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Weathering Effects on Cellulose Acetate Microplastics from Discarded Cigarette Butts

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Abstract:
Cellulose acetate, commonly used in cigarette filters, poses environmental concerns due to its questionable (bio)degradability and prevalent presence in nature. This study compares the weathering effects on two types of cigarette filters: traditional and newer filters used in heated tobacco devices (HTP). Microplastics were derived from used cigarette parts and then subjected to artificial aging. Analytical techniques (Thermogravimetry-Differential Scanning Calorimetry TG/DSC, Fourier-Transform Infrared Spectroscopic Analysis (FTIR)) and loose bulk density measurements were employed pre- and post-aging cellulose acetate of both types of samples. Despite increasing evidence influencing European Union (EU) directives on tobacco product disposal, there's a lack of systematic analysis on the weathering impact, especially concerning the touted environmental benefits of newer filters. Results indicate decreased particle size in cellulose acetate filters post-aging. Variances were observed in thermal behavior, yet FTIR spectra remained unchanged.

Keywords: **C**ellulose acetate; Cigarette filters; Microplastics; Artificial weathering; UV radiation impact, Polymer degradation

1. Introduction

Microplastics pose a global threat to aquatic and terrestrial ecosystems. Annually, around 4.5 trillion cigarette filters contaminate various natural environments (WHO, accessed 30.11.2023). Tobacco products significantly impact the environment from cultivation to disposal, releasing microparticles, and nanoparticles, carbon, and heavy metals (Belzagui et al., 2021; Moerman & Potts, 2011; Zafeiridou et al., 2018) . Cigarette filters, primarily composed of plasticized cellulose acetate fibers, degrade into microplastics, further aggravating environmental pollution. These plastics face diverse conditions like rain, abrasion, salt, temperature fluctuations, and crucially, UV radiation, hastening their breakdown (Erdal and Hakkarainen, 2022; Felipe da Silva et al., 2023; Hon, 1977; Poppendieck et al., 2020; Vanapalli et al., 2023). Cellulose acetate fibers degrade notably under Ultra Violet (UV) light, with significant changes observed beyond 235 nm wavelengths (Hon, 1977). Studies on their degradation have examined diverse environments, including soil, compost, freshwater, seawater, and artificial seawater (Araújo et al., 2022; Yadav & Hakkarainen, 2022). Recognizing this, the World Health Organization and the EU Directive emphasize reducing the impact of plastics like cellulose acetate in tobacco products (Directive (EU) 2019/904, accessed 30.11. 2023; WHO, accessed 19.5. 2023). Recycling these filters remains challenging due to their slow hydrolysis into cellulose and acetic acid, posing environmental risks (De Fenzo et al., 2020). The newer tobacco products, incorporating poly(lactic acid) (PLA) polymer films alongside cellulose acetate, contribute additional environmental strain (Bonanomi et al., 2020). However, both PLA and cellulose acetate undergo slow biodegradation under environmental conditions (Bonanomi et al., 2020). This study explores the impact of UV and visible light, simulating natural sunlight, on cellulose acetate comparably gained from classic and newer cigarette butts (ISO 4892-2, 2013; Q-LAB, accessed 30.11. 2023).

2. Materials and methods

2.1. Materials

The research involved the collection of used cigarette filters to create two distinct forms of cellulose acetate (CA) microplastics in powder form. These variations included: (a) powder derived from filters of conventional cigarettes and (b) powder sourced from cigarette filters used in HTP. To ensure the purity of the samples, all filters were meticulously separated from the remaining cigarette components, such as the wrapping paper, and great care was taken to prevent any contamination from tobacco or ash.

In the case of HTP filters, the process involved removing the biodegradable, pleated poly(lactic acid) film, which acts as a cooling plug for aerosol cooling purposes, but this part of filters was not the subject of this study. Subsequently, the CA cigarette filters were individually ground using a ball mill to create loose powder for each of the filter types.

All used cigarette filters obtained for this study from regular/classic cigarettes belonged to the same brand, specifically BOSS classic cigarettes manufactured by Tobačna Ljubljana d.o.o., Slovenia. Filters from heat tobacco devices, known as HTP or commonly recognized as IQOS ("I Quit Ordinary Smoking" by Philip Morris International, Inc., USA), were obtained under the brand name HEETS. For clarity, the CA filter samples were designated as classic and HEETS, respectively.

2.2. Methods

The samples were first milled and analyzed using FTIR, TGA/DTA analysis, and loose bulk measurements, then they were exposed to weathering in a standardized chamber for accelerated aging and analyzed again.

