QUANTIFICATION OF SHEDDING PROPENSITY OF POLYESTER FABRICS IN THE WASHING PROCESS

Tanja Pušić[*], Mirjana Čurlin[**], Ana Šaravanja[*], Kristina Šimić[*], Ivona Vidić Štrac[***], Nino Dimitrov[***]

[*] University of Zagreb Faculty of Textile Technology, Zagreb, Croatia
[**] University of Zagreb Faculty of Food Technology and Biotechnology, Zagreb, Croatia
[***] Croatian Institute of Public Health, Zagreb, Croatia

corresponding author: Tanja Pušić, e-mail: tanja.pusic@ttf.unizg.hr

Original scientific paper
Received: February 10th, 2024
Accepted: March 25th, 2024
HAE-2416
https://doi.org/10.33765/thate.14.4.1

ABSTRACT

Global microplastic (MP) pollution from primary and secondary sources is partly caused by the growing trend towards the use of plastics. One of the most important factors for the persistence of MP in the environment is their high resistance to degradation. The washing process has been identified as a risk and source of various pollutants in wastewater and numerous studies have been published. This study focuses on three different polyester fabrics: woven, knitted and double-faced plush fabrics, which were washed under standard conditions with the reference detergent ECE A at 60 °C for 40 min. Different methods were used to quantify the released fragments in a 5- and 10-cycle wash, to analyse the samples gravimetrically and to characterise the wastewaters by physicochemical parameters and filter cake. The results proved that the structure of polyester fabrics plays a role in shedding, although most fragments were released from all polyester fabrics in the first washing cycles.

***Keywords**: washing, polyester, shedding, fragments, wastewaters*

INTRODUCTION

The annual amount of approximately 8 million tonnes of microplastic (MP) particles entering the oceans has prompted experts, scientists, associations and society to identify the sources and size of plastic fragments, determine risks, improve and further develop analytical methods, adapt normative legal acts and define mitigation measures [1 - 3]. The primary sources of MP are used car tyres, boat coatings, plastic beads and pellets and cosmetic products, and the secondary sources are related to degradation products due to ageing and damage of plastics. In addition to the above sources, washing of synthetic textiles is thought to account for about 35 % of MP particles in aquatic ecosystems [4, 5]. The detachment of synthetic microfibres (MF) from textile structures leads to the occurrence of free MP and fibrous microplastics (FMP), which pose a threat to ecosystems [6, 7]. The particles released during the washing process are defined as MPs, microfibres and fragments, depending mainly on the author's area of expertise. MP particles have a size/diameter of less than 5 mm, and MF refer to fibres with a linear density of less than 1 denier or 1 dtex [8, 9]. A fibre fragment is a smaller piece of a textile fibre that is broken or separated from the construction of a textile product, so fibre fragments are often associated with MF as environmental pollutants due to their small size [8].

During the washing process, complex physicochemical mechanisms take place, which are caused by the interaction of textiles and the factors of the Sinner's circle (chemistry, mechanical agitation, temperature and time) [9, 10]. The intensity of the textile changes in the washing process depends on the structural parameters (type of flat product such as fabric, knitted fabric, non-woven fabric), the yarn (hairiness, type, cross-section) and the processing steps. Fibres that are released and loosened during the washing and the use of polyester textiles are formed from fibres that were fixed at both ends inside the material [11, 12]. Based on previous studies addressing the relationship between the tendency to pilling and the release of fragments during washing, no consistent position has been established. The generation of pilling is associated with the release of fragments during washing [13], while in [14] the effect of pilling is not associated with the release of microfibres. According to [15], the variables of the textile material had a greater influence on the release of fragments than the variables of the wash process. The reason for this lies in the fact that textiles are complex structures, so that no single variable appears to have a dominant effect.

This study is focused on three different polyester fabrics: woven, knitted, and double side weft plush, washed under the same process conditions harmonized with method 2A of HRN ISO EN 6330 [16]. The Sinner cycle factors included a reference detergent formulated according to European Colourfastness Establishment, ECE A [17], the temperature of 60 °C, duration of 40 min and the mechanical agitation of a Rotawash laboratory apparatus, Atlas, SDL, with the aim of quantifying the fragments released in a 5- and 10-cycle wash.

