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Researchof UV Aging of Secondary PolyethyleneTerephthalate in the Conditions of Central Asia

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In this regard, this work spent a year studying the process of photodestruction of painted recycled polyethylene terephthalate bottles in natural (Central Asia) and accelerated (UV climatic chamber) conditions under the influence of UV radiation. As a result of the studies, it was found that the average molecular weight of the transparent sample decreased to 7-8%, and the average molecular weight of the colored sample decreased to 15-36% in two different conditions. The resulting RPET color sources, in turn, worsen the physical and mechanical properties of the fiber after processing.

1. Introduction

Wide application of polyethylene terephthalate in the production of packaging for soft drinks and oils leads to the accumulation of a large amount of waste on dumps. On the example of the Republic of Uzbekistan, one can illustrate the relevance of this problem.In 2019, according to the Central Statistical Office, 56 thousand tons of polyethylene terephthalate were imported, which was processed into containers (bottles) for soft drinks and oils.After their use in the form of used containers, the same amount of household waste accumulates, as well as in dumps. In dumps, waste is exposed to sunlight, heat, and various aggressive environments. Among the listed influences, the most harmful, in the conditions of Central Asia, is high solar radiation, which contributes to photo and photo-oxidative destruction (Ernazarovaet al. (2022), Arantxa et al. (2023), Shubham et al. (2023)).Destructive processes over time lead to a change in the technological, physical, and mechanical properties of secondary polyethylene terephthalate (SPET).

One of the areas of SPET processing is the production of threads and fibers,Telli et al. 2023. An advanced technology for processing SPET into fibers and threads is extrusion followed by fibrillation, Sebeirt et al. 2022. This method is based on the extrusion of flexes (shapeless granules obtained by waste agglomeration) from SPET. In this case, one should expect the dependence of the technological and operational properties of SPET on storage conditions, i.e. depth of destruction processes.

It should be noted that photolytic and hydrolytic destruction (before and after) under the action of UV radiation is a change in the chemical composition of the surface of SPET products, Hosseini et al. (2007). It has been shown that the degradation of recycled SPET bottles under natural and accelerated weather conditions (340 nm, 13000 h) leads to a decrease in physical and mechanical properties, Philip et al. (2018).

Plastic bottles, PET, polyvinylchloride (PVC) and high density polyethylene reduce the transmission of UV rays with the help of dyes. As a matter of fact, manufacturers can add dye to the resin when molding plastic bottles to protect them from the sun and any other sources of ultraviolet radiation. Some colors are better for UV protection than others are. Darker shades such as blue, brown or black absorb UV rays better than lighter colors. While lighter colors cannot boast the same level of UV absorption, solid colors such as white or yellow can reflect incoming UV light to protect products.

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The simplest and direct way to quantify the degree of degradation of polymers is to measure changes in their mass. Since failure occurs at the surface, the rate of mass loss is closely related to the surface area of the plastic part, Tamada et al. (1993).In the light of the foregoing, this article is devoted to the analysis of the results obtained by exposure to UV-radiation on bottles of recycled polyethylene terephthalate of different colors during the year in natural and accelerated weather conditions.

2.Experimental part

For the experiment, waste SPET plastic containers of different colors were received from the recycling plant for waste SPET plastic containers immediately after the washing process. The samples were dried in a preheated oven at 160 °C for 60 min and ground into formless particles 8–10 mm in size.

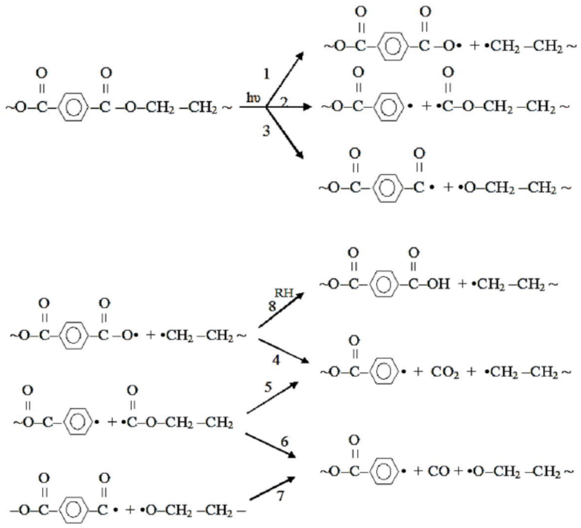
Table 1Standard conditions, which set in the UV climatic apparatus

Standard	Lamp A	Functions	/m^2/nm	Temperature °C	Time (hour)	Composition
ISO 4892-3 Cycle-1	UVA-340	UV Light Condensation UV Light	0,76 n/a 0,76	70 50 70	08:00 04:00 08:00	SPET invariouscolors

