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Microplastic pollution from synthetic textiles: quantitative evaluation and mitigation strategies

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Abstract

The present thesis focuses on microplastic pollution from synthetic textiles. Microplastics are defined as plastic fragments with dimensions less than 5 mm, which are gaining much attention due to their ubiquitous and possibly dangereous presence in marine environment. Washing processes of synthetic garments have been lately identified as responsible for about 35% of primary microplastic release in oceans and seas. Microplastics represent a threat for marine ecosystems, and consequently for humans, since they may be ingested by fauna, adsorb persistent organic pollutants and leach toxic additives. Moreover, recent concern has arisen regarding the possibility for humans to inhale microplastics released to air from wearing of synthetic garments, with still not understood consequences on health. In such scenario, this work has three major objectives: developing experimental procedures to quantify microfibres released to water and to air from synthetic clothes, investigating the role of textile characteristics and washing conditions in the release of microfibres, implementing mitigation strategies.

First of all, two quantitative methods were developed to evaluate the amount of microfibres released during washing processes at lab and real scale. The two developed procedures were compared in terms of results, effectiveness, costs and time consume and proved to be a useful tool for the evaluation of the extent of the release from textiles, allowing the identification of specific trends in the microplastic release, as a function of the textile nature and geometry, different detergents and washing conditions.

Then, a protocol involving tests with volunteers wearing commercial synthetic garments was set up to assess if microfibres are actually released by wearing clothes and if the quantities and dimensions pose a real threat for human health.

Finally, mitigation actions were proposed, based on the development of innovative finishing treatments of synthetic textiles, aimed at creating a thin coating on the surface of fabrics that could protect them during the stresses of wearing and washing, reducing the release of microfibres. The ecosustainability of such treatments was ensured by using natural or biodegradable polymers as finishing materials, instead of the conventional synthetic ones. The effectiveness of such treatments in mitigating the release of microfibres was tested by washing tests at lab scale, showing a very promising reduction of almost 90% of microfibres released by untreated fabrics.

Contents

Chapter 1 - Introduction

1.1 The plastic age

In 1945, Yarsley and Couzens praised in their book “Plastics” the benefits that this new class of materials could bring to the world, at the beginning of what they called “plastic age”. They described with optimism a world where man could make what he wants and needs using synthetic materials made from universally distributed substances.[1] In 1999, Brydson defined plastics materials as processable compositions based on macromolecules.[2] In the case of synthetic materials, such macromolecules are polymers, large molecules constructed frmany smaller structural units, covalently bonded together in any conceivable patterns.[3] Whereas the use of natural polymers may be traced back to the antiquity (i.e. mentions of natural resins like bitumen, amber and lac are reported in the Bible and in Roman and Indian writings), the early stages of synthetic plastics took place at the end of the 19th century.

In fact, in 1862, Alexander Parkes presented at the Great International Exhibition in London, a new material called “Parkesine”, an organic material obtained by cellulose nitrate and suitable for moulding. Also starting from cellulose nitrate and using camphor as plasticiser, in 1870 John Wesley Hyatt and his brother patented a new horn-like material known as “Celluloid”, which became a commercial success. Nevertheless, the first fully synthetic resin was invented in 1907 by the Belgian chemist Leo Hendrik Baekeland, named “Bakelite” after him. He discovered that heating a mixture of phenol and formaldehyde together with a catalyst, while applying a pressure, produces a thermosetting resin. Within few years, the material revealed to be a commercial success, used in many fields and in particular for electrical insulation. The plastic industry commenced its rise, with its major growth period starting from 1930. Polystyrene (PS), poly(vinyl chloride) (PVC), polyethylene (PE), poly(methyl methacrylate) (PMMA), Nylon and polytetrafluoroethylene (PTFE) were all developed during the ‘30s - early ‘40s, whereas polypropylene and polycarbonates were discovered in the mid-1050s.[2] In those years, Karl Ziegler and Giulio Natta developed the Ziegler-Natta catalysts, which paved the way to the massive industrial productions of polyolefins.[4] From 1950 to 2012, plastic growth had an average of 8.7 % per year, with plastics gradually replacing materials like glass, metal and paper.[5] It has been estimated that the amount of plastics (resins, fibres and additives) produced from 1950 to 2015 was 8300 million tons (Mt), around half of that produced in the last 13 years.[6]

The success of plastics preannounced by Yarseley and Couzens in 1945, is mainly due to the versatility of such materials, suitable for the most disparate applications. First of all, plastics are lightweight, strong, durable, corrosion-, chemical- and light-resistant, with high thermal and electrical insulation properties. Such range of properties along with their low-cost production, has driven the annual worldwide demand for plastics.[7,8] It is undoubtable that the use of plastics has brought remarkable benefits to human life. In fact, the application of plastics as food and water packaging have introduced important advantages like the possibility to control atmosphere and temperature inside the package, allowing a safe storage.[7] In addition, plastics applied in the building and transportation fields entailed also relevant reductions in terms of consumption of materials and fossil fuel energy. Clear example of significant energy savings is the new Boeing 787, made by 50 % of plastic composites that allowed to obtain a 20% less fuel costs.[9] Also, in the automotive sector, lots of metal parts have been progressively replaced by plastic composites.[5] The progresses in polymer science has also led to remarkable technological advances, even just considering that plastics represent around the 20% of the mass contained in electronic devices.[10] Polymers in combination with nanofillers like graphene[11] or carbon nanotubes[12] are used to develop composite materials for applications in different fields ranging from electronics (i.e. sensors), to aerospace, actuators, sporting goods and fuel cells. In particular, polymers are essential materials for the development of renewable energy resource, from photovoltaic cells,[13,14] to wind turbines.[15] Finally, the carbon based chemistry of polymers makes them compatible with biological tissues, allowing biomedical applications such as drug delivery, orthodontic therapy, vascular stents, orthopaedic implants and so on.[16]

In a nutshell, plastics have become indispensable to modern living and no longer represent only luxury and novelty as they did in the 19th century. In 2016, the global production of plastics was of 335 Mt, of which 60 Mt in Europe. Presently, plastic is mainly obtained from fossil materials. In fact, in Europe, the 4-6% of the overall consume of oil and gas is related to plastic production. The total converter demand of plastics was 49.9 Mt in 2016, of this quantity the 39.9 % was for packaging, the 19.7 % for building and construction, the 16.7% for various applications (i.e. furniture, mechanical engineering, appliances, medical etc.), 10% for automotive and the rest for electrical & electronics, household, leisure, sports and agriculture. In Figure 1.1, the European converter demand by polymer types in 2016 is represented.[17] All this data does not take into account the consumption of synthetic fibres that will be analysed in a subsequent section of this work.

As far as most of the predicted applications and advantages of plastics eventually became true, Yarsley and Couzens failed to foresee what has inevitably become the greatest drawback and natural consequence of its high durability: its disposal. Currently, there are three possibility for the end-of-life of plastics: recycling, thermal destruction, disposal in landfills. Regarding this latter possibility, not always the disposal occurs in controlled and managed sites, but very often it results in uncontrolled discarding in dumps or in the environment. [6] According to the European plastic industry association, in 2016 27.1 Mt of plastic waste were collected through official schemes: the 41.6% was treated for energy recovery, the 27.3% was disposed in landfills, the 31.1% was recycled both inside and outside Europe.[17]

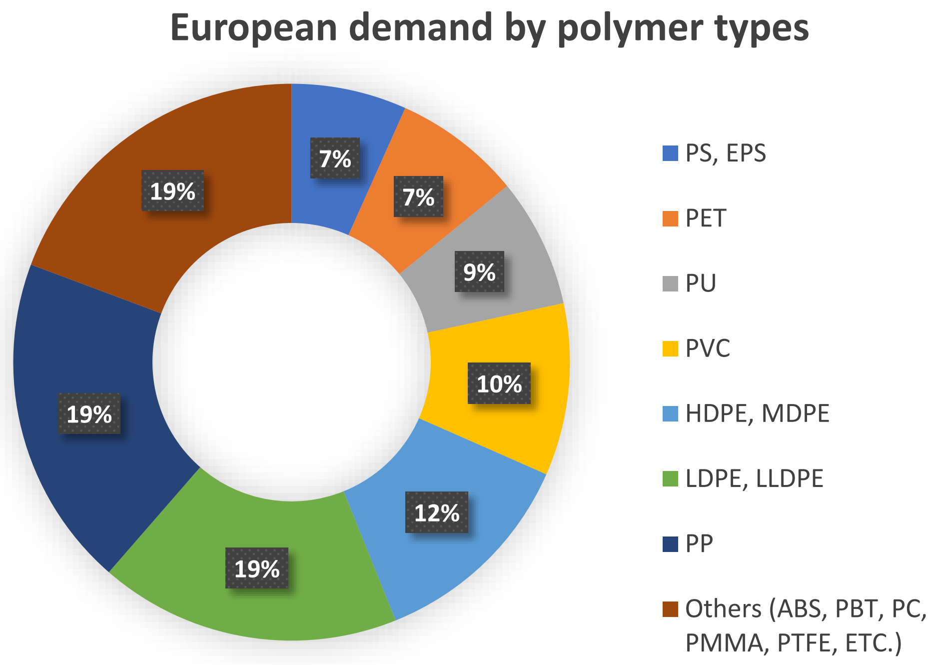

Figure 1.1. European plastics converter demand by polymer types in 2016 (source: Plastics Europe 2017).

In fact, much of the waste collected from western countries is shipped to countries with lower environmental standards, like China. This latter in fact, receives 56% by weight of plastic imports worldwide, with a serious lack of information available about how such waste is being handled.[5] A recent study has calculated that between 1950 and 2015, 6300 Mt of plastic waste have been generated, considering both primary and secondary (recycled) plastic. Regarding the disposal of such waste quantity, while the 12% (800 Mt) and 9% (600 Mt) was incinerated and recycled respectively, the remaining part ended up in landfills or in the natural environment. [6] As a consequence, the disposal of plastic in landfills or in the environment, coupled with the durability and resistance to degradation of such material, has caused one of the most serious environmental threat to our planet: plastic pollution.

Nowadays, plastic debris is ubiquitous and abundant in the environment and, despite the global recognition of the problem, it is still growing and will last for centuries even if immediately stopped.[18] In fact, it has been suggested to use plastic waste as a geological indicator of the so called Anthropocene era.[19] Moreover, it has been estimated that the current trends of plastic production and waste management could lead to the disposal of about 12,000 Mt of plastic waste in landfills or in the natural environment by 2050.[6] Thus, without an effective, well–designed and immediate management strategy of global plastic waste, the environmental consequences of this source of pollution will be irreparable.

1.2 Marine Plastic Pollution

The direct consequence of the massive plastic production and of the undoubtable lack of plastic waste management in many countries, has been the widespread presence of plastic debris in every corner of our planet, from the poles to the equator, from terrestrial habitats to remote islands. The warning signal of the seriousness of such environmental threat, have been marine ecosystems. In fact, most of the literature documenting the presence of plastics in our environment come from studies on marine habitats.[20,21,22] The first observations on the presence of plastic debris in marine ecosystems date back to the 1960s, when plastic fragments and pellets were found ingested by seabirds.[23] Since then, researches on this topic have come a long way and much more information is currently available on the impact of these pollutants on the environment,[24] or to their potential effects on human health.[25] Even if reliable data on the quantity of plastics present in marine environment are impossible to obtain, recent estimations have been made showing a very alarming scenario. In 2014, Ericksen et al. used an oceanographic model of debris distribution to estimate the amount and global dispersion of plastic pollution.[26] Maritime activity, watershed outfalls and population density were considered as main variables of the model, which used data from the Southern Hemisphere subtropical gyres and marine areas adjacent to populated regions. Results pointed out that at least 5.25 trillion of plastic particles are currently floating in the sea. Polymers like polyethylene, polypropylene and expanded polystyrene, due to their densities, represent the dominant floating debris, while heavier polymers like PVC, polyamides and PET tend to sink.[27] Nevertheless, even buoyant plastics do not remain in this floating status due to fouling with marine life and sediment or entanglement with other debris and then, they sink and settle down in deep water or sediment.[28] Once in the deep sea, degradation rates will be even slower because of darkness and cold.[25] Another study has found that plastic fishing gear can become negatively buoyant due to heavy fouling, but once they descend below the photic zone, the foulant colony would likely die due to lack of sunlight, allowing the plastic to float again. In this way, plastics become part of the marine ‘‘snow’’ (the natural detritus of the marine environment), and due to their buoyancy, they prevent marine snow from reaching the sea floor where it has an important role as sequestration vector for atmospheric CO_2, resulting in an alteration of the ecosystem.[29]

The sources of plastic debris in marine environment are essentially two: land-based or sea-based. The former includes litter intentionally left on beaches, material discarded in uncontained dumps and landfills, particles that pass-through wastewater treatment plants (the origin of such particles will be extensively treated in the following paragraphs). Instead, the latter comprises intentional or accidental loss of plastic items from ships, abandoned fishing gear or fishing packaging boxes, pellet spillage.[30] Polyolefins and nylons are predominantly used for fishing gears and around 18% of the marine plastic debris found in the ocean environment is attributed to the fishing industry. Instead, the contribution to plastic debris of land-based sources is around 80%.[31] A recent study has tried to estimate the annual input of plastic to the ocean from waste generated by coastal populations worldwide.[32] They defined "mismanaged" waste, material that is either intentionally littered or inadequately disposed, which could enter the water by inland waterways, wastewater outflows and transport by wind or tides. Considering 192 coastal countries with at least 100 residents, they based their evaluation on three factors: the mass of waste generated per capita annually; the percentage of waste that is plastic; the percentage of plastic waste that is mismanaged and has the potential to reach marine environment. Results showed that 275 Mt of plastic waste was generated in 2010 in these 192 coastal countries, with 4.8 to 12.7 Mt entering the ocean (Figure 1.2). They also ranked the top 20 countries waste producers, whose majority is represented by developing countries with a probable inadequate waste management system. According to their previsions, if no mitigation actions are applied, the amount of plastic waste flowing from land into the ocean will increase by an order of magnitude by 2025. Concerning the sea-based sources, despite since 1990 the dumping of rubbish at sea from ships has been prohibited under the international shipping regulation MARPOL Annex V, losses still occur. [32,33]

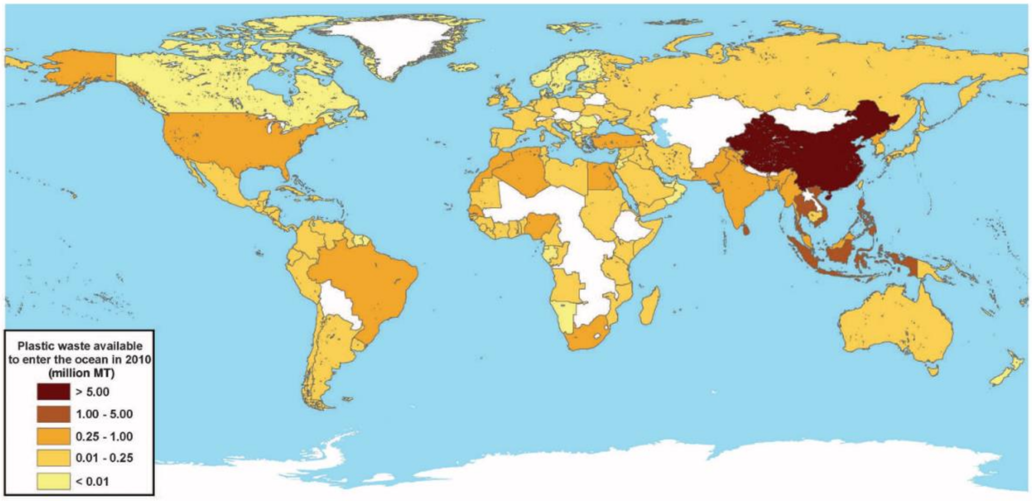

Figure 1.2. Global map with each country shaded according to the estimated mass of mismanaged plastic waste [millions of metric tons (MT)] generated in 2010 by populations living within 50 km of the coast.[a]

The durability and slow rate of degradation allow plastic debris to withstand the ocean environment for years to decades or longer.[34,35,36] Degradation my also become even slower due to fouling by marine organisms of plastic debris, which become partially shielded from UV light. Example of the persistence of plastic was the finding that some plastic fragments ingested by an albatross were related to an aeroplane shot down 9600 km away and 60 years ago.[18] In 1997, Laist identified over 250 species impacted by plastics either via entanglement or via ingestion. The list of this species comprises: turtles; penguins; albatrosses, petrels and shearwaters; shorebirds, skuas, gulls and auks; coastal birds other than seabirds; baleen whales, toothed whales and dolphins; earless or true seals, sea lions and fur seals; manatees and dugong; sea otters; fish and crustaceans.[37] The scientific literature that deals with the impact of plastic debris on marine fauna is wide and conspicuous, as well