EXPERIMENTAL

Materials

The polyester woven fabric (PES-WF) in plain weave with a unit area of 156 g/m^2, density of 27.7 threads/cm in the warp direction, 20 threads/cm in the weft direction and a fineness of 30.4 tex (warp direction) and 31.7 tex (weft direction) was used as a reference supplied by the Centre for Testmaterials B.V., Vlaardingen, Netherlands.

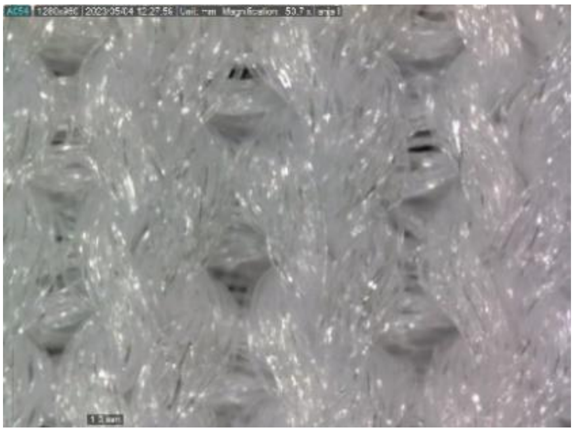
The polyester weft knitted fabric (PES-KF) with a unit area of 139 g/m^2, a horizontal density of 16 stitches/cm and a vertical density of 21 stitches/cm as a reference is supplied by the wfk - Cleaning Technology Institute e.V. Krefeld, Germany.

The double-sided weft woven polyester plush fabric (PES-DPF) with a unit area of 279 g/m^2 patterned in grey, red and yellow was purchased in the shop. One weft of the weft plush is basic and has a high-density structure (plain, twill), the other, the fleur weft, has lower density, i.e. it floats on the surface of the fabric [18]. In order to better visualise structural differences, the surface of all polyester samples was observed using digital microscope, Dinolite AM7013MZT, type Premier, Netherlands, Figure 1.

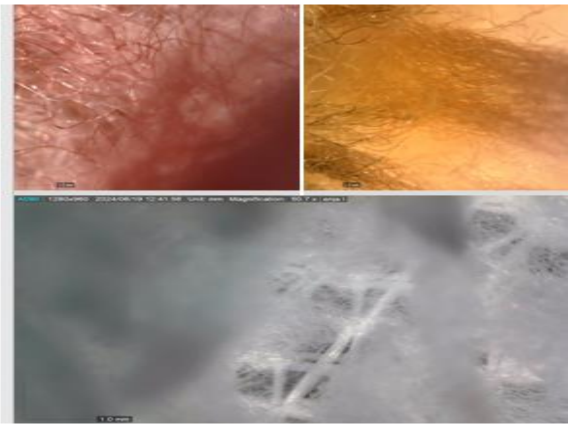
Washing process

Polyester fabrics were subjected to a washing process, bath ratio 1:7 under 10 cycles at 60 °C according to HRN EN ISO 6330 [18] using reference detergent ECE A (1.25 g/L) prepared in tap water in a Rotawash laboratory device, SDL Atlas, Rock Hill, USA for 40 min. The samples were rinsed in four cycles with tap water and dried at ambient conditions. The wastewaters after 5 and 10 wash and rinse cycles were collected for further analysis using physicochemical methods. The one step vacuum filtration of 5 and 10 wash cycles wastewaters was conducted using filter from glass fibres, GF (pore sizes 0.7 μm). The filter cakes after 10 wash cycles were isolated for analysis of filter residues. All samples for analysis are grouped in Table 1.

a)



b)



c)

Figure 1. Digital micrographs of three polyester fabrics surface, magnification 200x: a) PES-WF, b) PES-KF, c) PES-DPF

Table 1. Designation of samples

Samples	PES-WF	PES-KF	PES-DPF
fabrics washed 10 times	_10	_10	_10
wastewaters after 5 and 10 wash cycles	_5, _10	_5, _10	_5, _10
filter cakes	_10	_10	_10

Methods

The gravimetric method [19] was used to determine the degree to which the various textiles shed fibre fragments of all kinds, so polyester fabrics were weighed before and after 10 washes.