The effect of UV-radiation on the properties of SPET of various colors was determined according to ASTM G154 Model K035 - UV (climatic) application (TS EN ISO 9001:2008, Basaksehir/Istanbul, 220V AC (AC (10%), 50/60 Hz (verified UV climatic apparatus (ISO 4892-3 standard, 1-cycle: bulb UVA - 340 nm, 0.76 W/m^2/nm, UV light - 8 hours (70 °C), wind - 4 hours (50 °C)), UV - light - 8 hours (70 °C) - total - 20 hours) ((in the laboratory "TUFT AND GRASS"), Sang et al. (2020). UV - C is a subclass of ultraviolet radiation with a wavelength from 200 to 280 nm is missed in the spectrum of sunlight at the earth’s surface because wavelengths below 300 nm are absorbed by the ozone layer of the atmosphere, so the UV-A class (340 nm) was used.
The properties of SPET waste products were determined by the following methods: IR spectral analysis was carried out on a Shimadzu instrument, analysis of the melt flow index (MFR) State Standard 11645-73, ISO1133 ASTM D1238 (Document number CDN-17/0517, calibration date 20.01.2017, next calibration date 20.01.18, (in the laboratory “TUFT AND GRASS”); density according to State Standard 15139-69 by pycnometric method; characteristic viscosity in phenol: 1,2-dichloroethane (requirements State Standard 1942-86 for the first grade) =2:3 was determined according to the method given in the literature, Elamri et al. (2015), we used a capillary viscometer ADF-2 with a capillary diameter of 1.31 mm according to the State Standard 10028-81, Toroptseva et al. (1972).
The physico-mechanical properties of SPET waste products were determined by the following methods: before the bending test, the samples were kept at a temperature of 23 °C and a relative humidity of 50% for 88 hours. The test was carried out on a Computer Controlled Electronic Universal Testing Machine (“Jinan Meitesi Testing Technology Co., Ltd.”) in accordance with ISO 178. The modulus of flexural elasticity, flexural strength, and strain elongation were determined by testing five samples each. The test was carried out at a preload of 0.1 MPa and at a speed of 2 mm/min, Celic et al. 2022.

3.Results and discussions

The degradation of polymers under the influence of weather conditions is caused by many factors: solar radiation (ultraviolet, visible, infrared), oxygen, water (dew, rain, humidity, snow), heat (temperature) and other components such as dust, smoke, nitrogen oxides, sulfur dioxide, monoxide and carbon dioxide. In the process of processing and subsequent operation, as well as storage of PET, it is exposed to the complex effects of various chemical environments, temperature and oxygen, and their effect is increased by synergy. This leads to destruction proceeding with the breaking of bonds between atoms, Gewert et al. (2015), (2022), Moharir et al. (2019).The photo-degradation of PET is described by Norresh, which proceeds by photoionization (Norresh I) and macrochain termination (Norresh II). Photo-degradation is accompanied by cross-linking reactions or oxidation. The photo-oxidant includes oxygen and ultraviolet radiation. Photooxidative processes lead to a decrease in molecular weight, Singh et al. (2008).The formula given above shows the relevance of studying the impact of destructive processes on the technological and physical-mechanical properties of SPET. The results of these studies will make it possible to develop recommendations for the production of threads and fibers with reproducible properties. In this case, an important factor is the study of the color of the original HPET on the process of photooxidative processes.



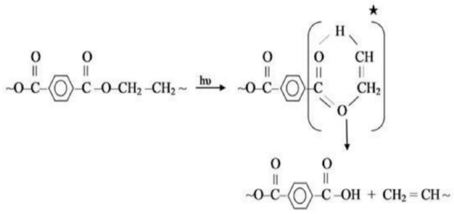


Figure 1. Type I Norresh mechanismFigure 2. Type II Norresh mechanism

Changes in properties during storage of SPET were studied in natural conditions at a natural testing area and in a climatic chamber, creating suitable conditions. The duration of the test is 1 year. At the same time, samples of the test were taken every 30 days to determine the technological and physic-mechanical properties (Table 2).The main criterion for controlling the process of photooxidative degradation is the average viscosity molecular weight (hereinafter referred to as the average molecular weight) of the initial SPET samples of various colors are given in Table. 2.