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[a] From Jambeck, J.R., Geyer, R., Wilcox C., Siegler T.R., Oerryman M., Andrady, A., Narayan, R., Law, K.L. 2015. Plastic waste inputs from land into the ocean. Science 347, 768-771. Reprinted with permission from AAAS.

summerised in extensive reviews.[20,22,24,25] Recently, a study has shown the health consequences of marine plastic pollution on the loggerhead turtle *Caretta caretta*, highlighting how both entanglement and ingestion could lead to serious injuries and even death of the animal. Three specimens of this turtle were collected stranded in Terceira Island, Azores (NE Atlantic): the first had to be amputated due to a piece of a nylon long line that was strangling its right forelimb causing a necrotic process; the second had swallowed a piece of swordfish long line which caused its death; the third had its left forelimb entangled in a bowl of floating debris and was already amputated when found (Figure 1.3).[38]

Figure 1.3. A specimen of Caretta caretta found in 2 April 2008 in Terceira Island, Azores, entangled in a bowl of plastic lines and with its left forelimb already amputated and cicatrized.[b]

Even one the scariest marine predator, the blue shark, can be seriously affected by plastic debris. A research activity carried out by a joint team of Italian marine

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[b] Reprinted from Marine Pollution Bulletin, 86, Barreiros, J.P., Raykov, V.S., Lethal lesions and amputation caused by plastic debris and fishing gear on the loggerhead turtle Caretta caretta (Linnaeus, 1758), 518–522, Copyright (2014), with permission from Elsevier.

scientists, has analysed plastic litter ingested by blue sharks caught in the Pelagos Sanctuary SPAMI (North-Western Mediterranean Sea). Results shown that 25.26% of sharks ingested plastic debris, and the type of litter most ingested was polyethylene sheet-like user plastic, widely used as packaging material.[39] Finally, another marine inhabitant that has been strongly exposed to plastic litter is the sperm whale. Between January and February 2016, 30 sperm whales stranded on different locations along the North Sea coast. The gastro-intestinal tracts of 22 of the carcasses were analysed, founding plastic debris like netting, ropes, foils, packaging material and a part of a car in 9 of the 22 individuals. Even if none of these items was responsible for the death of the whales, the findings demonstrate the high level of exposure to marine debris and associated risks for large predators.[40]

Another collateral problem of the presence of plastic debris in marine ecosystems, is related to the use of additives in plastic manufacturing. The aim of the incorporation of additives is the modification of the bulk properties of a polymer. According to their function, they can be classified into: fillers, plasticizers, flame retardants, colorants, UV stabilizers, anti-aging, cross-linking agents etc.[2] There has been speculation in the scientific community, if plastic can transfer such toxic substances in the marine environment, and, if ingested, to marine fauna.[41,42] Another issue arises from the fact that plastic debris can also adsorb and concentrate contaminants coming from other sources and so already present in marine ecosystems. The environmental consequences of both adsorbed contaminants and chemical additives, will be discussed in more details in the following paragraphs.

A fundamental aspect of the presence of plastic debris in seas and oceans is connected to their dimensions. It is considered that (with the exception of materials that have been incinerated) all the conventional plastics that have ever been introduced into the environment do not degrade, becoming smaller in size as a result of abrasion, weathering, and fragmentation.[43] Many studies suggest that wind, wave action, and density of plastic influence the spread of these fragments.[44,45] In the last decade, it has become clear that the problem of marine plastic pollution has had an unexpected turn that involves not only the macroscale level but also the micro one, with the discovery of the presence of "microplastics".

1.3 Microplastics: definition & sources

In 1971, marine scientists were carrying out a sampling campaign with plankton tows, to determine the effects of a nuclear power station on the ecology of Niantic Bay (northeastern Long Island Sound). They found spherical plastic particles in the tows and, interested about them, decided to investigate them in detail. The particles were polystyrene plastic, with an average diameter of 0.5 mm, and they also found that some fish species were ingesting them. The spherules appeared identical to polystyrene plastic "suspension beads", which are not usually marketed commercially, but are molded into a pellet shape before being sold to plastic fabricators.[46] Two years later, another plankton survey, this time in the North Atlantic, found plastic particles, different in shape and polymer type, but most of them with dimensions less than 5 mm. Like in the previous mentioned work, they collected polystyrene spherules and also polyethylene cylinders or disks, both of them used in plastic fabrication.[47] In 1990, a study on the presence of plastic debris on South African beaches, used for the first time the word "micro-plastic" to indicate artefacts with a diameter less than 20 mm.[48] Then, in a research paper in 2004, the term microplastic was reused to investigate the presence of microscopic plastic debris in sediments collected from beaches and from estuarine and subtidal sediments around Plymouth, UK.[44]

Nevertheless, it wasn't until 2009 that, during the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris, the scientific community agreed on a common definition of microplastics: plastic particles smaller than 5 mm. Though "micro" infers the need for microscopy to view these plastic pieces, due to the early state of research, it was chosen not to exclude visible components of the small plastic spectrum and thus set the upper limit at 5 mm. Another important outcome of the workshop was the differentiation between two main types of sources of microplastics. Borrowing terminology from atmospheric sciences, it was also decided to differentiate microplastic on the basis of their origins as "primary" microplastics if they are intentionally produced either for direct use or as precursors to other products, and "secondary" microplastics if they are formed in the environment from breakdown of larger plastic materials.[49] These definitions were later accepted by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) and by the United Nations Environment Program.[50,51] While the term "secondary" generically comprises any microplastics deriving from the fragmentation or weathering of larger plastic debris (i.e. bags, packaging etc.), the term "primary" includes more specific types of microplastics.

A recent report produced by the International Union for conservative of Nature (IUCN) drew up the following list of main sources of primary microplastics (Figure 1.4): [52]

- **Tyres:** the wear and tear of the outer part of tyres release particles made of a matrix of Styrene Butadiene Rubber mixed with additives and natural rubbers;[27]

- **Synthetic textiles:** washing processes of synthetic clothes cause the release of microplastics that through the sewage system reach marine habitats;[53]
- **Marine coatings:** during building, maintenance or use of boats, particles (i.e. polyurethane, epoxy, vinyl and lacquers) can detach from the coating of the vessels;[52]
- **Road marking:** made mainly of paint and thermoplastics, it can release microplastics from weathering or abrasion by vehicles;[52]
- **Personal care products:** synthetic "microbeads" (mainly made of polyethylene) have substituted natural exfoliants in a wide range of products, from hand-cleansers to toothpaste; [54,55]
- **Plastic pellets:** they can be spilled during manufacturing, processing transport or recycling and were the first microplastics detected in marine environment;[46]
- **City dust:** includes losses from abrasion of infrastructure, of objects, blasting of abrasives and intentional pouring (detergents). [52]

Besides synthetic clothes (this source is the main object of this work so will be treated later in details), primary microplastics that have gained more attention are microbeads. A recent work has analysed six major brands of facial scrubs, extracting polyethylene microbeads with mean diameters between 164 and 327 µm.[56] They also estimated that a single use of such products could release between 4594 and 94,500 microbeads. These latter ones have also been the first type of microplastics that has led to legislation actions by several governments worldwide. For instance, nations like UK and Canada have recently banned the use of microbeads in cosmetic products, while other countries like Italy and Ireland are about to do it.[57]

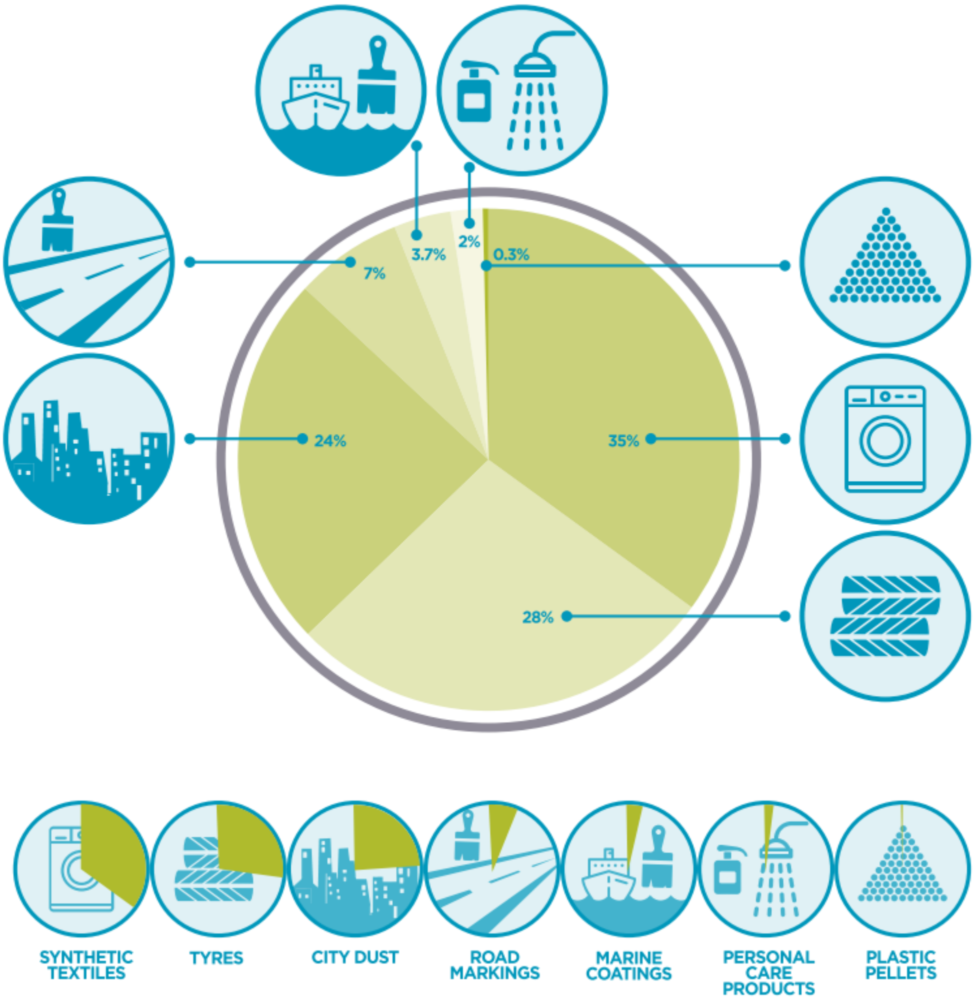

Figure 1.4. Global releases of primary microplastics to the world oceans by source (in %).[52]

1.4 Environmental impact of microplastics

Since 2011, the scientific literature on microplastic pollution have been continuously increasing, providing a conspicuous database on the occurrence of these pollutants.[58] Microplastics have been detected on beaches and in subtidal sediments worldwide;[53,59,60] in estuaries in UK and in China; [45,61] in rivers like the Rhine and the Meuse in the Netherlands and Germany,[62] in several French rivers,[63] in the Danube river;[64] in several lakes in northern and central Italy,[65,66] in the African Great Lakes,[67] in Canada and even in Mongolia.[68,69] Critical areas for plastic pollution are the subtropical gyres, where the debris tend to accumulate creating "plastic islands".[70,71] A recent work has investigated the concentration of microplastics in the South Pacific subtropical gyre, finding an average abundance of 26,898 particles/km^2 and average mass of 70.96 g/km^2.[71] Along with oceanic gyres, another area that have been indicated as a great accumulation zone for marine plastic pollution, is the Mediterranean Sea. In fact, sampling campaigns have found an average density of plastic of 1 item per 4 m^2, and 83% of the total number of collected items were microplastics.[72] Suaria et al. analysed the composition of microplastics floating in the Mediterranean Sea. They found that the most abundant polymer was polyethylene (52%), followed by polypropylene (16%), synthetic paints (7.7%), polyamides (6.6) and epoxy resins (5%), with other minor percentages of polymers like polystyrene, polyvinyl chloride etc.[73]

A wider alarming scenario comes from researches that have found microplastics even in the Artic and in the deep sea, demonstrating how these pollutants are ubiquitous and can also reach less accessible places.[74,75,76] In order to standardise the global dataset of plastic marine debris measured using surface-trawling plankton nets, van Sebille et al. used a statistical framework coupled with three different ocean circulation models. They calculated that 15 to 51 trillion microplastic particles accumulated in 2014, with the largest microplastic mass occurring in the North Pacific, while the greatest microplastic number was estimated in the Mediterranean and in the North Pacific.[77]

The widespread occurrence of microplastics in freshwater systems, sea and oceans, logically represents a threat for marine biota, since they can be ingested by zooplankton or other marine organisms, eventually entering the human food web. [78,79,80,81,82] Already in 1972, Carpenter et al., with their first account on the presence of polystyrene spherules in coastal waters, recognized the risk for fish to ingest them, founding these spherules in the guts of eight species.[46] Experiments on different types of zooplankton have clearly reported their capability to ingest both regularly and irregularly shaped microplastics, due to the fact that their dimensions overlap with those of natural food items.[80,83,84] Lusher et al. examined a sample of 504 of 10 different species front the English Channel, founding microplastics in 36.5% of them.[85]

Pegado et al. found 228 microplastics from gastrointestinal tracts of 26 specimens belonging to 14 species of fish from the Amazon River Estuary, categorizing them as pellets (97.4%), sheets (1.3%), fragments (0.4%) and threads (0.9%), with size ranging from 0.38 to 4.16 mm. The main polymers recognized were polyamide, rayon and polyethylene.[86] Several works have also highlighted how microplastics can be ingested by filter-feeders like mussels and oyster, and affect their respiration rates, immunology, reproductive capacity and filtration rates.[87,88,89]

Besides ingestion, microplastics may also present a toxic hazard to marine organisms. More in detail, three categories of compounds represent a toxic hazard in plastics:

- Persistent organic pollutants (POPs), already present in water and that can be adsorbed by microplastics;
- Additives added to plastics during their production;

- Residual monomers or oligomers.[28]

In the already mentioned study of Carpenter et al. in 1972, polychlorinated biphenyls (PCBs) were found on the surfaces of the collected polystyrene pellets. Since PCBs are not used in the manufacture of polystyrene, they hypothesized that the source of these PCBs was the seawater.[46]

In 2001, Mato et al. collected polypropylene (PP) resin pellets from four Japanese coasts, detecting the presence of (PCBs), dichlorodiphenyldichloroethylene (DDE) and nonylphenols (NP) in the pellets.[90] Since then, several studies have investigated the presence and sorption/desorption mechanism of hydrophobic organic pollutants in marine microplastics. Teuten et al. investigated phenanthrene (PHNH) sorption and desorption from polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE) and natural sediments.[91,92] Sorption capacity of PHNH for plastics was much higher than for sediments, while desorption rates of PHNH in seawater were significantly lower than for sediments. In 2012, Bakir et al. investigated the simultaneous sorption of two model POPs, PHNH and DDT onto PVC and Ultra-High Molecular Weight polyethylene, finding an antagonistic effect of DDT which interfere with the sorption of PHNH onto plastic.[93] Then, they carried on a broader analysis considering the potential for polyvinylchloride (PVC) and polyethylene (PE) to sorb and desorb ^{14}C-DDT, ^{14}C-phenanthrene (PHNH), ^{14}C-perfluorooctanoic acid (PFOA) and ^{14}C-di-2-ethylhexyl phthalate (DEHP). They evaluated the desorption rates of POPs both in seawater and under simulated gut conditions, studying the influence of pH and temperature to represent cold- and warm-blooded organisms. Their outcomes showed that desorption rates were faster with gut surfactant and simulating warm blooded organisms, with desorption under gut conditions up to 30 times greater than in seawater alone.[94] Other works have showed how polyethylene seems to accumulate more organic contaminants than other plastics such as polypropylene and polyvinyl chloride.[95,96]

Once verified that plastics can concentrate POPs in marine environment, the key question is if there is the real possibility to transfer such pollutants to marine organisms. At the moment, there is not a clear answer. A study conducted on fish exposed to a mixture of polyethylene with chemical pollutants adsorbed from the marine environment, discovered that the fish bioaccumulate the pollutants and suffer liver toxicity and pathology.[79] Transfer of contaminants from plastics and subsequent negative biological effects, were recorded also for lugworms exposed to contaminated microparticles of PVC.[97,98] Nevertheless, other scientific papers pointed out that the concentrations of plastics used in those experiments were higher compared to those typically reported in the natural environment and hence, there is uncertainty as to whether transfer of sorbed chemicals by microplastics is a quantitatively important route when compared to other pathways, such as respiratory or uptake from food, as suggested by calculations made with mathematical models.[99,100.101] In any case, the debate on the effects of microplastics on marine organisms is still open and need more scientific data, particularly in light of possible consequences on humans, since microplastics have been found in bivalves cultured for human consumption, in fish and bivalves sold for human consumption and even in sea salt.[81,82,102]

1.5 Microplastics from synthetic clothes

Among the different sources of microplastics, the most unexpected one is of course the washing processes of synthetic clothes. First accounts of synthetic fibres coming from clothes-washing machines were reported in sludge, sludge products, and sewage treatment plant effluents.[103,104] Such fibres were found to persist both in sludge produced by wastewater treatment plants as well as in treated wastewater effluent, and were also found in sludge byproducts of wastewater treatment plants (WWTPs), applied to agricultural land, up to 5 years after application.[104] In 2004, Thompson et al. found microplastics of fibrous shape (with diameter around 20 µm) in different samples collected from beaches and from estuarine and subtidal sediments in UK, and in plankton samples collected regularly since the 1960s along routes between UK and Iceland. They identified synthetic polymers like acrylic, polyamide, polyester and polypropylene.[44] Nevertheless, the first study that clearly pointed out how the washing of our clothes could be responsible for marine microplastic pollution, was the one of Browne et al. in 2011.[53] Through a forensic evaluation of microplastics from sediments collected on worldwide beaches (i.e. Australia, Oman, Chile, Philippines, Portugal, USA, Mozambique, UK, etc.), they discovered that the proportions of polyester and acrylic fibres used in clothing resembled those found in habitats receiving sewage discharges and effluents. Such result was the first warning signal that the presence of microplastic fibres in marine ecosystmes may be the consequence of the washing of clothes.