2.3. Milling process for samples preparation

The collected and prepared materials were first ground in a laboratory mill Millmix 20 (Domel, Slovenia) to micro particles (**Figure 1**). Millmix 20 is a vibrating ball mill with two 50 mL grinding drums, in which the grinding of cigarette filters from CA took place in two stages. The filling mass for grinding cigarette filters was up to 1 g. Cigarette filters from CA were first ground for 1 minute with three grinding bodies, 8 mm in diameter and with a frequency of 30 Hz, so that the filter fibers were separated, then they were ground for another 3 minutes with grinding bodies, with a diameter

of 25 mm, also with a frequency of 30 Hz. After milling, we sifted samples through a 63 μm sieve raster to ensure the homogeneity of the sample.

Figure 1. Prepared cellulose acetate microplastics from used cigarette butts samples: from classic cigarette filters (left) and from HEETS filters (right).

2.4. Artificial weathering

Cigarette filters, ground into fine particles, were meticulously placed within glass petri dishes and shielded by a layer of quartz glass to safeguard against contamination or any potential sample loss during exposure. These milled filters underwent accelerated aging for a period of 1000 hours (equivalent to 42 days) inside a Q-SUN Xe-3 UV chamber, manufactured by Q-Lab in Bolton, UK. The chamber was equipped with three powerful 1800 W xenon lamps, specifically calibrated to emit wavelengths akin to natural sunlight.

Throughout the exposure duration, the ground cigarette filters underwent thorough daily mixing and homogenization to ensure uniformity and consistency in the aging process. The samples were subjected to irradiation at a power level of 60 W/m^2 while maintaining a chamber temperature of 38 °C, while the black standard was maintained at a temperature of 65 °C.

2.5. Fourier-Transform Infrared Spectroscopic Analysis (FTIR)

In order to determine differences in the used material before and after artificial weathering for the cellulose acetate filters, attenuated total reflection Fourier-transform infrared spectroscopy (FTIR) was carried out using a FTIR Spectrum Two spectrometer (PerkinElmer, Waltham, MA, USA). The spectra were recorded from 400 cm^{-1} to 4000 cm^{-1}, with an average of four scans taken at a resolution of 4 cm^{-1}.

2.6. Thermal analysis

We performed TGA/DSC analysis, which simultaneously measures the change in heat flow and the change in mass of the polymer material, depending on temperature, time and atmosphere. The degradation/disintegration temperature of the polymer material is determined by the first derivative of the TGA curve. In addition, endothermic or exothermic processes in the sample are simultaneously monitored during the analysis with the help of a temperature sensor, which affect changes in the heat flow and are determined with the help of the DSC signal. Thermal properties of artificially aged and non-aged used cigarette filters were determined by simultaneous TGA/DSC thermogravimetric analysis, on a Mettler Toledo TGA/DSC 3+ device. A 40 μL aluminum pot was used for the characterization. The testing of both types of cigarette filters was carried out in a nitrogen atmosphere, with an N_2 flow of 20.0 mL/min, in a temperature interval from 25 °C to 600 °C and a heating rate of 10 °C/min. At 600 °C, we switched from nitrogen to oxygen atmosphere, with an O_2 flow rate of 20 mL/min, and maintained this temperature for another 20 minutes.

2.7. Loose bulk density

The loose bulk density of the samples was determined by measuring the mass (using a Mettler Toledo AT201 analytical balance; Mettler Toledo, Switzerland) of a known volume of the container, without tapping, at room temperature (23 ± 2) °C (European Medicines Agency, 2010).

3. Results

3.1. FTIR analysis

Using FTIR spectroscopy (**Figure 2**), we compared the spectra of unaged CA cigarette filters (blue spectra) with artificially aged CA filters (red spectra) and observed an almost unchanged course of the curves after 1000 h of exposure to UV radiation for both samples: classic cigarette filters and HEETS filters. Absorption bands characteristic of the acetyl group in the CA structure appear at the same wavenumbers in all unaged and artificially aged CA cigarette filters. Even the intensity of the absorption bands remained almost exactly the same for CA cigarettes after UV exposure.