The wastewaters collected after 5 and 10 washing cycles were characterised using physicochemical methods: pH, conductivity (κ), turbidity using nephelometric method (NTU), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS) and chemical oxygen demand (COD). A detailed description of the methods and conditions used can be found in the publication [20]. The particle size analyser, PSA 1090 LD, Anton Paar GmbH, Graz, Austria, was used to analyse the particle size distribution (PSD) in washing wastewaters. The Fraunhofer diffraction theory was used for the measurement and the computer support *Kaliope*® was used to determine the characteristic diameters D_{10}, D_{50}, D_{90}, shape factor (k) and the span value from the PSD curve [21]. All measurements were performed in replicate series of ten measurements in water as solvent, with the stirrer speed and pump speed set to medium.

Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) measurements were carried out using a micro-furnace pyrolyzer (EGA/Py3030D, Frontier Laboratories, Ltd., Koriyama, Japan) equipped with an auto-shot sampler (AS-1020E, Frontier Laboratories, Ltd., Koriyama, Japan). The pyrolyzer was interfaced directly to the split/splitless injection port of a GC/MS instrument (Shimadzu QP2010 Plus (Shimadzu

Corporation, Kyoto, Japan)). The GC injection port was connected to a quadrupole mass detector through a column system composed of a pre-column (Ultra ALLOY+-50, 2 m × 0.25 mm i.d. (internal diameter), coated with 10 µm film thickness of 50 % diphenyl and 50 % dimethylpolysiloxane (Frontier Laboratories, Ltd., Koriyama, Japan)), a separation column (Ultra ALLOY+-5, 30 m × 0.25 mm i.d. (internal diameter), coated with 0.5 µm film thickness of 5 % diphenyl and 95 % dimethylpolysiloxane (Frontier Laboratories, Ltd., Koriyama, Japan)) and a vent-free GC/MS adapter (Frontier Laboratories, Ltd., Koriyama, Japan). The detailed analytical conditions are listed in Table 2.

Table 2. Analytical conditions for Py-GC/MS used to detect MPs in samples

Instrument	Parameters	Settings
Pyrolyzer	Furnace temperature	600 °C
	Interface temperature	300 °C
GC	Injection port temperature	300 °C
	Column oven temperature	40 °C (2 min hold) → 280 °C (20 °C/min, 10 min hold) → 320 °C (40 °C/min, 20 min hold)
	Flow Control mode	Pressure 75 kPa
	GC/MS interface temperature	300 °C
	Injection mode	Split (split ratio: 1 : 50)
	Carrier gas	Helium (column flow rate: 0.98 mL min^{-1})
MS	Ion source temperature	250 °C
	Ionization method	Electron ionization (EI), 70 eV
	Scan range	*m/z 29−35*

For identification of the microplastic (MP) from filter cakes, each polymer in a sample was identified using the selected characteristic pyrolyzates of each polymer. For identification and quantitative analysis of pyrolyzates, software F-Search MPs 2.1 (Frontier Laboratories, Ltd.) was used. The calibration curves were validated using mixtures of 12 polymers - Microplastics standard calibration set (Frontier Laboratories Ltd., Japan). Mass of 0.4 mg MP samples was put in a sample cup, 0.4 mg of $CaCO_3$ was added and followed by Py-GC/MS measurements. Additionally, qualifications and identifications of the peaks in the chromatograms were confirmed by comparing the mass spectrum of each peak in the pyrogram with those in data search libraries of F Search all in one (ver. 3.7).