Textile industry is not a newcomer in the framework of environmental pollution. In fact, textile industry is recognized as one of the main polluters on earth for the harmful chemicals used, water and energy consumption, waste generation, transportation, and non-biodegradable packaging material.[105] As depicted in Figure 1.5, textile fibres are divided in two categories: natural and man-made. Natural fibres can be of animal, vegetable or mineral source, whereas the man-made ones are divided in regenerated and synthetic.[106] This last category, and object of interest of this work, represent almost the 60% of the annual global consumption of fibres, that is 69.7 Mt, used in the apparel industry. Over the last two decades, the global amount of fibres used for apparel has been increasing, mainly due to the massive consumption of synthetic fibres. In fact, the market of synthetic fibres has recorded an increase close to 300% over the same period.[52] The IUCN, has estimated that the release of microfibres by washings of synthetic clothes contributes by about 35% to the global release of primary microplastics to the world oceans, thus becoming the main source of microplastics.[52]

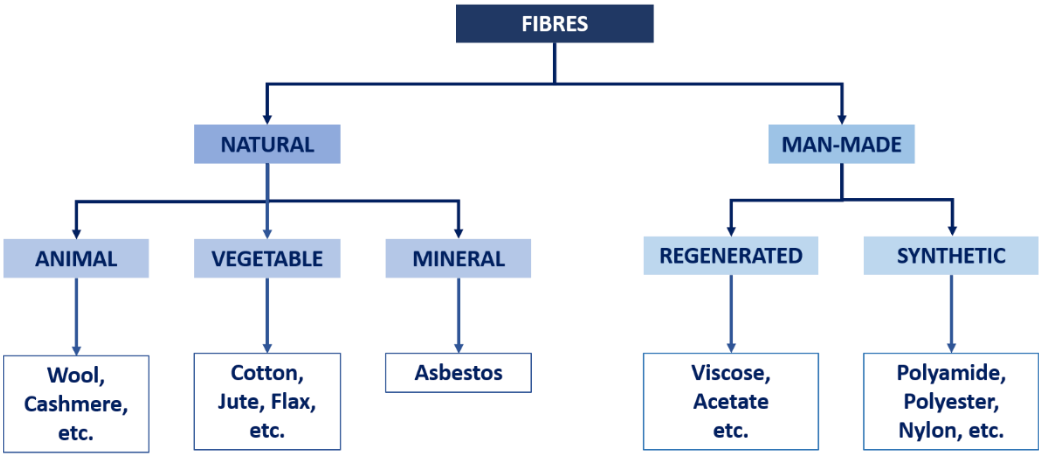

Figure 1.5. Classification of textile fibres.

The release of microplastics from synthetic clothes may be caused by the mechanical and chemical stresses that fabrics undergo during a washing process in a laundry machine. It has been debated if such "microfibres" can, and if yes in what proportion, be blocked by wastewater treatment plants (WWTPs). A first report on the efficiency of a WWTP on Swedish west-coast highlighted that even if the retention of microplastics in the WWTP was very high, >99 %, still the number of microplastics ≥300 µm was substantial.[107] Sutton et al. investigated the abundance of microplastic at nine sites in San Francisco Bay (California, USA), analysing also microplastics in final effluent from eight wastewater treatment plants that discharge in the Bay.[108] They found out that wastewater effluents contained a considerable microplastic contamination, with a great abundance of microfibres. Moreover, they did not observe a substantial difference between microplastic contents coming from tertiary and secondary filtration WWTPs. Sampling from three WWTPs in Sidney (Australia), showed an average of 0.28, 0.48 and 1.54 microplastics per liter of final effluent in tertiary, secondary and primary treated effluent, respectively.[109] Even with such low concentrations, considering the large volumes of effluent discharged to the aquatic environment, WWTPs have the potential to act as a pathway to release microplastics given, as concluded also by another study on the stepwise removal of microlitter in a tertiary level WWTP in Finland, which found that 1.7×10^6 to 1.4×10^8 microplastics per day was discharged into the sea trough wastewater effluents. [110] Other works have also investigated the role of WWTPs as pathways for microplastics, proposing methods to collect and identify microplastics from effluents like focal plane array-based micro-Fourier-transform infrared imaging.[111,112,113] In general, the results coming from all these investigations on microplastics and WWTPs, must be handled conservatively, due to differences in methodologies (e.g., mesh filters sizes, chemical analyses) and seasonal variation of water fluxes.[30] It must also been taken into account that global estimations of the amount of microplastics that can pass through WWTPs are not feasible since the type of plant varies according to the country and moreover, some countries with lower infrastructure do not collect and treat most part of their wastewater.[51]

Nevertheless, despite the differences among the studies, it cannot be argued that WWTPs represent an entrance route for microplastics to the aquatic environment, particularly for microfibres. Cesa et al. have reviewed all the works which analysed field samples where textile fibres were considered dominant, highlighting how microfibres can be found in beaches worldwide, in the water of Pacific Ocean, North Sea, Atlantic Ocean and even in the Artic and in deep sea sediments.[30] Another study have revealed that polyethylene terephthalate (PET) microfibres (length range: 62-1400 µm, width 31-528 µm, thickness 1-21.5 µm) were ingested by the zooplankton crustacean Daphnia magna, causing an increased mortality of the specie.[114] Textile fibres were also found in fishes and shellfish on sale for human consumption, sampled from markets in Makassar, Indonesia, and from California, USA.[81]

In conclusion, taking into account all the data and information gathered on microplastic pollution caused by washing processes of synthetic clothes, it arises the need of deeper studies on the mechanisms that cause the release of such fibres from textiles during washing, investigating parameters of influence, and evaluating the real amount of microfibres that come out from a washing machine. Then, such information will provide insights on how to mitigate such source of pollution in the most effective way.

1.6 Aim of the work

The main objective of this thesis is to shed a light on one of the newest, more alarming, and controversial sources of pollution: the release of microplastics from synthetic textiles. In order to reach such ambitious goal, this study will focus on the development of quantitative evaluation methods to assess the actual impact of the release of microfibres from synthetic fabrics, then will present possible mitigation strategies based on ecosustainable textile treatments.

In Chapter 2, two different evaluation procedures are presented to quantify the amount of microfibres released during washing processes of synthetic textiles. The first procedure was developed for washing tests at lab scale, starting from standard methods used in textile industry. It is based on the use of a laboratory simulator of real washing processes, and on further filtration of washing effluents with analysis of the filter by scanning electron microscopy, to quantify the number of microfibres released. The effectiveness of such procedure was assessed first, and it was applied to identify possible textile and washing parameters which could influence the release of microfibres. The second procedure was applied instead to a real household washing machine, whose wastewater underwent a multistep filtration process. The reliability of such procedure was tested by washing commercial clothes with commonly used washing parameters. Moreover, the effect of different types of garments, in terms of textile composition and characteristics, on the release of microfibres was also investigated. Finally, the two developed procedures were compared in terms of results, effectiveness, costs and time consume.

Another aspect of microfibre pollution was studied in Chapter 3, where the possibility of the release of microfibres from synthetic textiles to air was evaluated. The need of such type of investigation arose from recent articles[115,116] which have highlighted the risk of inhalation of synthetic fibres with unknown consequences on human health. A protocol involving tests with volunteers wearing commercial synthetic garments was set up to assess if microfibres are actually released by wearing clothes and if the quantities and dimensions pose a real threat for human health. Furthermore, the influence of textile parameters on the release to air was also studied.

Finally, in Chapter 4, mitigation actions are proposed. The approach reported in this part is aimed at preventing microfibre pollution starting from its initial source, synthetic textiles, starting from the development of innovative finishing treatments of synthetic textiles, aimed at creating a thin coating on the surface of fabrics that could protect them during the stresses of wearing and washing, reducing the release of microfibres. The ecosustainability of such treatments was ensured by using natural or biodegradable polymers as finishing materials, instead of conventional synthetic ones. In fact, the first treatment is based on the use of a natural polysaccharide, pectin, easily extracted from fruit peels, whereas the second one involves the application of two biodegradable polymers, poly(lactic acid) and poly(butylene succinate-co-butylene adipate). Such finishing materials were applied using two different techniques: a chemical grafting in the case of pectin, an electrofluidodynamic method for the biodegradable polymers. Both treatments were optimized in order to not compromise textile properties of the treated fabrics, and their effectiveness in mitigating the release of microfibres was tested by lab tests.

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Chapter 2 - Evaluation and quantification of microplastic release from synthetic clothes during washing

2.1 Introduction

The global framework of clothes washing procedures adopted worldwide is difficult to estimate due to the obvious difference in uses and consumes between countries, and also for the lack of data and records in continents like Africa, Central and South Americas. It has been estimated that globally more than 840 million domestic washing machines are used, consuming annually around 20 km^3 of water and 100 TWh of energy, with high variability in models and conditions of operation.[1] During the European Life+ project MERMAIDS, a household washing habit survey was conducted from October to December 2014 in Europe.[2] The majority of the respondents were from Spain, France, Italy, Netherlands, Belgium, Portugal and Germany. The data acquired in the survey have permitted to define that the most common washing machine brands are Bosch, Whirpool, LG, Indesit and AEG and 90% with a capacity between 5 and 8 Kg. Moreover, cotton program resulted to be one of the most used programs for all kind of clothes except for delicates. Furthermore, the results obtained by the survey indicated that:

- the most used washing temperatures are 30-40° C;
- wash cycles usually last between 1h and 1h 30min;
- most centrifugation programs used are between 800 and 1000 rpm;

- the consume of water is between 30 and 50 liters per wash cycle;
- the average of washes per household and per year is 352.54, that is 6.7 washes/household*week.

Considering these data, and the fact that they are related only to the washings in Europe, it is undoubtable that the quantity of wastewater from washing machines is enormous and acts as a route for microplastics. In such scenario, it is of striking importance to evaluate the real environmental impact of washing processes of synthetic clothes, starting from quantifying the microplastics that can be released during a wash and identifying possible parameters of influence.

In 2009, Browne et al. tried to evaluate the number of fibres discharged into wastewater from laundry processes. They used 3 different front- loading washing machines (Bosch WAE24468GB, John Lewis JLWM1203 and Siemens Extra Lasse XL 1000), and washed 3 different types of clothes (polyester blankets, fleeces, shirts). They washed at 40 °C and 600 R.P.M., without using any detergents since they blocked the filter-papers used to filter the effluents. They concluded that each garment can shed more than 1900 fibers per wash, all garments released a number of fibers per liter of effluent higher than 100 with more than 180% from fleeces.[3] Despite such values have been the only available for a while, there are concerns about the validity of them, since no more information were provided in the article about the evaluation procedure, particularly about the filter pore size and the counting procedure of the fibres.

Between 2016 and 2018, several works aimed at evaluating microplastic release from washing were published. Hartline et al. applied a gravimetric method to evaluate the release of microfibres during washings of 5 types of commercial jackets, with different compositions of synthetic fibres. Two types of wash trials were conducted: on new garments and on garments that, having been washed once as “new” garments, were then mechanically aged. The tests were carried with a top-load (Whirlpool model WET3300XQ) or front-load (Samsung model WF42H5000AW/A2) residential-type washing machine, without using any detergents. For the trials in the top-load washing machine they used the following program: 29.6 °C warm cycle, 30 min; 12 min wash, 14 min rinse, and 4 min spin. Instead, the program used for the tests in a front-load machine was: 29−41 °C warm cycle, 24 min; 8 min wash, 10 min rinse, and 6 min spin (1200 rpm). Only a part of the wastewater was collected and filtered through two inline hand-cut Nitex nylon filters, the first with a 333 µm pore size the second with 20 µm pore size. Across all experiments, the recovered microfibre mass per garment ranged from approximately 0 to 2 g, and the amounts recovered from top-load machine tests were approximately 7 times those from front-load machines. Moreover, the garments mechanically aged via a 24 h continuous wash showed an increased mass release compared to new garments.[4]

Pirc et al. analysed six identical fleece blankets, using a front-loading Bosch model Maxx7 VarioPerfect, and washing only with water, with detergent and with detergent plus softener, up to 10 consecutive washing cycles. Their selected washing program had a duration of 15 min, temperature of 30 °C, and spinning of 600 rpm. The wastewater was filtered through a stainless steel filter with 200 × 200 µm pores. Relative fibre release was calculated as percentage of the initial blanket mass. Results shown that the use of detergent and softener did not significantly influence emission and that after 8 washing cycles, the emission decreased and stabilized at approx. 0.0012 wt%.[5]

A similar approach was used by Napper et al., who tested three synthetic jumpers: 100% polyester (black), 100% acrylic (green) and 65% polyester/35% cotton blend (blue). From each garment, a 20 cm × 20 cm square was cut from the back panel, sewed at the edges with cotton thread, and washed in a Whirlpool WWDC6400 washing machine. The effluents were filtered through a nylon sieve with 25 µm pore size, attached to the end of the drainpipe. They performed washings with duration of 1h 15min and 1400 R.P.M., varying temperature (30 °C and 40 °C), detergent (absent i.e with only water, bio-detergent, non bio-detergent) and conditioner (absent, present), and recorded data after the fifth wash since they observed a stabilization of the amount of released microfibres after the first five washes. They gravimetrically evaluated the amount of fibres released and through a conversion formula, estimated the following numbers of microfibres released per 6kg of washing load: 137,951 microfibers for the polyester-cotton blend, 496,030 microfibers for the polyester fabric, 728,789 microfibers in the case of the acrylic. No clear trends were observed regarding the use of detergents and conditioners.[6]

Another work by Sillanpää et al. performed wash trials on four different types of polyester textiles and two garments of cotton, using a front-load washing machine (Bosch WAE28477SN) and liquid detergent. The washing program was 40 °C, spin-dry rate 1200, and total duration 75 min and up to 5 washing cycles were performed. Only an aliquot of wastewater for each washing test was filtered under vacuum through filters of 0.7 µm pore size and around the 10% of the filter area was observed under an optical stereomicroscope to count the microfibres released. The number of microfibres released from polyester and cotton textiles in the first wash varied in the range 2.1×10^5 to 1.3×10^7 and the mass ranged from 0.12 to 0.33% w/w, such amounts showed a decreasing trend in sequential washes.[7]

Carney Almroth et al. dealt with this issue with a different approach, focusing on textile characteristics. They studied polyester (polyethylene terephthalate), polyacrylic (polyacrylonitrile) and polyamide fabrics, with different knitting factors using a laboratory simulator of real washing processes, a Gyrowash one bath 815. They washed fabric samples at 60 °C for 30 min with a liquid detergent, filtering the washing water through a glass filter with 1.2 µm pore size. A sampled part of the filter was observed by using a light microscope to quantify the number of microfibres released. The outcomes of such work pointed out that polyester fleece fabrics released more fibres, with an average of 7360 fibers/m^{-2}/L^{-1} in one wash, compared with polyester fabrics which released 87 fibers/m^{-2}/L^{-1}. They also found that loose textile constructions shed more, as did worn fabrics, and high twist yarns are to be preferred for shed reduction.[8]

Considering all these studies conducted up to now, it is still necessary to develop effective experimental procedures to evaluate microfibres released during washing processes, both at lab and real scale and to correlate the release with washing parameters and textile properties. In fact, washing and textile parameters must be singled out and investigated to understand the role for instance of temperature, time, water hardness and mechanical action. For this purpose, the following paragraphs illustrate two experimental procedures to evaluate the microplastic release at lab and real scale; such procedures were applied to study the influence on the release of different textile and washing factors and were confronted to assess their effectiveness.