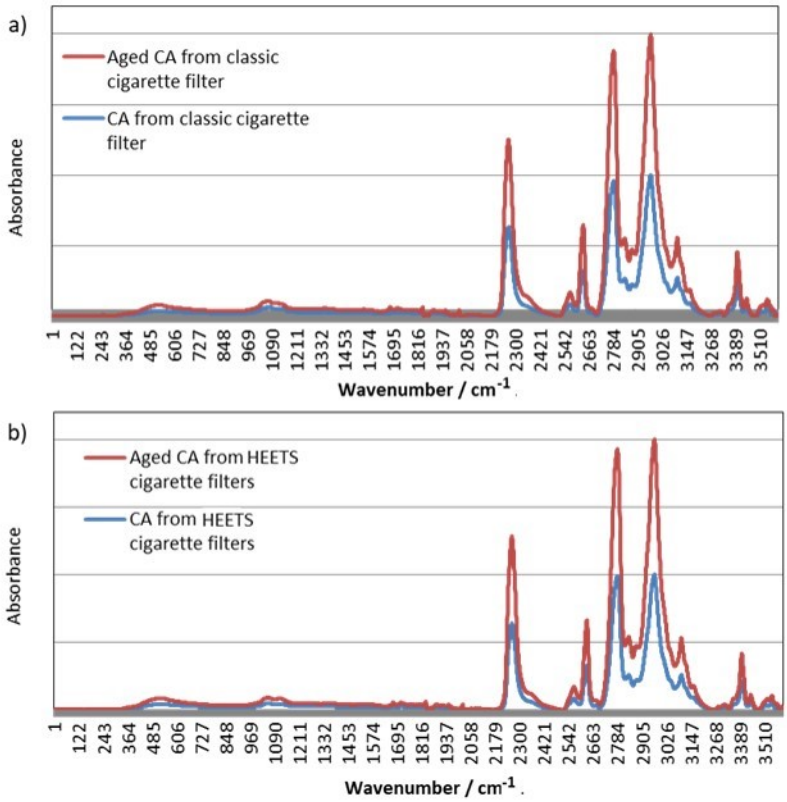

Figure 2. FTIR spectra of CA microplastics from used cigarette butts (a) from classic cigarette filters and (b) from HEETS filters.

3.2. Thermal analysis

The degradation of cigarette filters was assessed through simultaneous TGA/DSC analysis (**Figure 3**). In unaged CA cigarette filters, the initial mass loss commenced at a marginally lower temperature (Td1), coinciding with an endothermic peak around 138 °C. This peak is linked to the evaporation of absorbed moisture or volatile organic components trapped in the filter during smoking. Additionally, it corresponds to the decomposition of plasticizers present in the cigarette filter manufacturing process (De Fenzo et al., 2020). The absorbed water and volatile organic components in artificially aged CA cigarette filters were slightly reduced (-5.8 % for CA classic – Figure 3a and -8.6 % for CA HEETS – **Figure 3b**) due to their prior elimination through elevated temperature UV exposure for 1000 hours. Subsequently, used CA cigarette filters exhibited greater mass loss, attributable to washing and the release of chemical compounds, aligning with findings reported by other researchers (Joly & Coulis, 2017).