RESULTS AND DISCUSSION

The washing process of textiles should be considered through the mutual interaction of material and medium. The factors of the Sinner's circle in the standard washing process of the investigated polyester fabrics are related to the hydrodynamics, the alkaline medium and ingredients of the ECE A standard detergent as well as the temperature of 60 °C. Since the factors of the washing process are constant, the effects of the fabric properties are possible. Table 3 shows the changes in fabrics weight after 10 wash cycles compared to the untreated fabric samples, expressed as mass increase/loss.

Table 3. Change in the mass of the samples during 10 wash cycles

Change in mass (%)	PES-WF_10	PES-KF_10	PES-DPF_10
increase	0.73	0.32	-
loss	-	-	0.82

The results in Table 3 show an increase in the mass of polyester woven and polyester knitted fabrics and a loss in the mass of double-sided plush fabric, which could indicate differences in the quantity of fragments released. The increase in the mass of woven and knitted fabrics can be explained by the presence of residues on the surface caused by the deposition of calcite from tap water or insoluble detergent components, e.g. zeolites. The alkaline hydrolysis of the surface of PES-

WF and PES-KF in the washing bath at 60 °C can lead to a change in the surface, e.g. porosity [22], which can influence the increased deposition of residues. The mass loss of PES-DPF_10 indicates released fragments and the absence of depositional residues on the sheared pile and hairy surface. The physicochemical indicators of the wastewater from 5 and 10 wash cycles listed in Table 4 can be more or less meaningful in the evaluation of the effluents load.

The results in Table 4 show a minor influence of the number of wash cycles on the wastewater parameters TSS, TS and TDS. The conductivity of the wastewater is influenced by the number of wash cycles. The values were reduced with increasing number of wash cycles. The type of polyester fabric also had an impact, the highest value was recorded for the wastewater PES-DPF_5 and the lowest for PES-KF_10. The turbidity of the wastewater at 10 wash cycles is lower than the values at 5 cycles, especially for PES-DPF. The comparison of the wastewater parameters of 5 and 10 wash cycles in Table 4 shows an influence of the wash parameters and the water as a medium, which manifests itself in the reduction of the turbidity and the ion load of the wastewater.

The greatest differences in the quality of the wastewater were found in the COD parameter, which is highest for PES-DPF and lowest for PES-KF. The influence of the wash cycles is very pronounced in the PES-DPF_10 wastewater, which indicates chemical contamination. Extreme COD values can be influenced by the structural parameters and tendency to shed in washing process.

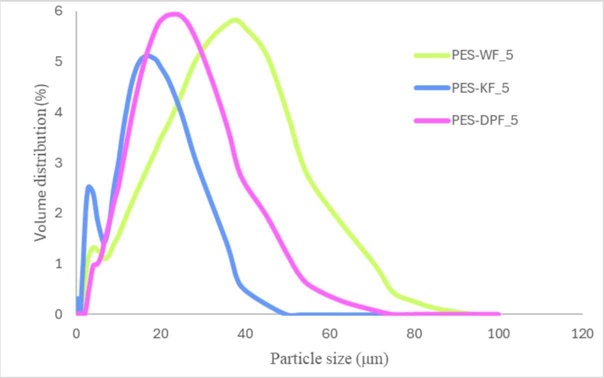
The results of the particle size distribution (PSD) in washing effluents of 5 and 10 washing cycles of polyester woven fabric (PES-WF), polyester knitted fabric (PES-KF) and double-sided woven polyester plush fabric (PES-DPF) are shown as PSD curve in Figure 2, and its characteristic parameters, shape factors (k) and span values are displayed in Table 5.