2.2 Evaluation of microplastic release from lab scale washing tests of synthetic clothes[c]

The quantification of microfibres released from standard fabrics due to laundering and the correlation of the release with fabric properties is reported in this paragraph. Moreover, the influence on the microplastic release of washing detergents (in liquid and powder forms), additives (i.e. softener, oxidizing and bleaching agents), washing parameters (i.e. temperature, time, water hardness and mechanical action) and washing conditions (domestic and industrial), was evaluated. In order to reach this main objective, a new procedure was developed to evaluate the microfibre release during wash trials from standard fabrics simulated at lab scale. Such procedure consists in the filtration of washing waters and the analysis of the filter surface by scanning electron microscopy (SEM). The application of a counting procedure allowed performing a direct quantification of the number and the dimension of the microfibres released. Compared to some previous works, the present study also differs because it analyses microfibres with very low dimensions.[4,5,6] In fact, a filter with a small pore size (5 µm) was used, allowing the detection of microfibres that could escape through filters with a greater pore size (20 and 330 µm pore size in Hartline et al.[4]; 200 µm pore size in Pirc et al.[5]; 25 µm pore size in Napper et al.[6]). Three different synthetic fabrics, woven polyester, knitted polyester and woven polypropylene, were investigated and quantitative information was collected about the amount and dimension of microplastics

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[c] The work presented in this paragraph has been published as: De Falco, F., Gullo, M. P., Gentile, G., Di Pace, E., Cocca, M., Gelabert, L., Brouta-Agnésa, M., Rovira, A., Escudero, R., Villalba, R., Mossotti, R., Montarsolo, A., Gavignano, S., Tonin, C., Avella, M., 2018. Evaluation of microplastic release caused by textile washing processes of synthetic fabrics. Environmental Pollution 236, 916-925. DOI: 10.1016/j.envpol.2017.10.057

released during washings simulating domestic conditions. The results obtained were correlated with the type of fabric, of detergent, with washing parameters and conditions, in order to identify specific trends in the release.

2.2.1 Materials and Methods

Materials

Three different commercial standard fabrics (Testfabrics Inc. USA) were selected for the washing experiments: plain weave polyester, double knit jersey polyester and plain weave polypropylene. The fabric type, code and the weight (g/m^2) provided by the manufacturer, along with the fibre length, are reported in Table 2.1.

Table 2.1. Fabric type, code, weight and fibre length

Type of Fabric	Code	Weight (g/m^2)	Fibre length (mm)
Plain weave polyester	PEC	126	35
Double knit jersey polyester	PEP	200	-*
Plain weave polypropylene	PP	170	50

* PEP yarns are made of continuous fibres.

The identity of each fabric type was confirmed by Fourier Transform Infrared (FTIR) spectroscopy. The spectra are reported in Figures S2.1-S2.3 of the Supporting Information (SI). Untwisted yarns (both warp and weft for woven fabrics), removed from the selected fabrics, were analyzed by optical microscopy using a Stereo microscope Lynx S115 (Vision Engineering, UK).

The detergents used in domestic and industrial washing experiments, are listed in Table 2.2.

Table 2.2. Laundry products tested during domestic and industrial washing methods.

Type of product	Code	Composition*	Dose (mL of liquid or g of powder /15L water)**	Washing pH ***	Type of washed fabric
			Domestic washings		
Distilled Water	R		-	7.0	PEC, PEP, PP
Light Duty Detergent (LDD, Liquid)	DL	Anionic and non ionic surfactants, fabric care additives, enzymes	60 mL	7.4	PEC, PEP, PP
Heavy-duty detergents (HDD, Powder)	DP	Anionic and non ionic surfactants, percabonate, tetraacetylethylenediamine, enzymes	73 g	10.7	PEC, PEP, PP
Oxy-product (liquid)	OL	Hydrogen peroxide, anionic and non ionic surfactants	85 mL	5.2	PEC
Bleach (liquid)	BL	Hypochlorite	100 mL	9.7	PEC
Softener (liquid)	SL	cationic surfactants, silicones	40 mL	4.6	PEC
			Industrial washings		
Distilled Water	R		-	7.0	PEC
Standard alkaline detergent solution	DL2	Surfactant, sodium hydroxide (in accordance with UNI EN ISO 105-C12)	-	12-12.5	PEC
Sapo Igienbucato	IB	Nonionic detergent, anionic detergent, other organic components	22.5 mL	8.2	PEC
Oxitex	OXI	Whitening based O_2 (Acid 6-phthalimido)-peroxyhexanoic.	15 mL	4.5	PEC

* The composition and brief description of the used detergent is detailed in the SI

** Dose is the amount of detergent as recommended by the manufacturer.

*** Washing pH is the pH of the liquor determined by using a pHmeter

Washing Process

Washing tests of synthetic standard fabrics were conducted in Linitest apparatus (URAI S.p.A., Assago, Italy), as laboratory simulator of a real washing machine, operating in both domestic and industrial conditions, in order to correlate fabric characteristics and/or washing conditions/laundry products with the extent of microfibres released. A detailed description of the Linitest apparatus is reported in the SI.

In particular, simulations of domestic washing tests were performed according to the ISO 105-C06:2010 standard method used for testing the color fastness of textiles to domestic and commercial laundering, using the liquor ratio (liquor:specimen) 150:1 vol/wt, corresponding to 150 ml of liquor per gram of fabric, where liquor means the solution constituted by water plus the dose of detergent. One cycle of the employed washing process simulates five domestic washing cycles (ISO 105-C06:2010). Fabric specimens, with a size of 9 x 9.30 cm^2, were sewed with a cotton thread in order to avoid the release of fibres from the cut edges. Then, such fabric specimens were placed in the steel containers of Linitest, containing 10 steel balls, and washed for 45 min at 40˚C using distilled water for the reference wash, R, and distilled water plus the dose of detergent for the others (see Table 2.2). The sewing was effective in preventing the release from the edges, as observed in preliminary washings reported in the SI.

In order to evaluate the effect of other washing parameters on microfibre release, a set of experiments was performed changing time, temperature, mechanical action and water hardness. For all these washings, the same commercial liquid detergent was used with a dose of 65 mL/15L water and washing pH of 8.1. In this case, the reference washing test C0 was performed with liquid detergent in distilled water as medium, while the other washing conditions were obtained by changing the parameters mentioned above. In Table 2.3, the used washing conditions are summarized.

Another set of washing tests was carried out according to the UNI EN ISO 105-C12 standard method, which specify the operations to simulate an industrial washing process. For industrial washings, fabric specimens with a size of 16 x 8 cm^2 were sewed on the sides with a cotton thread in order to obtain a “bag” of 8 x 8 cm^2 (bag), as illustrated in Figure S2.6 in the SI. These bags were filled with 25 steel balls and placed in the steel containers, along with other 25 steel balls, and washed for 60 min at 75˚C using distilled water for the reference washes, and solutions containing detergent for the other tests (see Table 2.2).

All the washing tests performed are summarized in Tables 2.2 and 2.3. Each washing test was repeated three times.

Table 2.3. Wash trials performed changing the washing parameters.

Condition	**Temperature (ºC)**	**Time (min)**	**N° Steel Balls**	**Medium**	**Type of washed fabric**
C0	40	45	10	Distilled water	PEC
C1	60	45	10	Distilled water	PEC
C2	40	45	0	Distilled water	PEC
C3	40	90	10	Distilled water	PEC
C4	40	45	10	Hard water (27 ºd)	PEC
C5	40	45	20	Distilled water	PEC

Filtration

The washing effluents, obtained from the wash tests, were filtered by means of a peristaltic pump (Mettler Toledo, flow rate 100 ml/min) connected with Tygon tubes, throughout polyvinylidene fluoride (PVDF) filters (Durapore®, Merck Millipore), see Figure 2.1a, with an average pore width of 5 µm and a diameter of 4.7 cm. Then, 400 ml of Milli-Q water at 70°C were fluxed in the filtration system, since such amount of water was found optimal to avoid an excess of detergent on the filter surface. The filters were dried at 105 ºC for 30 min. The washing effluents coming from a single washing test, whose volume was more than 150 ml depending on the weight of the tested fabric, were filtered through only 1 filter that was analysed as described below and never reused. Since each washing test was repeated three times, three filters per type of wash were obtained. In total 68 filters were analysed.

To avoid cross contamination of fibres among the different washes, the Linitest apparatus and the filtration devices were carefully rinsed with distilled water after each test. In detail, after each filtration, tygon tubes were cleaned fluxing about 2000 ml of Milli-q water while the filter holder was rubbed with a toothbrush to remove any residues of detergent or microfibres, then rinsed with Milli-q water. 1 filter per wash was used and never reused. Moreover, cotton lab coats and nitrile gloves were worn during all the experimental work.

Counting Method

In order to determine the amount of microplastics released during the washing tests, the filter surfaces were analysed using a Scanning electron microscope, SEM, Quanta 200 FEG (FEI, The Netherlands). SEM observations were performed in low vacuum mode (P_{H_2O} = 0.7 torr), using a large field detector (LFD) and an accelerating voltage of 30 kV. The observations were conducted on filters mounted on a circular sample stage (diameter 7 cm) by using adhesive tape. Due to the low vacuum conditions that prevent charging effects also on non electrically conductive samples, the filter surfaces were not modified, pretreated or coated with any kind of metal layer. The quantitative determination of the amount of microfibres released was performed using the procedure described below, and named as "counting method" from now on. For each filter sample, 21 electron micrographs were acquired along two orthogonal diameters of the circular filter (see Figure 2.1b). This sampling was chosen since it permits to observe the filter from the border to the centre of its surface. Every micrograph represents a rectangular area (Ar) of the filter surface, equal to 7.8 mm^2.

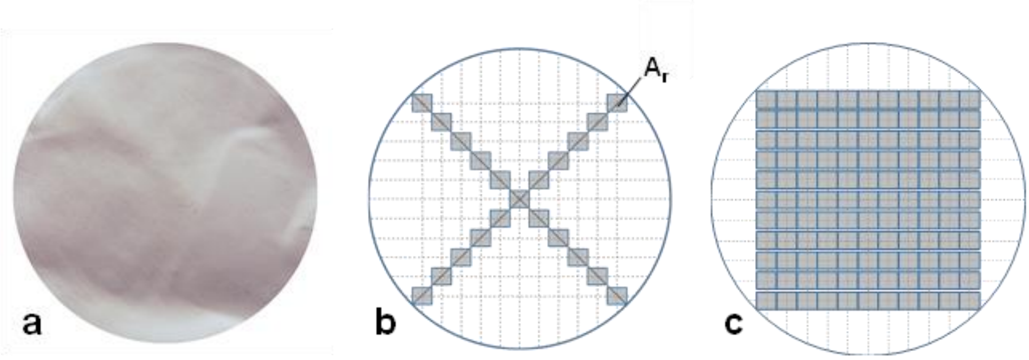

Figure 2.1. a) Optical image of a PVDF filter; b) position of the acquired micrographs (Ar) along the filter used in the counting method; c) position of the acquired 121 micrographs of the filter (extended counting method) used to validate the counting method.

The amount of microfibres, n_i, in each micrograph was determined by a visual observation with the help of the public domain software ImageJ (release 1.43u). The number of fibres per unit area, C_i, for each *i*-image, was calculated according to equation 1:

$C_i = n_i/A_r$ Equation 1

where n_i is the number of fibres of the *i*-image and A_r is the area of a single rectangle, 7.8 mm^2. The total number of fibres per filter, N, was determined by using equation 2

$$N= \bar{C}_i \cdot A_{tot} \qquad \text{Equation 2}$$

where $\bar{C}_i$ is the average number of fibres per unit area calculated as $\bar{C}_i = \frac{(\sum_{i=1}^{21} C_i)}{21}$, and A_{tot} is the total area of the filter (1709.4 mm^2).

In order to validate the counting method, an extended counting method was used. In detail, the counting procedure described above was applied on 2 filters obtained from different washings. Then, the resulting N value obtained for each filter was compared with the number of fibres determined by analysing a wider filter surface. In particular, for these filter samples, 121 electron micrographs were acquired as schematized in Figure 2.1c. These 121 micrographs cover an overall area of 943.8 mm^2, that is 55% of the total area of the filter. Using this extended counting method, the number of fibres per filter was calculated by using equation 3

$$N= \bar{C}_j \cdot A_{tot} \qquad \text{Equation 3}$$

where $\overline{C_j}$ is the average number of fibres per unit area obtained as $\overline{C_j} = \frac{(\sum_{j=1}^{121} C_j)}{121}$, and A_{tot} is the total area of the filter (1709.4 mm^2). The compatibility between the two methods was determined through two-Sample t-test and non parametric Mann-Whitney U test.

Several washing tests were conducted changing fabric type or detergent or washing condition, and each test was replicated three times. Three filters were obtained by the triplication of each washing test, and underwent the described counting method to determine N per each filter, the average N value among the three filters (N_a) and the related standard deviation (SD). No accumulation of microfibres was observed on preferential zones of the filter surfaces.

Since the tested fabrics differ for weight (g/m^2) and fabric specimens used for washing trials present the same size, the number of fibres released per each type of wash was normalized to the weight of the washed fabrics.

Statistics

Statistical analysis of the number of fibres per unit area, C_i, for each *i*-image, was carried out to compare the various washings by using OriginPro 8.5 software. The Ci values of the 3 filters collected from the triplication of the same washing test, were averaged before the statistical analysis, thus representing a medium distribution of the fibres, actually counted on the micrographs, along the two diagonals of a filter. The Kolmogorov-Smirnov normality test was used to determine whether data, from each filter, was drawn from a normally distributed population. The compared Ci values came from filters representing two or more different type of wash. In order to assess the differences between the washes per material type/detergent/condition, two-sample t-test and one-way analysis of variance (ANOVA) with Tukey's posthoc test were used for normally distributed data. The non-parametric Mann-Whitney U (MWU) and Kruskal-Wallis (KW) tests were applied when the assumption of normality was not valid. All tests were applied to assess correlation between number of fibres released and type of fabric, used detergent, washing conditions and industrial and domestic washings. A 5% significance level was used for all statistical tests; p values <0.05 indicate significant difference among the data.

Microfibre sizing and weight estimation

SEM micrographs of the filter surfaces were analysed by ImageJ to measure the length and diameter of the microfibres released. For each washing trial, the average values of the length, L, and diameter, D, were evaluated along with the standard deviation, based on the measurements of 25 microfibres per filter.

The weight in gram of microfibre released per kg of fabric washed, was estimated from the average number of microfibres released, Na, assuming the fibres were of cylindrical shape, following equation 4.[6]

Grams of microfibre/kg fabrics = $1000 \cdot N_a \cdot \left(\pi \cdot \frac{D^2}{4} \cdot L\right) \cdot \rho$ Equation 4

Where ρ is the density of the material.

2.2.2 Results and Discussion

Firstly, the counting method set up was validated by applying an extended counting procedure, in which a wider filter surface was analysed. With this aim, two filters, collected from two different washing experiments on woven polyester, were analysed. Filter 1 was collected from a washing with only water and filter 2 from a wash with liquid detergent. Each filter was counted twice: using the counting method and the extended counting method. The results from each method were statistically compared. This comparison was performed to confirm that the counting method (performed on 21 SEM images/filter) gives results comparable to an extended counting method (performed on a large area of each filter). In Figure 2.2, the values obtained by applying the counting method and the extended counting method on the filters, are graphed. The results, at a significant level of 0.05, indicated that there is no difference between the two methods, allowing to conclude that the counting method set up can be used to evaluate the amount of microfibres released during washings (filter 1: p=0.53 - MWU; filter 2: p=0.40 - t-test).