Table 2Average molecular weight of original SPET samples of different colors

Samples, 12.03.2021.	Characteristic viscosity, [η], (dl/g)	Molecular weight, [*Mn*], (g/mol)
Transparent	0,68	21869
Transparent 1	0,62	19565
Blue	0,639	20290
Green	0,63	19946
Brown	0,55	16936
Kefirbottle (whiteopaque)	0,45	13298

The data in the Table 2 show that the average molecular weight of HPET has different values. Moreover, it is the highest (21869 g/mol) for PET used to produce transparent bottles and the lowest for producing kefir bottles (13298 g/mol). This, apparently, is due to the fact that brown and kefir bottles have a certain aging period, because in the case of the same age of aging, due to the same technology of their production, the probability of deeper destructive processes is unlikely. Accordingly, the used samples of bottles do not have the same starting characteristic. The effect of exposure to atmospheric air and sunrays, as well as photooxidation in a climatic chamber on the average molecular weight of SPET is shown in Table 3 and 4.

Exposure of samples of PET bottles of transparent, transparent 1, blue, green, brown colors for 12 months, showed that the color of bottles staining effects on the destructive processes occurring in SPET. The most resistant to photooxidative degradation turned out to be SPET, in the composition of which there is no dye - transparent at all. During the year of aging, its average molecular weight k decreased from 21869 to 19946 g/mol by 8.8%. The degree of destruction of SPET containing pigments of other colors is as follows: transparent 1 - 17.2%, blue - 18.4%, green - 18.8%, brown - 36%, white (kefir bottle) - 32.8%. These data show that the highest degree of degradation during this aging period was observed in SPET used to produce brown bottles - 36%. Apparently, the initial molecular weight of SPET also affects the depth of degradation (21869 for transparent and 16936 for brown). In addition, the presence of dyes in the SPET composition cannot be excluded. Dark pigment - brown contributes to a more complete absorption of UV-rays, which leads to a deeper destruction (36%).

Table 3 Average molecular weight of SPET samples subjected to natural aging for 12 months

Months Year/2021-2022 years	Samples											
	Transparent		Transparent 1		Blue		Green		Brown		Kefir (whiteopaque) (22.03.2021)	
	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)
12.03	0.,68	21869	0.62	19565	0.639	20290	0.63	19946	0.55	16936	0.45	13289
12.04	0.675	21675	0.612	19262	0.63	19946	0.62	19565	0.535	16381	0.445	13120
12.05	0.67	21482	0.6	18807	0.625	19756	0.612	19262	0.52	15802	0.428	12519
20.06	0.665	21289	0.58	18055	0.6	18807	0.6	18807	0.5	15098	0.42	12238
27.07	0.65	20712	0.57	17680	0.56	17307	0.56	17307	0.4	11539	0.35	9824
27.08	0.65	20712	0.558	17233	0.558	17233	0.558	17233	0.395	11365	0.34	9487
27.09	0.65	20712	0.556	17158	0.558	17233	0.558	17233	0.395	11365	0.33	9152
27.10	0.65	20712	0.556	17158	0.558	17233	0.547	16824	0.395	11365	0.33	9152
27.11	0.65	20712	0.55	16936	0.558	17233	0.547	16824	0.39	11192	0.325	8925
07.03	0,63	19946	0.53	16196	0.54	16565	0.53	16196	0.38	10847	-	-

Table 4 Average molecular weight of SPET samples tested in the climatic chamber(44-cycles,8800 hours), (12months)

Months Year/2021-2022 years	Samples											
	Transparent		Transparent 1		Blue		Green		Brown		Kefir (whiteopaque) (22.03.2021)	
	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)	[η] dl/g)	[*Mn*] (g/mol)
12.03	0.68	21869	0.62	19565	0.639	20290	0.63	19946	0.55	16936	0.45	13289
17.04	0.668	21404	0.585	18242	0.615	19375	0.59	18430	0.49	14735	0.395	11365
12.05	0.65	20712	0.56	17307	0.54	16565	0.57	17680	0.44	12943	0.33	9152
23.06	0.640	20328	0.545	16750	0.525	16012	0.554	17084	0.42	12238	0.31	8488
26.07	0.638	20252	0.541	16602	0.522	15902	0.551	16973	0.39	11192	0.29	7832
27.08	0.638	20252	0.539	16528	0.522	15902	0.551	16973	0.388	11123	0.29	7832
28.09	0.638	20252	0.536	16418	0.522	15902	0.551	16973	0.386	11054	0.29	7832
30.10	0.638	20252	0.531	16233	0.52	15829	0.55	16936	0.383	10951	-	-
02.12	0.638	20252	0.53	16196	0,52	15829	0.55	16936	0.38	10847	-	-
07.03	0,62	19565	0.51	15463	0.51	15463	0.534	16344	0.36	10163	-	-