Table 4. Physicochemical parameters of 5 and 10 wash cycles wastewaters

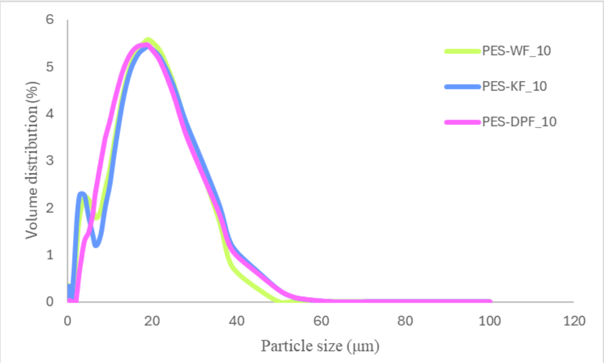
Wastewater	TSS (mg/L)	TS (mg/L)	TDS (mg/L)	pH	κ (µS/cm)	Turbidity (NTU)	COD (mg O_2/L)
PES-WF_5	121.2	634.6	552.9	7.97	811.0	70.2	191.0
PES-WF_10	124.5	663.0	527.8	8.06	740.0	50.7	183.5
PES-KF_5	123.5	561.5	459.6	7.90	752.9	75.3	79.3
PES-KF_10	141.0	575.0	486.3	7.90	717.5	69.9	63.3
PES-DPF_5	66.0	678.3	560.2	8.57	982.8	75.7	368.0
PES-DPF_10	69.0	682.4	550.1	8.49	814.3	46.4	601.0

Table 5. Characteristic parameters of the PSD curves of wastewater after 5 and 10 wash cycles of PES-WF, PES-KF and PES-DPF

Wastewater	D_{10}	D_{50}	D_{90}	Mean (µm)	k	Span
PES-WF_5	3.127	22.913	47.313	25.515	1.065	1.929
PES-WF_10	2.416	12.588	27.124	14.298	1.122	1.960
PES-KF_5	1.889	9.647	21.938	11.199	1.135	2.079
PES-KF_10	2.028	11.054	24.484	12.625	1.114	2.035
PES-DPF_5	6.1022	18.095	34.980	20.618	1.833	1.596
PES-DPF_10	4.805	13.716	27.580	15.962	1.833	1.661



a)

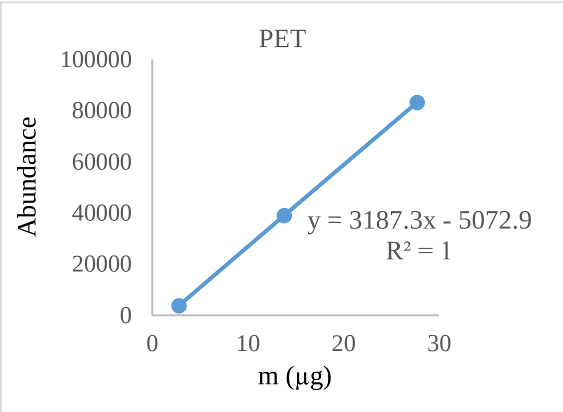


b)

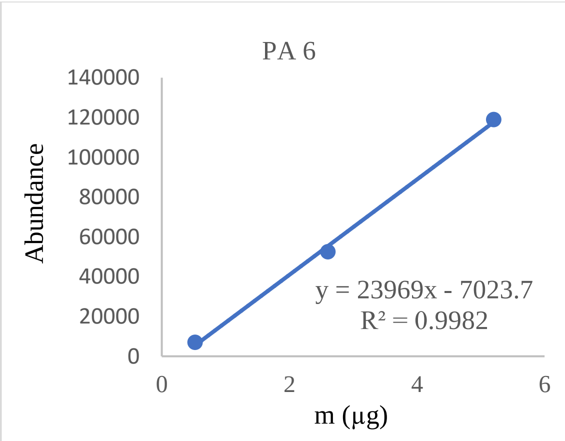
Figure 2. PSD curves of wastewaters: a) PES-WF_5, PES-KF_5 and PES-DPF_5, b) PES-WF_10, PES-KF_10 and PES-DPF_10

The results in Table 5 show that the particles with the smallest diameter and the smallest volume distribution are present in the wastewater PES-KF_5. The volume distribution as well as the size of the particles released from PES-WF_5 and PES-DPF_5 is larger, highlighting the PES-WF structure characterised by larger released particles, up to 100 μm, Figure 2. Based on the values of the D_{50} parameter, it can be seen that half of the particles present in the wastewater PES-WF_5 are smaller than 22.913 μm and half are larger than that. With increasing number of washing cycles, a smaller range of particle sizes (up to 60 μm) and slight differences in the ratio between smaller and larger particles were observed in all wastewaters, Figure 2. All parameters obtained (D_{10}, D_{50} and D_{90}) for the wastewater of PES-KF increase with increasing number of wash cycles, and for the wastewater of PES-WF and PES-DPF the parameters obtained decrease with increasing number of wash cycles. The influence of fabric type and the higher release of fragments during the first few washes is present, which is consistent with previous results on release during the first few washes of a new item [23].