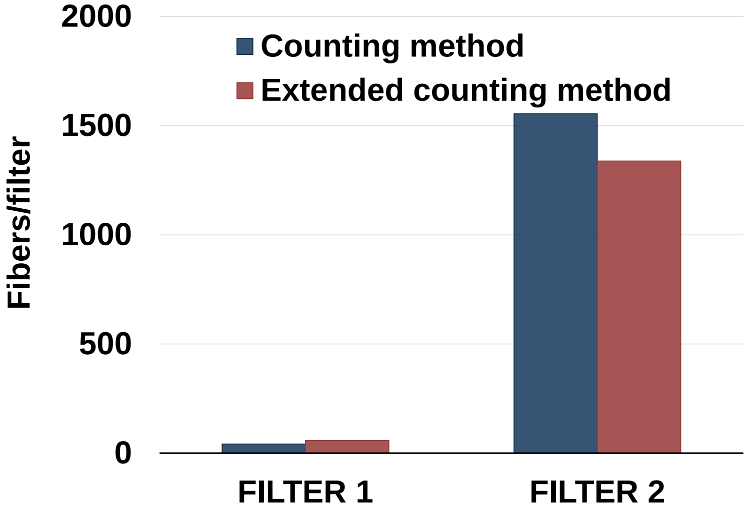

Figure 2.2. Comparison of the number of fibres per filter obtained for two different washes, by using the counting method and the extended counting method.

Figure 2.3 reports the results obtained from the three different fabrics, PEC, PEP and PP, washed in Linitest apparatus under domestic conditions with water, R, as reference, and with liquid, DL, and powder detergents, DP. In the same Figure, an example of SEM micrographs for each wash trial, is reported. In order to highlight the presence of microfibres on the filters, the fibres in the reported micrographs were coloured in dark grey using a digital image editing software. The digitally edited SEM images are identified as false colour SEM images from now on. The amount of microfibres released ranged from hundreds to thousands microfibres per filter and the values depended on the kind of fabric tested and on the washing conditions/laundry products. In fact, taking into account PEC, the washings performed with only water produced a release of 162 ± 52 microfibres per gram of fabric that increased to 1273 ± 177 using liquid detergent, and to 3538 ± 664 using powder detergents; a similar trend was obtained for PEP and PP. In fact, taking into account PEC, the washings performed with only water produced a release of 162 ± 52 microfibres per gram of fabric that increased to 1273 ± 177 using liquid detergent, and to 3538 ± 664 using powder detergents; a similar trend was obtained for PEP and PP.

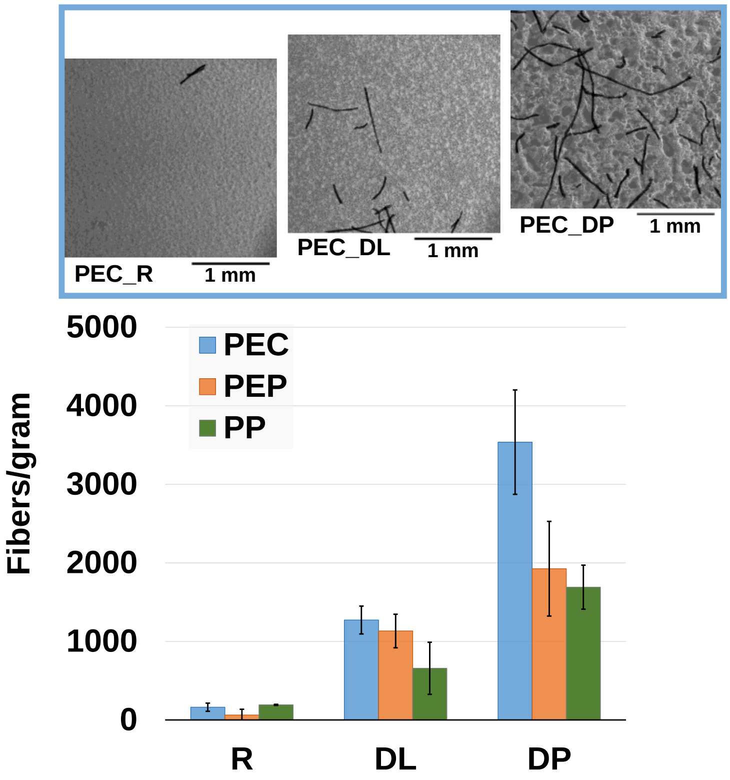

Figure 2.3. Number of fibres per gram of fabric (Na ± SD) released from woven and knitted polyester (PEC and PEP, respectively) and woven polypropylene fabrics (PP), during domestic washing simulations performed with water (R), liquid detergent (DL) and powder detergent (DP). In the upper part of the figure, SEM images of the filters collected by simulating washings of PEC with water, liquid detergent and powder detergent, are reported (false-colour SEM images).

These findings indicate that the use of detergents, both in liquid and powder form, induce an increase of microfibre release. In particular, the powder product favours the microfibres shedding more than the liquid one.

It is reported that washing products may significantly reduce the mechanical action during laundering. This tendency is ascribed to the presence of foam, generated by surfactants, and to the absorption of surfactants on fibre surfaces. The first reduces the beating and rubbing actions, thus preventing fabric damage, while the surfactants reduce the friction among fibres.[9] In the performed experiments these effects were not detected since the composition of the used detergents, in term of amount of surfactants, was not modified. Moreover, it should be considered that only weakly or moderately foaming detergents are permissible in Europe, where the horizontal axis drum-type washing machines are the most common, in order to avoid overfoaming that reduces the washing performance. For these reasons, foam regulators are commonly used to minimize detergent foaming tendencies.[10]

The higher release of microfibres caused by powder detergent could be explained taking into account that it contains inorganic compounds insoluble in water, like zeolite, that could cause friction with the fabrics. Moreover, the increase in the amount of microfibres released could be also related to the higher pH of the powder detergent. In fact, as reported in literature, though alkali-based detergents are effective in removing soil, there is some evidence that they can induce chemical damage on polyester fabrics by means of slow surface hydrolysis.[9] In addition, it is important to note that the powder detergent can also induce a significant error (underestimation) into microfibre determination since, as observable in Figure 2.4 for PEC samples, the powder detergent induced on the filter the formation of a thick layer in which the microfibres were partially or completely embedded, thus making difficult their numerical determination.

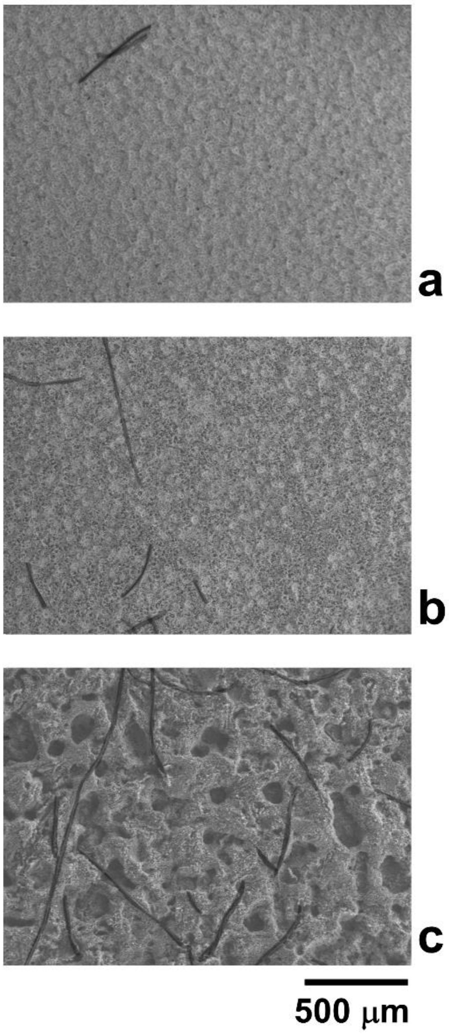

Figure 2.4. False-colour SEM images of filter surfaces containing microfibres coming from PEC washed under domestic condition with: water (a), liquid detergent (b) and powder detergent (c).

Statistical analysis confirmed that the amount of microfibres released differs significantly depending on the detergent used during the washing (PEC: p=0.00 - ANOVA; PEP: p=0.00 - KW; PP: p=0.00 - ANOVA). Tukey post hoc test revealed that the average number of microfibres released from PEC samples, washed by using powder detergent, was significantly higher than all other values obtained by washing with water or liquid detergent (p=0.00 in both cases

- ANOVA). Furthermore, the amount of microfibres released from PEP DL and PEP DP samples were significantly higher than PEP R (p=0.00 in both cases - KW). In the case of PP samples, the statistical analysis highlighted that the amount of microfibres released from PP DP samples was significantly higher than PP DL and PP R samples (p=0.00 in both cases - ANOVA). Usually, the main factor of loss of fibres from a textile is pilling, that consists in fibres entanglement on the textile surface and thus in the formation of fibre balls or pills during processes like washing or wearing. As reported in literature, this phenomenon is relevant particularly for knitted fabrics.[11] In the tests performed in the present work, however, this phenomenon was not observed and, as a result, knitted polyester released less microfibres than the woven one (see Figure 2.3). In order to understand the mechanism of microfibre release, an optical microscopy analysis was carried out on untwisted yarns (both warp and weft for woven fabrics), removed from the selected fabrics. As it can be observed in Figure 2.5a, the surface of the knitted polyester yarn is characterized by low hairiness, that consists of small fibres that protrude from the main yarn core.[12] In fact, the yarn is made of continuous fibres with a very low twist. Figures 2.5b and 2.5c, show that the weft and the warp yarns of woven polyester are characterized by a different structure: the warp is a doubled yarn and the weft is a single yarn. Both yarns present a high hairiness. The weft and the warp yarns of woven polypropylene, Figure 2.5 d – e, are both doubled yarns and with high hairiness. Since some of the analyzed fabrics, PEC and PP, present similar hairiness but opposite trends in the release, see Figure 2.3, this parameter could not be directly related to the release. A textile parameter that could instead influence the microfibre shedding, is the length of the fibres that compose the yarn. PEP yarns are made of continuous fibers (see Figure 2.5a), whereas PEC and PP yarns are made of short staple fibres with a length of 35 and 50 mm respectively (see Table 2.1). Such difference could affect the release of microfibres. In fact, shorter staple fibers could more easily slip away from the yarn during a wash, leading to a higher microfibre release, as observed for PEC and PP. Finally, the weight (g/m^2) of the fabrics, reported in Table 2.1, gives an indication of the material mass per unit area. The highest is this value, the highest numbers of fibres are present per unit area. However, as observed before, the microfibres released could not be related to the number of fibres present per unit area, since PEP, that has the greatest weight, is also the fabric that released less microfibres.

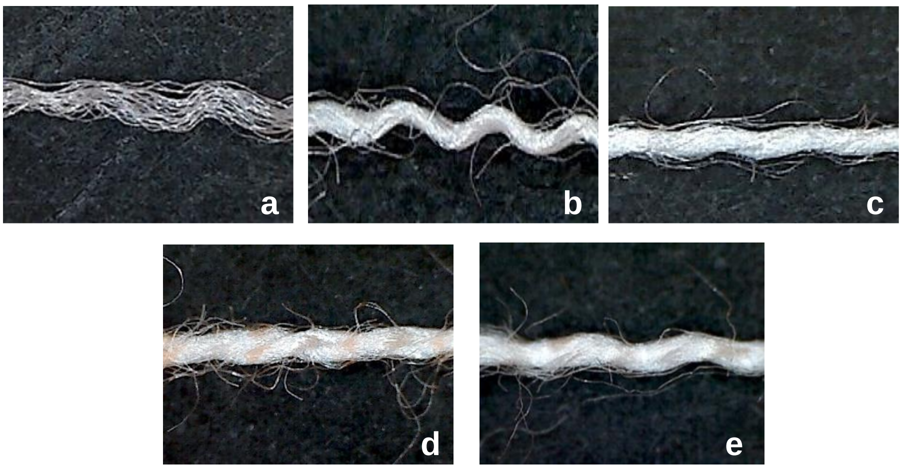

Figure 2.5. Optical microscope images of a) continuous polyester yarn from PEP; b) a staple polyester weft yarn, c) a staple polyester warp yarn from PEC; d) a staple polypropylene weft yarn, e) a staple polypropylene warp yarn from PP.

Besides the fibres counting, SEM micrographs were also analysed to determine the average dimensions (length and diameter) of the microfibres released. The results indicated that PEC microfibres were 340 ± 292 µm in length and 14 ± 3 µm in diameter. Similarly, PEP microfibre length was 478 ± 408 µm and the diameter was 20 ± 6 µm. PP microfibres showed a length of 339 ± 247 µm and a diameter of 19 ± 6 µm. The microfibre dimension was found independent from the detergent used. The weight in grams of microfibres released per kg of fabric washed was estimated using equation 4. Such approximation was necessary since the weight of microfibres released per filter was not determinable by gravimetric method. The grams of microfibres released per kg of fabric in the case of PEC fabrics were 0.012, 0.092, 0.255 in the washings with water, liquid detergent and powder detergent respectively; 0.013, 0.235 and 0.399 g/kg of PEP microfibres were released during the washings with R, DL and PD. Finally 0.017, 0.057 and 0.146 g/kg of fabrics were released in the case of PEP washed with R, DL and DP.

Moreover, the analysis of quantitative results obtained by applying the counting method indicate that, passing from lab-scale to household washings, a typical 5 kg wash load of polyester fabrics could release an impressive number of microfibres, in the range of 6,000,000-17,700,000, corresponding to 0.43 – 1.27 g of microfibres, depending on the type of detergent used.

Since woven polyester produced the greatest release of microplastics, further investigations were carried out on this type of fabric using the detergents OL, SL and BL (see Table 2.2), as described in the experimental section. The results are shown in Figure 2.6a, indicating that the washings performed with the softener, SL, and with the bleaching agent, BL, induced a reduction of fibre loss compared to PEC DL and PEC OL. In particular, the amount of microfibres released from PEC DL and PEC OL were significantly different from PEC R ($p=0.01$ and $p=0.00$ respectively - ANOVA). This trend could not be correlated to the pH of the different detergents since, for instance, OL and SL have a similar pH but affected the release in opposite ways. These results indicate a mitigating effect of the softening and bleaching agents on the number of microfibres released by the fabrics. Concerning the softener, its effect can be explained by its ability to reduce the friction between fibres,[13,14] allowing microfibrils to lay parallel to the fibre bundle[15] and thus decreasing damaging and breaking phenomena. The extension of such explanation also to the bleach liquid, should be carefully considered since it appears to be in contradiction with precedent studies performed on cotton fabrics.[16,17] For such reason, further experiments would be needed to establish the role of bleaching agents on microfibre release. A relevant observation is that this trend is different with respect to that reported in other studies where the use of softeners resulted in an increase of the fibre release from fabrics.[18,19] Nevertheless, it is to be noted that in the cited works, the main mechanism of fabric deterioration during washing is pilling, not evidenced in our study.

Finally, it was estimated that the use of a softener during the household washing of a 5 kg wash load of polyester fabrics, could reduce the release of microfibres more than 65% (total release about 4,150,000 microfibres) with respect to the amount released during the washing under the same conditions but only with a liquid detergent (about 6,000,000 microfibres).