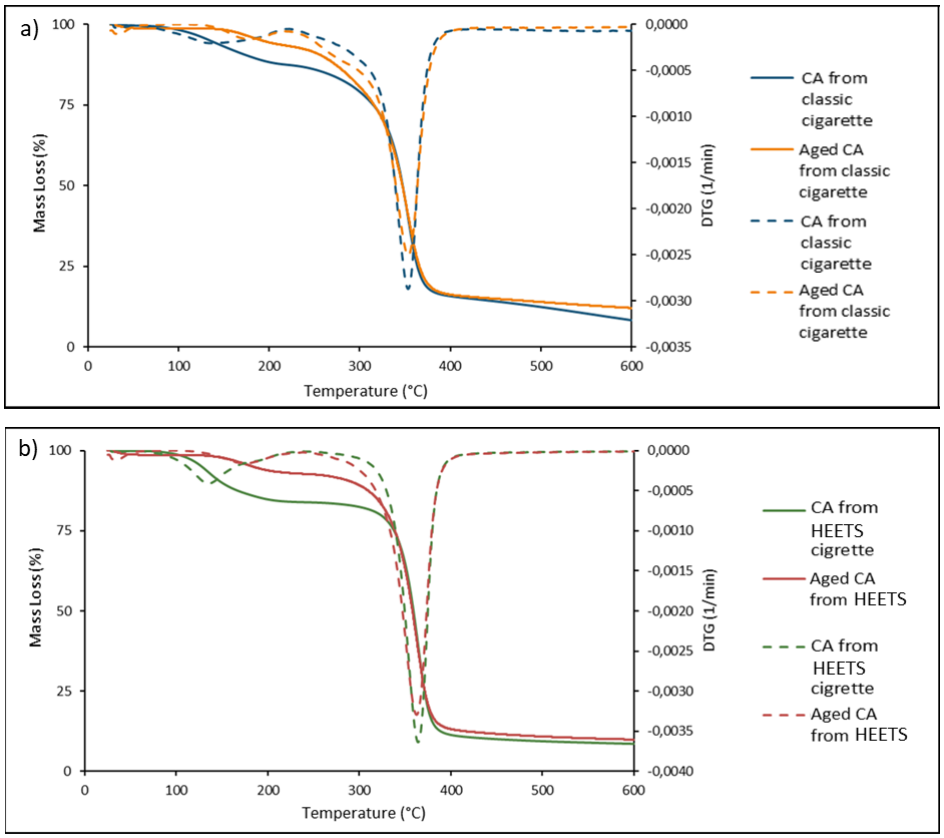

Figure 3. TGA/DTG analysis of unaged and artificially aged (a) CA classic and (b) CA HEETS cigarette filters.

Moreover, the degradation of CA in these filters occurred in a single step. This breakdown involves the degradation of sugars, lignin, pectin, and hemicellulose (Baker, 1987), alongside the deacetylation/depolymerization process of CA (De Fenzo et al., 2020), impacting the breakdown of glucosyl bonds (Barud et al., 2008). The organic CA component's decomposition temperature (Td2) in CA HEETS cigarette filters was approximately 367 °C, slightly higher compared to CA classic cigarette filters, which decomposed around 358 °C. This variance also manifests in the decay rate (ΔY), marginally higher in both unaged and artificially aged CA classic filters. This distinction might be linked to differences in filter composition, manufacturing processes of CA fibers, and maybe the method of using these filters.

The exothermic peak indicating the soot decomposition (Tds), observed in both unaged and artificially aged CA cigarettes, emerged at approximately 600 °C and is primarily influenced by carbon content. The heightened proportion of soot in artificially aged CA cigarette filters resulted from UV radiation exposure, impacting particle size reduction and an increase in their specific surface area. This effect was confirmed through loose bulk density measurements.

3.3. Loose bulk density

We conducted loose bulk density measurements on both unaged and artificially aged classic and HEETS cigarette filters (**Table 1**). Notably, all artificially aged CA cigarette filters exhibited a higher loose bulk density. After artificial aging, the loose bulk density of CA classic filters was increased by approximately 14 %, while for CA HEETS it was risen by about 9 %. Moreover, for all CA HEETS cigarette filters it was marginally higher than that of classic cigarette filters indicating the presence of smaller particles in the case of HEETS filters. This variance could potentially stem from differences in the

manufacturing process of the filters. However, it's plausible that the increased loose bulk density might also be linked to the distinct usage method between classic cigarettes, which burn, and CA HEETS. It might be associated with reduced filter contamination by chemicals or moisture. Such contamination typically causes particle adhesion, resulting in the formation of agglomerates.

Table 1. Results of average loose bulk density of unaged and artificially aged CA cigarette filters.

Samples	Non-aged	Aged (1000 h xenon chamber)	Changes in loose bulk density (%)
CA classic	0.21	0.24	14.3
CA HEETS	0.34	0.37	8.8

4. Discussion

We investigated the impact of UV light on the aging process of CA samples gained from cigarette filters. Analysis via FTIR spectra revealed no discernible differences between the spectra taken before exposing the samples to UV radiation and those obtained after controlled UV exposure. The observed trends are comparable to reports in the literature on the degradation of CA cigarette filters, where the authors also determined the unchanged chemical structure of microfibers from used CA cigarette filters after exposure to fresh water and natural sunlight for 18 months (Belzagui et al., 2021) and after exposure to 5 different environmental conditions for 720 days (Bonanomi et al., 2015).

However, complementary analyses including TGA/DSC evaluations and loose bulk density measurements showcased notable alterations in cellulose acetate samples derived from traditional cigarette filters versus those from HEETS filters.

Significantly, the exposure to UV light induced changes in the thermal stability of the samples and led to an increase in loose bulk density. These findings indicate evident physical transformations occurring during exposure to UV radiation.

5. Conclusion

Conclusively, our investigation demonstrates that UV light, an integral part of the solar spectrum, did not visibly induce chemical changes in cellulose acetate within a controlled 1000-hour exposure to accelerated UV radiation (approximation of sunlight). Therefore, it can be inferred that even discarded cigarette butts, which are exposed to sunlight containing UV radiation, do not undergo significant chemical alterations. Nonetheless, it's important to note that cigarette butts in the environment experience a variety of other influences, including abrasion, temperature fluctuations, and UV radiation, contributing to the breakdown of cigarette filters into microplastic particles. Intriguingly, these microplastics exhibit enhanced thermal stability when exposed to UV light.

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Conflicts of Interest: The authors declare no conflict of interest.

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