For identification of the MP from filter cakes, each polymer in a sample was identified using the selected characteristic pyrolyzates of each polymer. Calibration curves with correlation coefficients, $R^2 > 0.99$ showed presence of MPs, PET (polyethylene terephthalate) and PA 6 (polyamide 6), in the sample of filter cake PES-DPF_10 with their probability level and retention index (RI) obtained from standard calibration curves, Figure 3 and Table 6. Identified MPs in the filter cake PES-DPF_10 in the Table 6 are specified by retention time (RT) and the limit of quantification (LOQ).



a)



b)

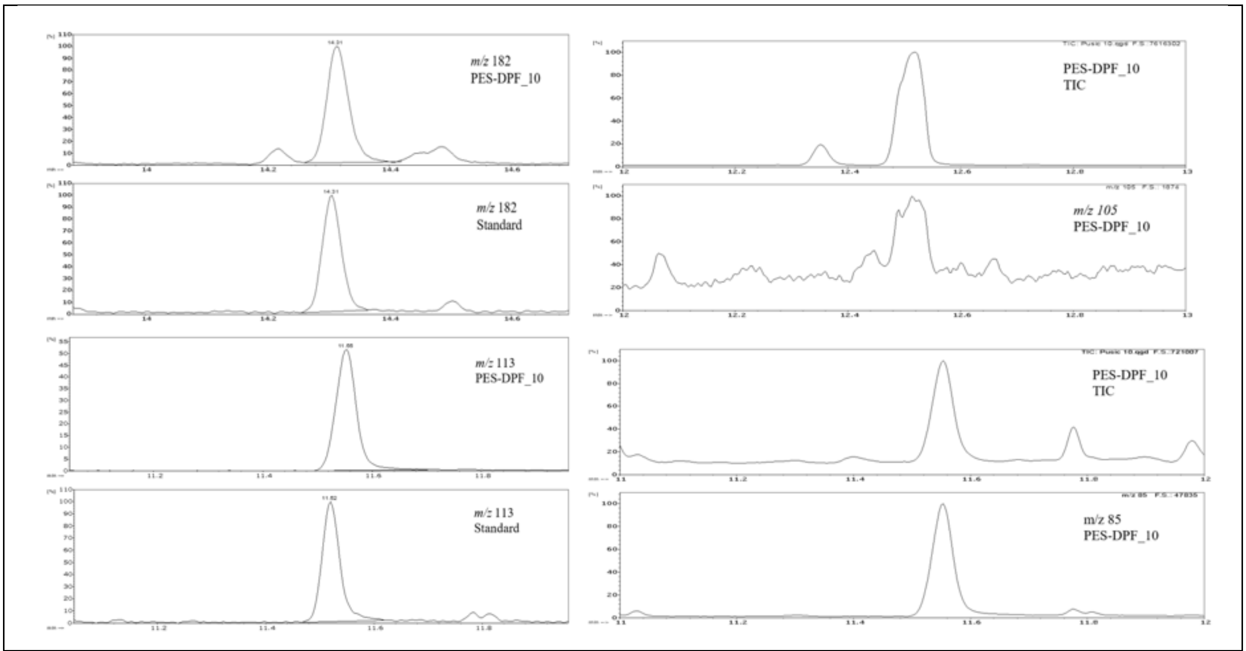
Figure 3. Calibration curves for MPs analysis: a) PET, b) PA 6