The amount of microplastics released during the washes performed by changing the washing parameters (temperature, time, mechanical action, water hardness), as described in Table 2.3, is reported in Figure 2.6b. The obtained results indicate that higher temperature (C1), washing time (C3) and mechanical action (C5) produced an increase of microplastics release, even if the recorded differences were not very significant. In fact, ANOVA analysis indicated no substantial difference among the washes (p=0.30). These outcomes could be explained considering a synergistic effect between the detergent and the washing parameter. The higher temperature could increase the surface hydrolysis of polyester fabrics caused by the alkaline detergent, as well as a longer washing time could extend the fabric exposure to the chemical damage induced by the alkaline detergent. Moreover, the increased water hardness could induce fabric abrasion during the test. In fact, as reported in literature for cotton fabrics, the use of hard water in laundering accelerated accelerates the rate of abrasive damage.[20]

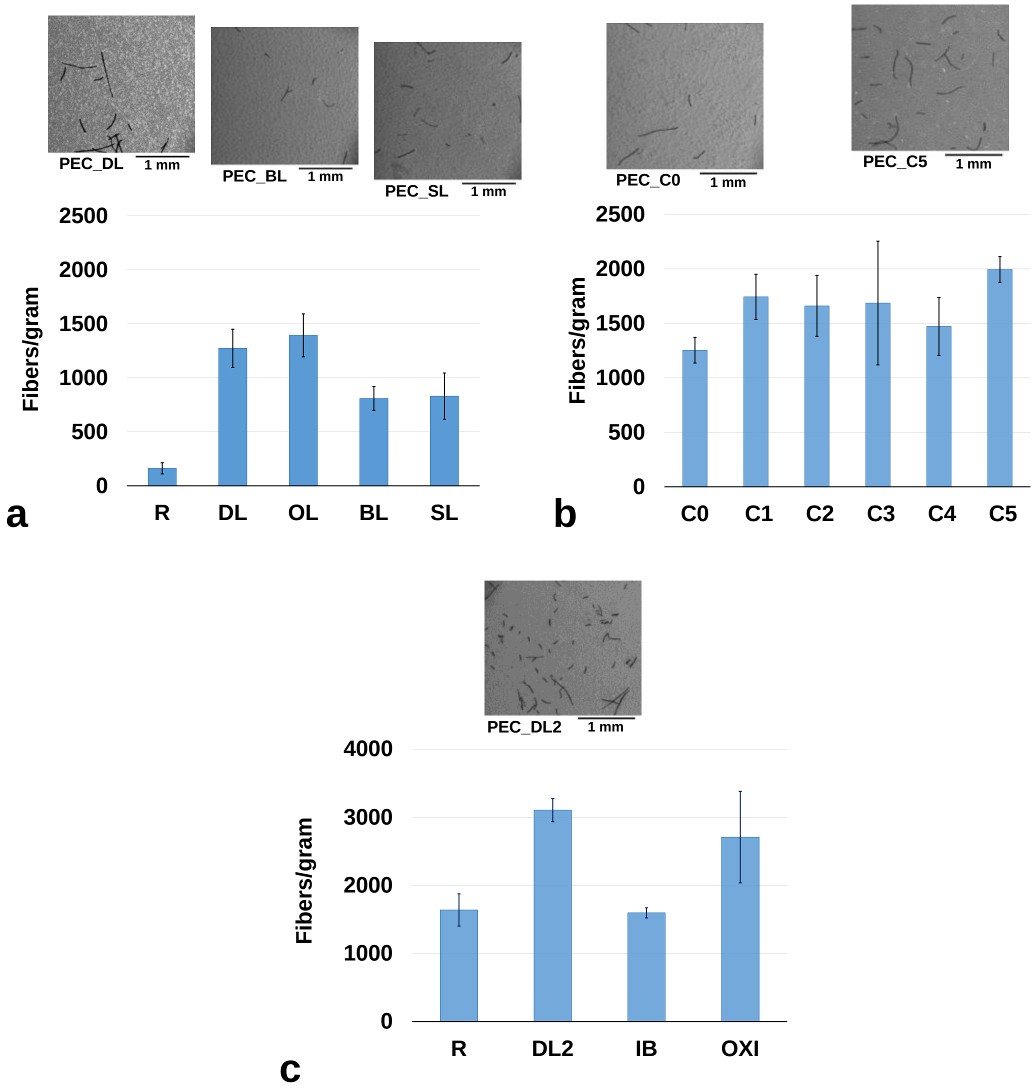

Figure 2.6. Counting results (Na ± SD) related to domestic washing simulations on woven polyester (PEC) with: a) different types of detergents, in the upper part SEM images of the filters collected by washing with DL, BL and SL are reported; b) different washing conditions, in the upper part SEM images of the filters collected by simulated washing with conditions C0 and C5 are reported; c) industrial washing simulations, in the upper part SEM images of the filters collected by washing with DL2 are reported (false-colour SEM images).

Finally, a last set of experiments was performed to simulate the impact of industrial laundry facilities on the environment, an aspect of the microfibre problem that has never been considered before. In this respect, industrial washings in Linitest were performed on woven polyester, as it showed the worst results in the domestic trials, upon washings with water, as reference, and with three laundry products. The results are graphed in Figure 2.6c. As expected, due to the more aggressive washing conditions, in all cases the release of microfibres was greater than that obtained under domestic washing conditions. The presence of liquid detergents such as DL2 and OXI induced an increase of microfibre loss, whereas the release obtained by using IB was closer to R. However, also in this case, no significant difference among all these washes was detected by ANOVA analysis ($p=0.28$). The pH of the detergents seemed to not affect the release, since DL2 and OXI have an opposite pH but a similar influence on the release.

The size and material type of fibres encountered in marine sediments and fauna have been the focus of different researches.[1,21] In agreement with the data reported, the size of the microfibres released during our washing tests ranges from 20 to 2000 μm in length. As known, microfibres can be ingested by marine organisms as reported for polyethylene terephthalate textile microfibres (length range: 62–1400 μm, width 31–528 μm, thickness 1–21.5 μm), that were ingested by crustacean Daphnia magna, causing an increased mortality of the specie.[22] Moreover, textile fibres were also found in fishes and shellfish on sale for human consumption, sampled from markets in Makassar, Indonesia, and from California, USA.[21] On the basis of such data, the size of the microfibres evaluated in this work matches the size range with potential negative effects on aquatic organisms.

2.2.3 Conclusions

In this work, an analytical protocol based on the filtration of the washing effluents of synthetic fabrics and on the analysis of the filters by scanning electron microscopy, was developed. Such protocol differs from others reported in literature because it is based on the direct quantification of low dimension microfibres (filter pore size 5μm) released during washing trials.[4,5,6] The adopted protocol proved to be a useful tool for the evaluation of the extent of the release from textiles, allowing the identification of specific trends in the microplastic release, as a function of the textile nature and geometry, different detergents and washing conditions.

Results showed that woven polyester released the highest number of microfibres with respect to knitted polyester and woven polypropylene during washing under domestic conditions, independently of the used detergent. Additional trials performed on woven polyester pointed out that the lowest release of microfibres was obtained by using a softener, due to its ability of reducing the friction among the fibres. Further studies are needed to better understand the role of bleach liquid in the decrease of the number of microfibres released. Regardless the type of fabric, the results indicated that powder detergent, higher temperature, higher water hardness and mechanical action increased the microplastics release. Finally, as expected, industrial washings produced a significant release of microfibres.

The approximate number of microfibres released from a typical 5 kg wash load of polyester fabrics was calculated to be more than 6,000,000 and it is influenced by the type of detergent used. Considering the different efficiency of WWTPs and the amount and the dimensions of the microfibres collected in this work, a significant part of them could potentially reach marine environment with negative effects on aquatic organisms. These results clarify key factors (fabric and detergent types, wash conditions and parameters) involved in the microfibre release caused by washing processes of synthetic textiles, which should be taken into account for the development of mitigation strategies to reduce microfibre pollution. Further experiment to examine the effect of laundry in real conditions will be performed to corroborate the results obtained in lab scale on standard textile.

2.2.4 Supporting Information

FTIR spectra of the tested fabrics

FTIR Spectra of fabrics were recorded at room temperature by means of a Perkin Elmer Spectrum 100 FTIR spectrometer, equipped with an attenuated total reflectance accessory (ATR). The scanned wavenumber range was 4000–650 cm^{-1}. All spectra were recorded at a resolution of 4 cm^{-1}, and 16 scans were averaged for each fabric. The FTIR spectra are reported in Figures S2.1-S2.3.

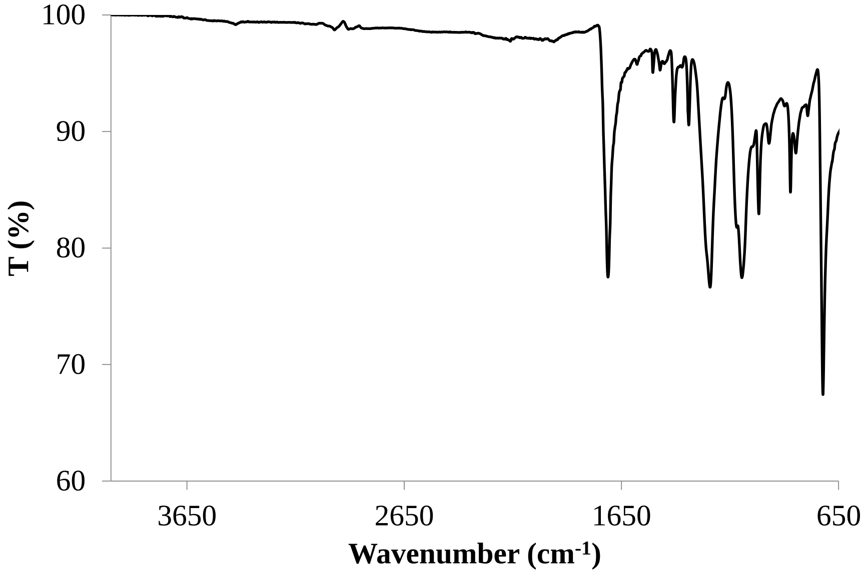

Figure S2.1. FTIR Spectrum of woven polyester (PEC).

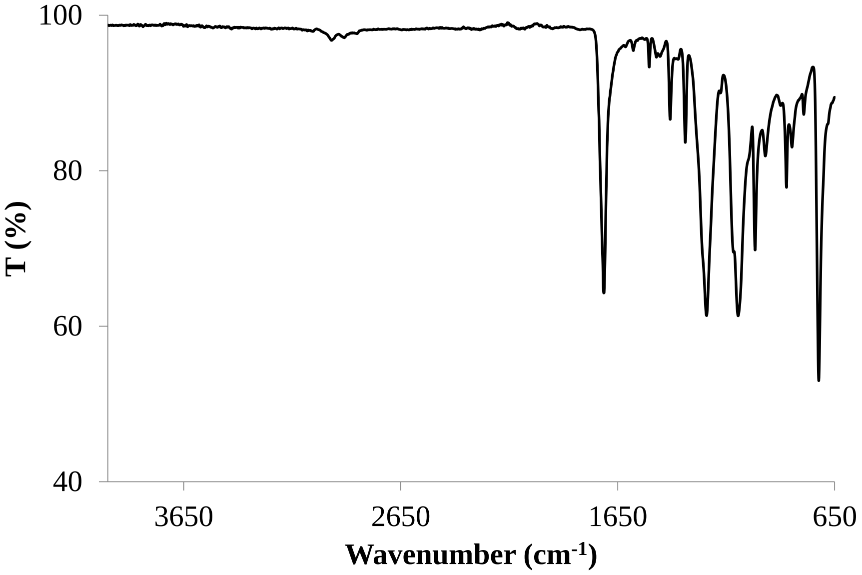

Figure S2.2. FTIR Spectrum of knitted polyester (PEP).

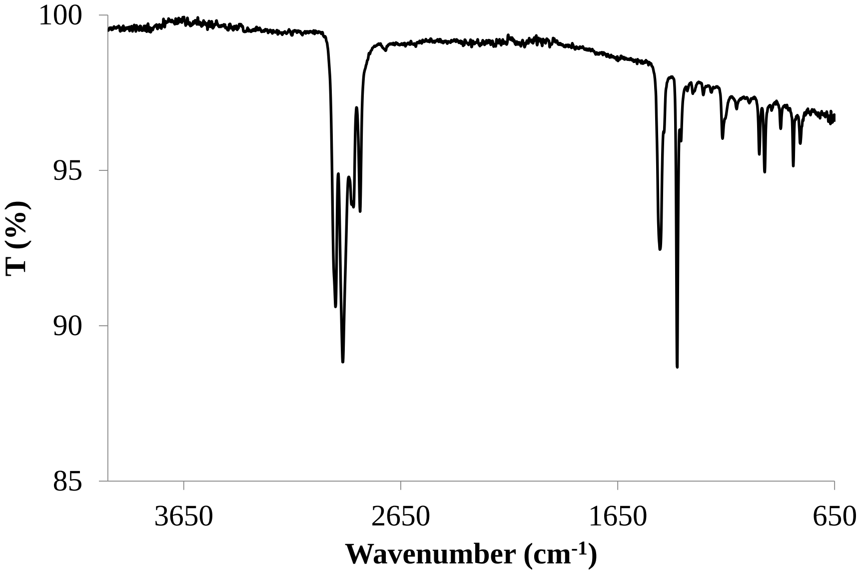

Figure S2.3. FTIR Spectrum of woven polypropylene (PP).

Detergent Composition

The general composition of detergent used in domestic washings are:

- LDD (liquid): anionic surfactants (sodium laureth sulphate, sodium alkylbenzene sulfonate C10-13 LIN), non ionic surfactants (fatty alcohol ethoxylate C12-18 7EO), fabric care additives (styrene/acrylates copolymer, CP vinylpyrrolidone-vinyllimidazole), enzymes (lipase, amylase, mannanase).
- HDD liquid: anionic surfactants (sodium dodecylbenzenesulfonate, sodium palm kernelate, sodium C12-15 pareth sulphate, sodium laureth sulfate), non ionic surfactants (C12-14 pareth-7, C14-15 pareth-7), enzymes (protease, amylase).
- HDD powder: anionic surfactants (sodium dodecylbenzenesulphonate), percabonate, sodium sulphate, zeolite, sodium carbonate, sodium silicate, sodium bicarbonate, non ionic surfactants (C12-15 pareth-7), Tetraacetylethylenediamine (TAED), enzymes (Subtilisin, Amylase).
- Oxy-product (liquid): hydrogen peroxide, anionic surfactants (sodium laureth sulfate), non ionic surfactants (fatty alcohol ethoxylated C12-C18 7EO).
- Bleach (liquid): sodium hypochlorite.
- Softener (liquid): cationic surfactants (dehydrogenated tallow hydroxyethylmethylammonium methosulfate), silicones (polymethylsiloxane).

The characteristics of the detergents used in industrial washings are:

- Alkaline detergent solution (pH 12-12,5) with 5 g/l of surfactant and 1 g/l of sodium hydroxide (in accordance with UNI EN ISO 105-C12). The detailed description is reported in Table S2.1.

Table S2.1. Composition of the alkaline detergent solution.

Substance	Concentration (wt%)
Sodium alkylbenzene sulfonate	0.425
Non ionic surfactants	6
Sodium citrate dihydrate	5
Ethylnaphthidate - HEDP	1
Matasilicate anhydrous	42.3
Polymaleic acid	2
Foam inibitors (phosphoric acid esters)	3
Sodium carbonate	39.5
Wet	0.475

- SAPOIGIENBUCATO. (pH 8.2). Composition: (15-30%) of Nonionic detergent, Anionic detergent, other organic component. Dose = 1.5 ml/l; This detergent was supplied by Rampi (Italy). SAPOIGIENBUCATO is a sanitizing detergent to the high concentration of last generation plug that replaces the detergent powder and is suitable for washing all types of fabrics, cotton, synthetics, linen and coloured fabrics that restores freshness, cleanliness and hygiene.
- OXITEX. Whitening based O2 (Acid 6-phthalimido)- peroxyhexanoic. This detergent was supplied by Rampi (Italy). (Dose = 1 ml/l; pH washing solution = 4.5). It is a unique auxiliary material for detergents, which readily delivers superior bleaching performance and disinfection at low temperature and under mild conditions in comparison with percabonate, perborate or other bleaching compound.

Linitest apparatus

The Linitest consists of a water bath containing a rotatable shaft which support radially, stainless containers (diameter 75± 5 mm, high 125 ± 10 mm and capacity of 550 ± 50 ml). The bottom of the containers is placed at 45±10 mm from the centre of the shaft.

The wash trials were performed according to specific normative which specify the operations to simulate a domestic or industrial washing process. The fabric specimens, prepared as described in the manuscript, were placed inside the stainless containers together with the opportune bath and steel balls.

The containers assembly was rotated at a frequency of 40 ± 2 min-1. The temperature of the water bath was thermostatically controlled to maintain the test solution at the described temperature ± 2 °C. In Figure S2.4**,** images of the Linitest apparatus are reported.

Figure S2.4. Linitest apparatus.

Evaluation of the sewing

The release from the edges was evaluated on preliminary washings preformed on woven polyester samples sewed and not sewed, under domestic condition by using liquid detergent. Washing effluents where filtered according to the procedure described in the Materials and Methods section. The filter surfaces were observed by means of scanning electron microscopy. Such analysis led to the conclusion that in the case of not sewed fabric samples, the filter surface was characterised by the presence of a large number of fibers entangled and the detachment of whole parts of the yarn that make impossible to apply the counting procedure (see Figures S2.5). This effect was not observed for sewed fabric samples.

