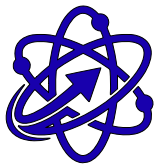
Sample	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Crystallinity (%)
Control	75	245	27
6 mo natural	78	249	33
1000 h UV	80	250	34

where  $\Delta H_f$  is the measured enthalpy of fusion,  $\Delta H_{cc}$  is cold-crystallization enthalpy (if present), and  $\Delta H_f^0$  is the reference enthalpy for 100 % crystalline PET ( $\approx 140$  J·g<sup>-1</sup>), your reported change from 27 → 34 % is a robust indication of increased crystalline mass fraction. Explicitly state the  $\Delta H_f^0$ , scan rate, and whether  $\Delta H_{cc}$  was subtracted.

history from permanent morphological change. A true material change will persist in the second heating after erasing history during a fast melt/cool cycle.

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<sup>-1</sup> and a broad hydroxyl band at 3400 cm<sup>-1</sup>, 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 ( $\approx 6,5$  % 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 [4,18,19,20,21,22,23,24,25,26]. 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 ( $\text{TiO}_2$ ,  $\text{ZnO}$ )** 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  $\text{TiO}_2$  or  $\text{ZnO}$  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.

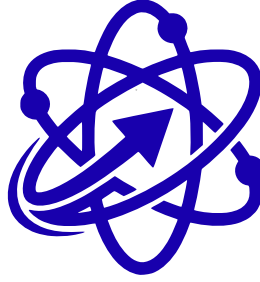
Overall, safe and durable use of sPET in environments with intense solar radiation requires a comprehensive approach that includes chemical stabilization, surface protection, and material modification.

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