Table 6. Quantitative (Q) results of MPs in the filter cake PES-DPF_10

	Polymer	Prob. (%)	Q (µg)	RT (min)	LOQ (µg)
Filter cake PES-DPF_10	PET	88.2	13.8	14.31	1.5
	PA 6	98.6	5.62	11.55	0.25

The qualifications and identifications of peaks in the chromatograms were confirmed by comparing the mass spectrum of each peak in the pyrogram with those in data search libraries of F Search all in one, ver. 3.7. Figure 4 represents characteristic extracted ion chromatograms (EICs) with qualifier ions (indicator and confirmation m/z values) for different polymers (PET, PA 6) from the filter cake of the sample and compared with an EICs from MPs standard from the calibration curve and additionally compared from the total ion current (TIC) at the same retention time (RT). All m/z values from filter cake PES-DPF_10 match retention times of MP standard.

The presence of PA 6 in the filter cake cannot be linked to the polyester fabric PES-DPF_10. The contamination of this sample purchased in the shop was possible and further research efforts will focus on identifying the contaminants.



a b

Figure 4. Extracted ion chromatograms (EICs): a) PET, b) PA 6 in the sample of filter cake PES-DPF_10 with their corresponding indicator and confirmation m/z values

CONCLUSION

In subsequent washes, the mass of the woven and knitted polyester fabrics was higher, while the mass of the double-sided plush fabric was lower than the mass of the original fabric samples. This could indicate differences in the amount of fragments released. The results of the particle size analysis and the phenomena described can be attributed to the structural properties, which interact differently with the parameters of the washing process and thus contribute more or less to the fragment release. Most fragments were released from all analysed polyester fabrics in the first few washing cycles. The analysis of the filter cake PES-DPF_10 by Py-GC/MS should be clarified due to the presence of polyamide. The quantitative analysis of the filter cakes (PES-WF_10 and PES_KF_10) will be extended to other samples to show differences in the amount of released fragments.

REFERENCES

[1] A.P. Periyasamy, Environmentally Friendly Approach to the Reduction of Microplastics during Domestic Washing: Prospects for Machine Vision in Microplastics Reduction, Toxics 11(2023) 7, Article number: 575. https://doi.org/10.3390/toxics11070575

[2] S. Raja Balasaraswathi, R. Rathinamoorthy, Effect of fabric properties on microfiber shedding from synthetic textiles, The Journal of The Textile Institute 113(2022) 5, 789-809. https://doi.org/10.1080/00405000.2021.1906038

[3] L. Tiffin, A. Hazlehurst, M. Sumner, M. Taylor, Reliable quantification of microplastic release from the domestic laundry of textile fabrics, The Journal of The Textile Institute 113(2022) 4, 558-566. https://doi.org/10.1080/00405000.2021.1892305

[4] M.A. Browne, T. Galloway, R. Thompson, Microplastic-an Emerging Contaminant of Potential Concern?, Integrated Environmental Assessment and Management 3(2007) 4, 559-561. https://doi.org/10.1002/ieam.5630030412

[5] R. Rathinamoorthy, S. Raja Balasaraswathi, A review of the current status of microfiber pollution research in textiles, International Journal of Clothing Science and Technology 33(2021) 3, 364-387. https://doi.org/10.1108/IJCST-04-2020-0051

[6] C.R.S. de Oliveira, A.H. da Silva Júnior, J. Mulinari, A.P. Serafini Immich, Textile Re-Engineering: Eco-responsible solutions for a more sustainable industry, Sustainable Production and Consumption 28(2021), 1232-1248. https://doi.org/10.1016/j.spc.2021.08.001

[7] E. Hernandez, B. Nowack, D.M. Mitrano, Polyester Textiles as a Source of Microplastics from Households: A Mechanistic Study to Understand Microfiber Release During Washing, Environmental Science and Technology 51(2017) 12, 7036-7046. https://doi.org/10.1021/acs.est.7b01750

[8] AATCC TM212-2021: Test Method for Fiber Fragment Release During Home Laundering, The American Association of Textile Chemists and Colorists, 2021.