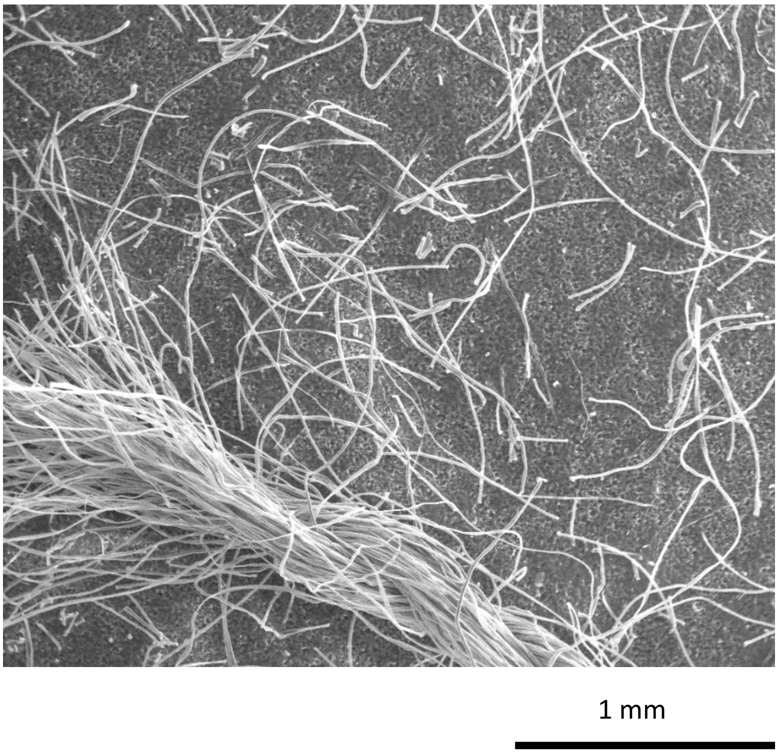

Figure S2.5. SEM micrograph of a filter surface to assess the edge effect.

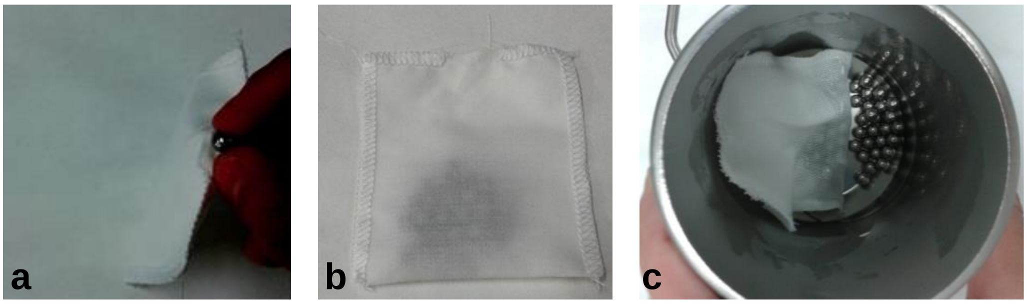

Figure S2.6. Preparation of fabric samples for the industrial washing process: a) insertion of stainless steel in the fabric; b) fabric bag with 25 stainless steel inside; c) view of the inside part of the apparatus used for the washing process.

2.3 Evaluation of microplastic release from synthetic clothes during real scale washing tests

In order to evaluate the real impact of domestic washings into the environment, a study on the release of microfibre during washings of real commercial clothes was performed. Wash trials were carried out in a household washing machine, whose wastewater was collected and filtered. The entire volume of effluents was filtered to obtain more reliable data not affected by errors due to the sampling of only an aliquot. The wastewater was filtered through decreasing porosity filters in order to understand, besides the amount of microfibres released, also their dimensions. The trials had two main objectives: (1) obtaining reliable quantitative data about microplastic release from commercial synthetic clothes during washings in real household laundry machines; (2) identifying possible influences of textile characteristics on the release. To this purpose, the only variable factor in the trials was the type of washed garments, while the washing program and detergent used were kept constant.

2.3.1 Materials and Methods

Materials

Four types of commercial garments were kindly supplied in more than one item by Plastic Soup Foundation (Amsterdam, the Netherlands): a blue t-shirt (100% polyester, code BT), a green sleeveless blouse (100% polyester of which 65% is recycled polyester, code GB), a red t-shirt (100% polyester, code RT), a green long sleeved top (the front is made of 100% polyester and the back is made of a blend of 50% cotton and 50% modal, code GT). The identity of each fabric type was confirmed by Fourier Transform Infrared (FTIR) spectroscopy. Fabrics were observed using a Leica M80 optical microscope to assess textile characteristics. The commercial liquid laundry detergent used in the washing tests has the following composition: 5-15% of anionic and non ionic surfactants; < 5% of soap and phosphonates; optical whitening agents; enzymes and perfume.

Washing tests

Washing tests were performed using a Bosch washing machine series 4 VarioPerfect WLG24225it with the following program for synthetics at 40°C, 1 h 47 min and 1200 rpm. The commercial liquid detergent was used in the dose recommended by the supplier. Each washing tests was performed on new garments. More items of the same type of garment were washed together in order to reach a washing load of 2 ÷ 2.5 kg. Two replicates of each wash tests were performed. Ten consecutive washing cycles were performed on BT and GB in order to evaluate the microfibre release vs washing time; the garments were dried at air between the cycles, to simulate real laundry habits. Cross-contamination of fibres between washes was prevented by running two consecutive empty washing cycles, the first at 60 °C, 1200 rpm, 2h 15 min, the second at 40 °C, 1200 rpm for 30 min.

Filtration

The analytical procedure adopted to determine the quantity of released microfibres consisted in the filtration of wastewater coming directly form the drainpipe of the washing machine, with a 400 µm pore size mesh. The wastewater was recovered in tanks and filtered by means of a peristaltic pump (SP 311/60 Velp Scientifica) connected with Tygon tubes, throughout a nylon net filter with a 60 µm pore size (Merck Millipore) and then through a nylon net filter with a 20 µm pore size (Merck millipore). Finally, 300 ml of the filtered wastewater were further filtered through a PVDF membrane of 5 µm pore size (Durapore®, Merck Millipore); greater volumes were impossible to filter due to the clogging of the filter for its very small pore size. A drawing of the filtration system is reported in Figure 2.7. When clogging of the filters occurred, the filtration was stopped, clogged filters were removed and stored, new filters were applied and the filtration restarted. At the end of each tank, 1L of distilled water was poured into, the tank was shaken, and the water filtered. Such procedure was carried out twice for each tank to collect possible fibres that remained attached on the surface of the tanks. Finally, 1L of distilled water at 70 °C was fluxed in the filtration system to clean the filters from excess of detergent. All filters were dried in oven at 105° for 1 h and then weighted. They were weighted before and after the filtration in order to evaluate the amount in grams of microfibre released, that was normalized for the washing load.

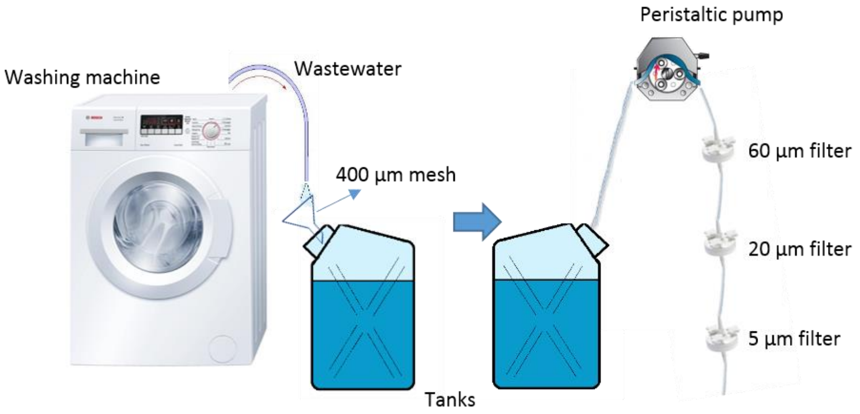

Figure 2.7. Drawing of the filtration system

To avoid cross contamination of fibres among different filtrations, Tygon tubes, filter holders and tanks were cleaned with distilled water and with a jet of compressed air. Cotton lab coats and nitrile gloves were worn during all the experimental work.

Thermogravimetric analysis

To asses the nature and relative amount of microfibres released during washing of the green long sleeved top made of polyester, cotton and modal, a thermogravimetric analysis was performed on about 5 mg of microfibers recovered on the filter with 60 µm pore size as well as on neat samples, about 5 mg, cut from the front and the back of the top. Samples were placed in an open platinum pan and heated from 30 to 800 °C at the rate of 10 °C min^{-1} under nitrogen atmosphere (flow rate: 40 mL min−1) in a Pyris 1 TGA from Perkin–Elmer (Waltham, MA, USA).

2.3.2 Results and Discussion

The selected garments were analysed using an optical microscope, to obtain information on their textile features. In general, textile fibres are spun into *yarns*, defined as assemblies of fibres twisted in different way along fibre axis. The fibers constituting the yarns can be *staple fibres*, of comparatively short length, and *filaments*, which are fibres of indefinite length.[23] Yarns are mainly arranged in two structures: *woven fabrics* produced by interlacing two sets of yarns, the warp which runs in a lengthways direction and the weft which runs in a widthway direction and *knitted fabrics* produced by interlacing loops of yarn.[24] Moreover the *hairiness* is defined as the presence of small fibres that protrude from the main yarn core.[12] In Figure 2.8, the optical micrographs acquired on fabric surface and on the yarns for each type of garment are reported. As evidenced in Figures 2.8a-d both BT and RT are knitted fabrics with low hairiness, the yarn is made of continuous filaments and presents a low twist. GB (Figure 2.8e) is a woven fabric with low hairiness. The two yarns constituting the woven are reported in Figures 2.8f-g. and are both constituted by filaments with the weft characterized by a higher twist than the warp.

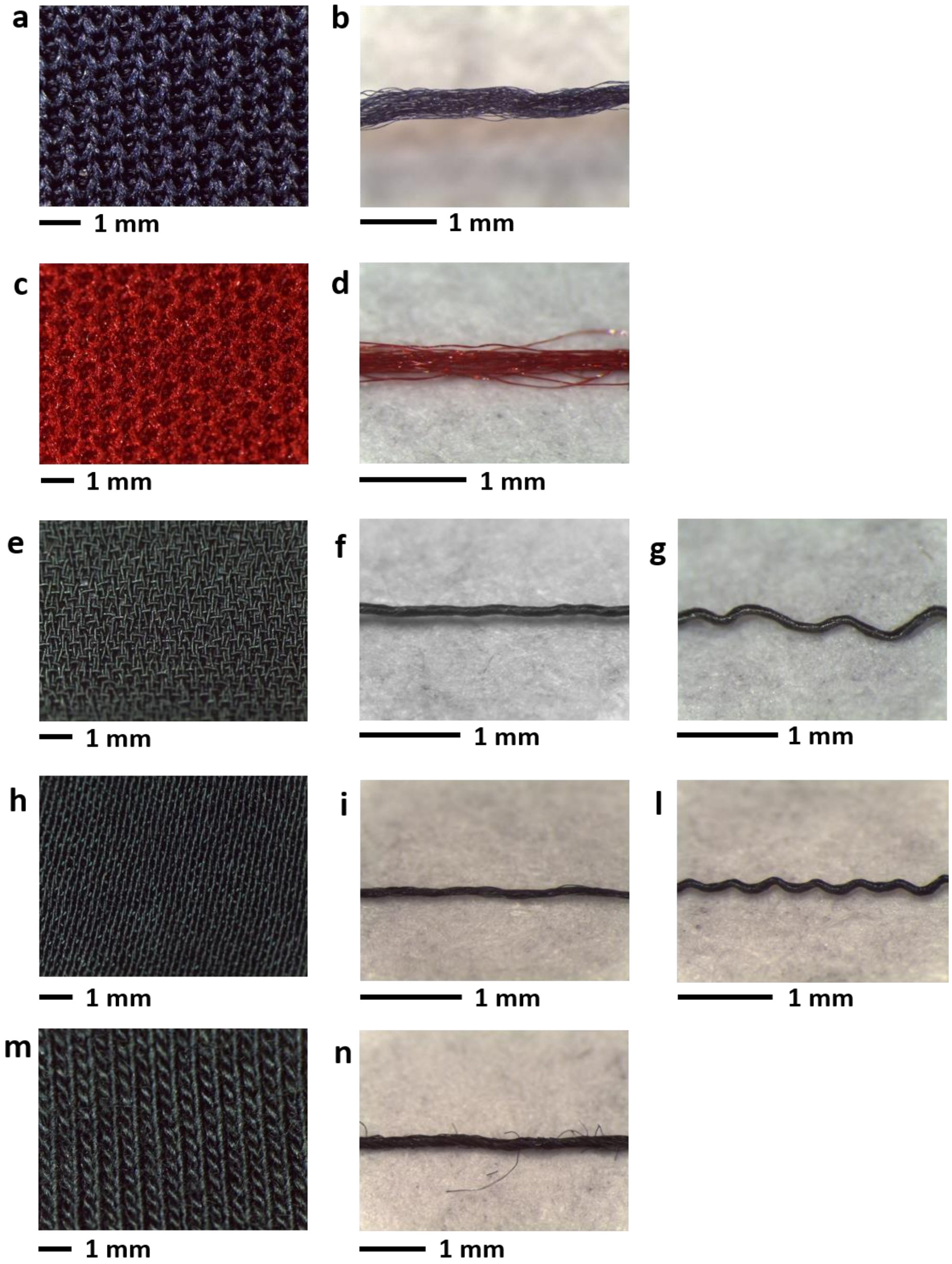

Figure 2.8. Optical micrographs of: blue t-shirt (BT) a) plane surface, b) yarn; red t-shirt (RT) c) plane surface, d) yarn; green blouse (GB) e) plane surface, f) warp yarn, g) weft yarn; green top (GT) front polyester part h) plane surface, i) warp yarn, l) weft yarn; GT back modal/cotton part m) plane surface, n) yarn.

Finally, GT presents a double structure, observable in figures 2.8h and 2.8m. The front part of the top (Figure 2.8h) is in 100% polyester, woven with low hairiness and with both yarns made of continuous filaments (Figures 2.8i-l), with a moderate twist in the case of the warp and a higher one for the weft. The back of the top (Figure 2.8m) is in a blend of 50% cotton and 50% modal, knitted with higher hairiness, the yarn is made with shorter fibres (Figure 2.8n), moderately twisted.

The clothes underwent wash tests to quantify the release of microfibres during washing. Each test had a washing load of about 2 ÷ 2.5 kg in order to simulate the mechanical action of more garments washed together. It was chosen to use the same liquid detergent because the aim of the work was to investigate the influence on the release of different types of garments. The results of the microplastic released after the first wash for all garments are depicted in Figure 2.9.

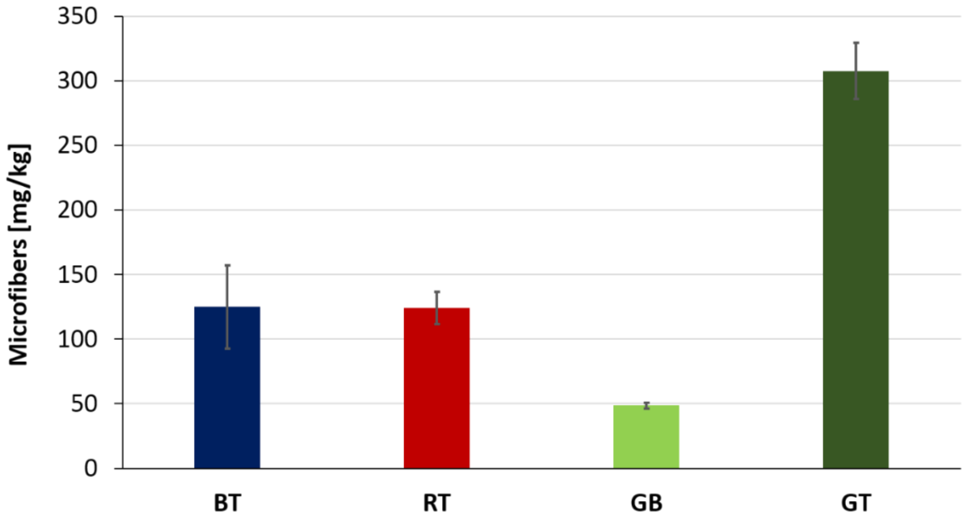

Figure 2.9. Quantity of microfibres released (expressed in mg/kg) from blue t-shirts (BT), green blouses (GB), red t-shirts (RT) and green tops (GT).