Similar results were obtained when studying aging in a climatic chamber for 44 cycles, 8800 hours, which is equal to the annual aging period, and the degree of aging in both cases is almost the same within the experimental error. It allows determining the suitability of waste for processing by accelerated tests in a climatic chamber. It should also be noted that exposure for 12 months, both in the testing area and in the climatic chamber, does not lead to significant changes in the color, shape of the color and shape of the bottles

Moreover, the results of aging, both in the testing area and in the climatic chamber, do not differ significantly. The density of SPET shows structural changes in the polymer (Table 5). It should be noted that according to State Standard R 51695, SPET density is regulated within 1.38–1.42 g/cm3 [24]. Moreover, the lower bound is typical for amorphous, and the upper - is for crystalline PET. The density data presented in Table 5 indicate a predominantly amorphous structure of SPET.It should be noted that the highest value of the degree of crystallinity (45%) is observed in the case of transparent bottles due to the absence of a dye in the PET composition, which can also affect the polymer structure. Blue and green pigments contribute to the formation of the crystal structure.Therefore, these pigments contained in HPET contribute to the formation of a crystalline structure (15.8 and 12.5%).

Table 5 Technological properties of SPET samples

Indicators / SPET Samples	Flow index of melt, (g/10min)			Density, (g/sm^3)					
	1a	2b	3c	1a	$X_{кр}$ %	2b	$X_{кр}$ %	3c	$X_{кр}$ %
Transparent	38,75	37,90	36,15	1,39	45	1,37	29,1	1,36	20,8
Transparent 1	36,45	33,15	32,65	1,345	8,3	1,34	4,1	1,338	2,5
Blue	36,00	34,75	32,35	1,354	15,8	1,349	11,6	1,34	4,1
Green	35,22	34,25	33,00	1,35	12,5	1,348	10,8	1,34	4,1
Brown	33,05	32,00	31,95	1,34	4,16	1,336	0,83	1,32	-
Kefir (whiteopaque)	27,00	25,14	22,05	1,27	-	1,25	-	1,23	-

*1a - zero point; 2b - exposed to UV radiation for 12 months; 3c - tested in a climatic chamber (44 cycles, 8800 hours 12 months).

The degree of crystallinity (X_{cr}) is calculated by the formula:

$$X=\frac{\rho-1,335}{1,455-1,335}$$ Andrady (2017)

which: ρ is the sample density. It is expected that the density of crystalline PET is 1.455 g/cm3, completely amorphous - 1.335 g/sm3

Brown and white pigments are beneficial to the formation of an amorphous structure. The SPET used to produce kefir bottles is characterized by a lower density than the standard state values. Therefore, using the formula given in Profaizer et al. (2007), it was not possible to calculate the degree of crystallinity. Apparently, this is due to the fact that PET modified with another polymer, which has a lower density than PET, was used to produce bottles.Sufficiently high resistance of dyed and undyed SPET to UV-radiation, heat, and air oxygen does not cause a significant decrease in physico-mechanical properties (Table 6).

Table 6 Influence of aging in the polygon and climatic chamber on the physic-mechanical properties of SPET samples

Indicators / SPET Samples	Bendingstrength (MPa)			Elongationatbendingstrength (%)		
	1a	2b	3c	1a	2b	3c
Transparent	81	80	79	4,5	4,4	4,4
Transparent 1	78	76	75	5,5	5,4	5,45
Blue	79	78	77	4,7	4,65	4,55
Green	77	76	75	4,8	4,7	4,65
Brown	74	72	71	5,8	5,6	5,4
Kefir (whiteopaque)	71	69	68	4,4	4,3	4

*1a - zero point; 2b - exposed to UV radiation for 12 months; 3c - tested in a climatic chamber (44 cycles, 8800 hours 12 months).

Similar results were obtained in the work, Al-Azzawi (2015). This, apparently, is due to the relatively low degree of destruction (Tables 2 and 4).The results of the studies show that PET containers that have lain in dumps for 12 months can be used after preliminary washing, drying and grinding and separation from extra neousimpurities (label, lid, etc.).

Thus, complex studies were carried out to identify the duration of aging of PET - containers on the technological, physical, and mechanical properties of SPET. It was found that after 12 months of aging in natural conditions, PET containers can be recycled into products.

4. Conclusions

Based on the results of studying the physico-chemical properties of samples of non-ferrous SPET sources stored for a year under natural and accelerated conditions, the following conclusions were made:
- Physical and chemical properties of both samples under two different conditions that the average molecular weight decreased to 8-36%;
- Blue and green samples are in the crystal structure.

It was found that after 12 months of aging in natural conditions, PET containers can be recycled into products. Our next research will be devoted to the study of the technological properties of each stage of the spinning system ("VarioFil® R+") in the production of polyester fiber from mixed-colored SPET.

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