[9] S.A. Hosseini Ravandi, M. Valizadeh, Properties of Fibers and Fabrics That Contribute to Human Comfort, in: Improving Comfort in Clothing, ed.: G. Song, Woodhead Publishing Limited, 2011, 61-78. https://doi.org/10.1533/9780857090645.1.61

[10] E. Smulders, Laundry Detergents, Wiley-VCH Verlag GmbH & Co. KGaA, Düsseldorf, 2002, 224.

[11] J. Kurz, Laundering in the Prevention of Skin Infections, in: Textiles and the skin, eds.: P. Elsner, K. Hatch, W. Wigger-Alberti, S. Karger AG, Basel, Switzerland, 2003, 69-91. https://doi.org/10.1159/000072238

[12] C. Palacios-Mateo, Y. van der Meer, G. Seide, Analysis of the polyester clothing value chain to identify key intervention points for sustainability, Environmental Sciences Europe 33(2021), Article number: 2. https://doi.org/10.1186/s12302-020-00447-x

[13] M.C. Zambrano, J.J. Pawlak, J. Daystar, M. Ankeny, J.J. Cheng, R.A. Venditti, Microfibers generated from the laundering of cotton, rayon and polyester based fabrics and their aquatic biodegradation, Marine Pollution Bulletin 142(2019), 394-407. https://doi.org/10.1016/j.marpolbul.2019.02.062

[14] G. Dalla Fontana, R. Mossotti, A. Montarsolo, Influence of sewing on microplastic release from textiles during washing, Water, Air, & Soil Pollution 232(2021), Article number: 50. https://doi.org/10.1007/s11270-021-04995-7

[15] A. Hazlehurst, L.Tiffin, M. Sumner, M. Taylor, Quantification of microfibre release from textiles during domestic laundering, Environmental Science and

Pollution Research 30(2023), 43932-43949. https://doi.org/10.1007/s11356-023-25246-8
[16] HRN EN ISO 6330:2021: Tekstil - Postupci pranja i sušenja u kućanstvu za ispitivanje tekstila.
[17] R. Nayak, S. Ratnapandian, Care and Maintenance of Textile Products Including Apparel and Protective Clothing, CRC Press, Taylor and Francis Group, London, 2018. https://doi.org/10.1201/b22481
[18] Desinatura tkanina, Hrvatska tehnička enciklopedija, 204. https://tehnika.lzmk.hr/tehnickaenciklopedija/desinatura_tkanina.pdf, Accessed: June 13, 2024.
[19] HRN EN ISO 4484-1:2023: Tekstil i tekstilni proizvodi - Mikroplastika iz tekstilnih izvora - 1. dio: Određivanje gubitaka materijala iz tkanina tijekom postupka pranja.
[20] T. Pušić, B. Vojnović, M. Čurlin, I. Bekavac, T. Kaurin, K. Grgić, K. Šimić, Z. Kovačević, Assessment of Polyester Fabrics, Effluents and Filtrates after Standard and Innovative Washing Processes, Microplastics 1(2022) 3, 494-504. https://doi.org/10.3390/microplastics1030035
[21] M. Čurlin, T. Pušić, B. Vojnović, N. Dimitrov, Particle Characterization of Washing Process Effluents by Laser Diffraction Technique, Materials 14(2021) 24, Article number: 7781. https://doi.org/10.3390/ma14247781
[22] I. Čorak, A. Tarbuk, D. Đorđević, K. Višić, L. Botteri, Sustainable Alkaline Hydrolysis of Polyester Fabric at Low Temperature, Materials 15(2022) 4, Article number: 1530. https://doi.org/10.3390/ma15041530
[23] N.J. Lant, A.S. Hayward, M.M.D. Peththawadu, K.J. Sheridan, J.R. Dean, Microfiber release from real soiled consumer laundry and the impact of fabric care products and washing conditions, PLoS ONE 15(2020) 6, e0233332. https://doi.org/10.1371/journal.pone.0233332

Funding: This research was funded by Croatian Science Foundation, grant number HRZZ-IP-2020-02-7575.