BT and RT released 125.0 ± 32.1 mg/kg and 124.1 ± 12.4 mg/kg of microfibres, respectively. Both t-shirts have the same fabric structure and yarn characteristics, so it is not surprising their same behavior during washing tests. These results indicate a very high reproducibility into the amount of microfibre released by knitted polyester fabrics made with yarns constituted by continuous filaments. Instead, GB released 48.6 ± 2.2 mg/kg of fibres, a value less than the half of that released from BT and RT. Such difference could be related to the fact that the yarns constituting GB have a higher twist compared to those of BT and RT, and are assembled into a woven structure, resulting in a more compact assembly that could make more difficult for fibres to slip from the fabric. At the moment, it is not possible to ascertain if the different polyester composition among GB (made of 65% recycled polyester) and BT and RT (made of 100% polyester) could have a role in such behavior. The greatest amount of microfibres released came from GT, with a value of 307.6 ± 21.8 mg/kg. Such result is almost three times those obtained for BT and RT. GT has the most complex textile structure with a front polyester woven part and a back cotton/modal knitted part, that should have different behaviors in the release.

The multistep filtration procedure allowed to separate the aliquots of microfibres recovered on the 400 µm mesh, the 60 µm and 20 µm pore size filters. The additional filtration on a filter with 5 µm pore size, allowed to obtain an approximate concentration of mg of microfibres per liter of water effluent. The different quantities of microfibre recovered on each filter are reported in Figures 2.10 and 2.11.

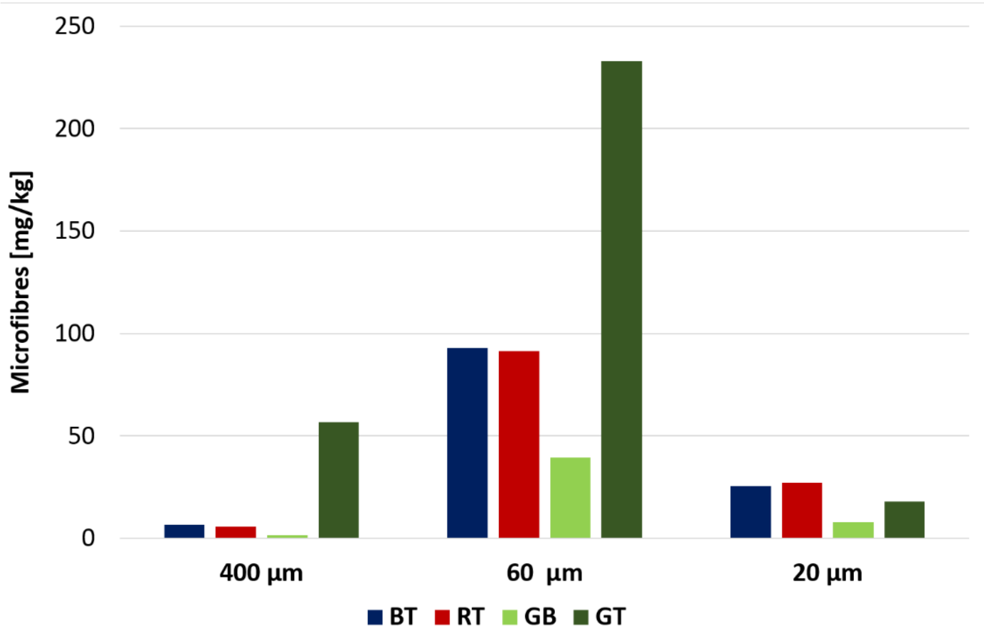

Figure 2.10. Aliquots of microfibres recovered on 400, 60 and 20 µm filters (expressed in mg/kg), from blue t-shirts (BT), red t-shirts (RT), green blouses (GB), and green tops (GT).

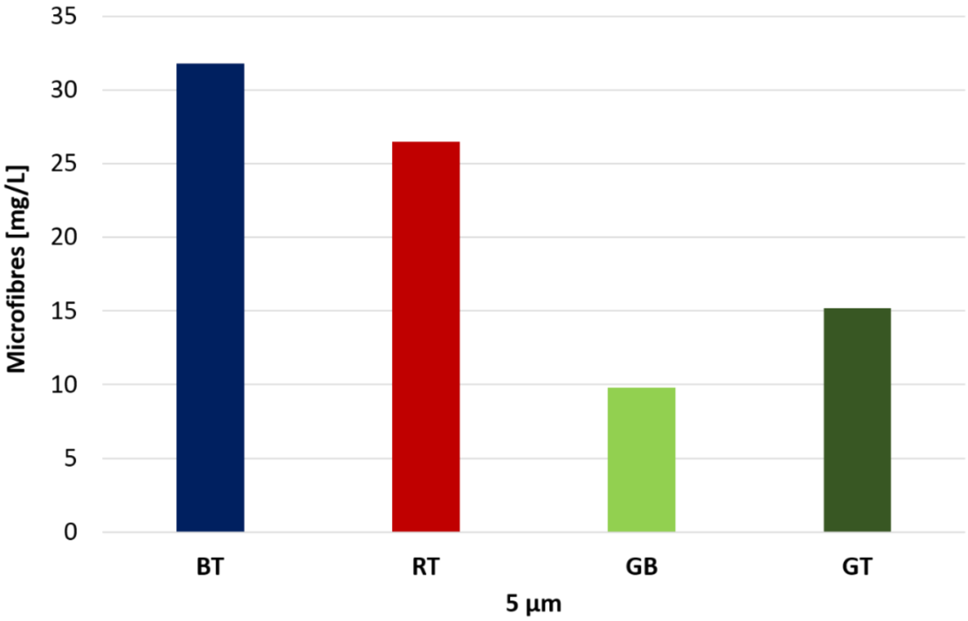

Figure 2.11. Aliquots of microfibres recovered on 5 µm filters (expressed in mg/L), from blue t-shirts (BT), red t-shirts (RT), green blouses (GB), and green tops (GT).

Regardless the type of garment, results pointed out that the greater aliquot of microfibres released was the one collected on the filter of 60 µm pore size; pictures of the filter appearance after filtration are shown in Figure 2.12. These findings indicate that most of the fibres that detach from the fabrics have dimensions compatible with such pore size.

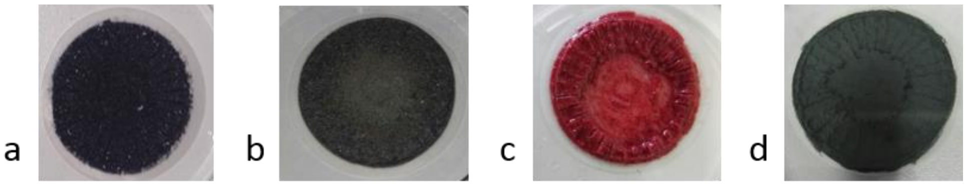

Figure 2.12. Pictures of the fibres recovered on 60 µm filters from the washing of a) blue t-shirts (BT), b) green blouses (GB), c) red t-shirts (RT) and d) green tops (GT).

The 400 µm mesh blocked similar amounts of fibres for BT and RT (6.7 and 5.6 mg/kg, respectively), very low for GB (1.4 mg/kg) and significantly high for GT (56.8 mg/kg). The same trend GT>>BT,RT>GB, was observed also for the fibres recovered on the 60 µm filter, whereas fibres collected on 20 and 5 µm filters showed a different behavior. In fact, for both of them, the fibres released from BT and RT were of similar amounts (20 µm: 25.5 mg/kg for BT, 27.0 mg/kg for RT; 5 µm: 31.8 mg/L for BT, 26.5 mg/L for RT) but slightly greater than the amount released from GT (20 µm: 18.0 mg/kg; 5 µm: 15.2 mg/kg). For all garments the 60 µm filter was able to retain around 75 ÷ 80 % of the total amount of microfibres released per wash. For BT, RT and GB, 400 and 20 µm filters retained around 5% and 20 % of the total release but, in the case of GT, such values were reversed (400 µm: around 20%; 20 µm: around 5%).

Thermogravimetric analysis was performed on GT fibres recovered from 60 µm filter, since it was the most abundant fraction, with the aim to understand the composition of the microfibres released.

Figure 2.13 reports the thermogravimetric curves of GT cotton/modal back part, GT polyester front part, and of GT fibres from 60 µm filter.

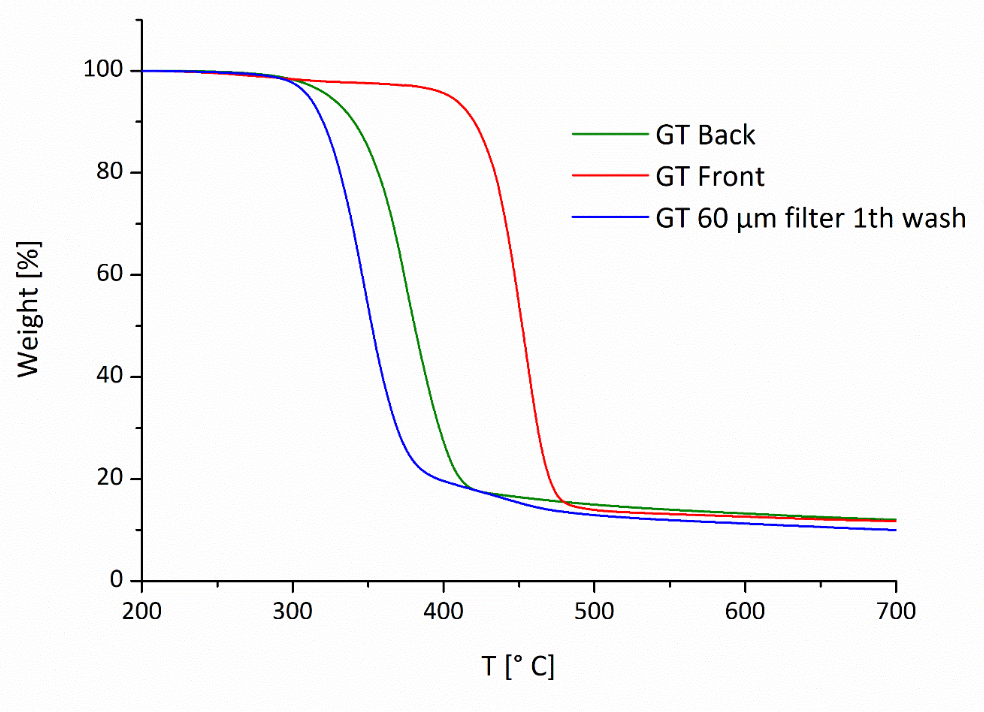

Figure 2.13. Thermogravimetric curves of GT cotton/modal back part, polyester front part, fibres form 60 µm filter.

GT front presents a single step thermal degradation, with a temperature of max weight loss (T_{max}) of 454° C, due to the decomposition of the main chain of polyester.[25] The GT back part has also a single step degradation but shifted to lower temperatures with a T_{max} at 377° C ascribable at cellulosic degradation of the blend cotton/modal. It is reported in literature that cotton and viscose have a similar thermal degradation behavior, with the degradation of viscose starting at lower temperatures compared to cotton.[26,27] However, in the analysed sample of GT back, no difference in the degradation of both materials was detected. Instead, the aliquot of microfibres recovered on the 60 µm filter presents a two-step thermal degradation: the first start at 200° C and has a weight loss of around 81% (T_{max} = 348° C). the second starts at 406° C and loose around 9% of weight (T_{max} = 450° C). Comparing such results with the thermal degradations of GT front and back part, it appears clear that the first step could be attributed to the degradation of the cotton/modal part of the aliquot, whereas the second step is ascribable to the degradation of polyester. Then, around the 80% of the amount of microfibres released from GT during washing are of cellulosic nature, released from the back part. An explanation to such behavior can be looked for in the textile differences between GT front and back part. This latter is composed by yarns with short staple fibres that could more easily be released from the fabric compared to the continuous filaments more twisted of the woven structure of the front. In fact, as reported in literature, in natural fibres staple length is not well defined and every batch of fibres consists of fibres varying in length over a wide range.[28]

Another part of the activity was dedicated to investigating the release of microfibres during subsequent washing cycles. Due to their completely different behavior, BT and GT were selected to undergo up to 10 washing cycles. Figures 2.14 and 2.15 summarize the results of this investigation. After 4th -5th cycles, microfibres released from BT reached a plateau, exhibiting the same trend in the aliquot recovered on the 60 µm filters. On the contrary, the release from GT showed a slightly decrease after 4th-5th cycles but no plateau was reached up to the 10 cycle. A similar trend was recorded for the aliquots from the 60 µm filters, with a constant decrease until the 4th cycle, followed by an oscillating pattern. Also in this case, a thermogravimetric analysis was performed on the aliquots of fibres recovered on 60 µm pore size filters after the 1st, 5th and 10th washing cycles.

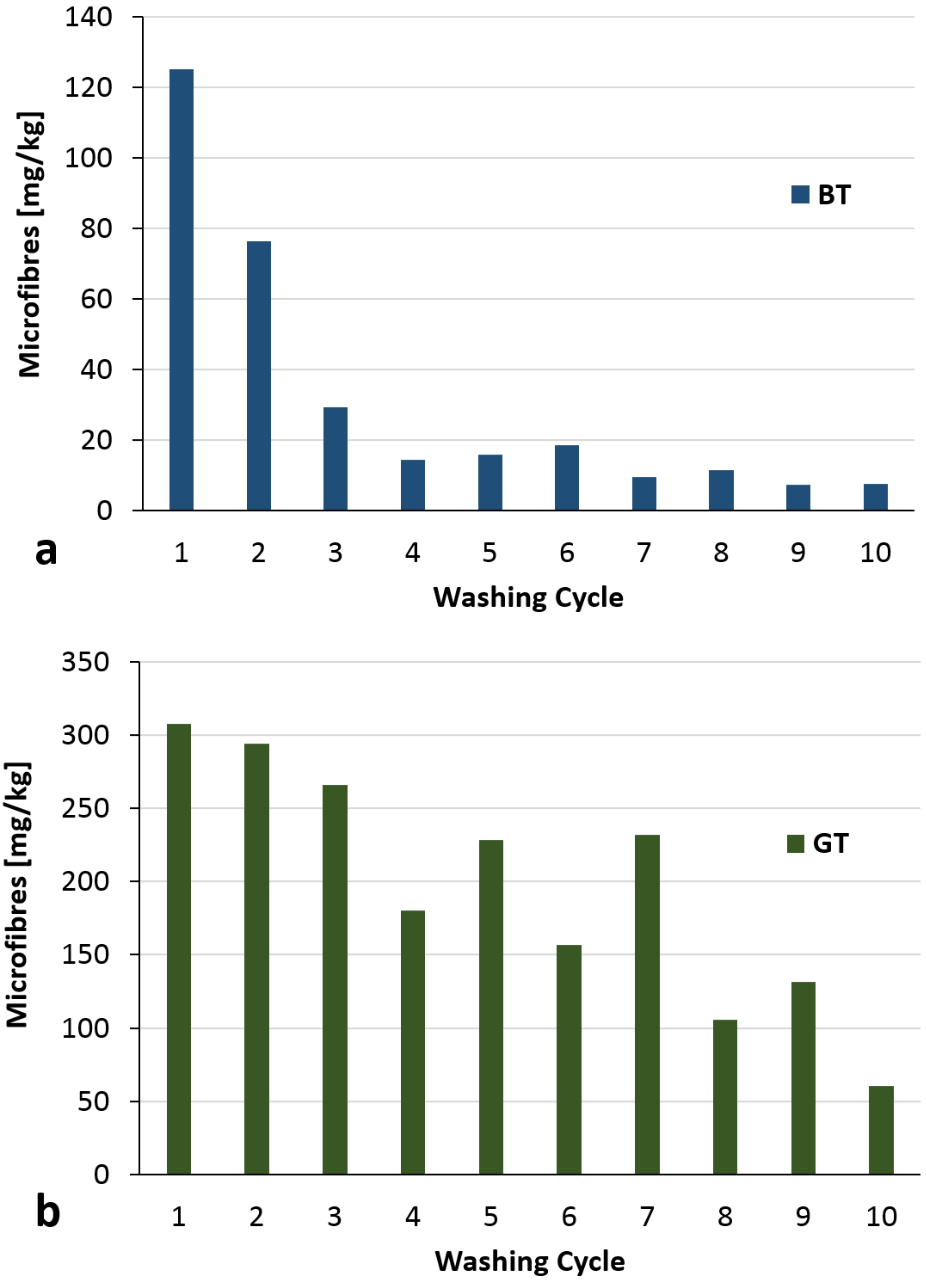

Figure 2.14. Amount of microfibres released (expressed in mg/kg) from blue t-shirts (BT) and green tops (GT) during 10 washing cycles.

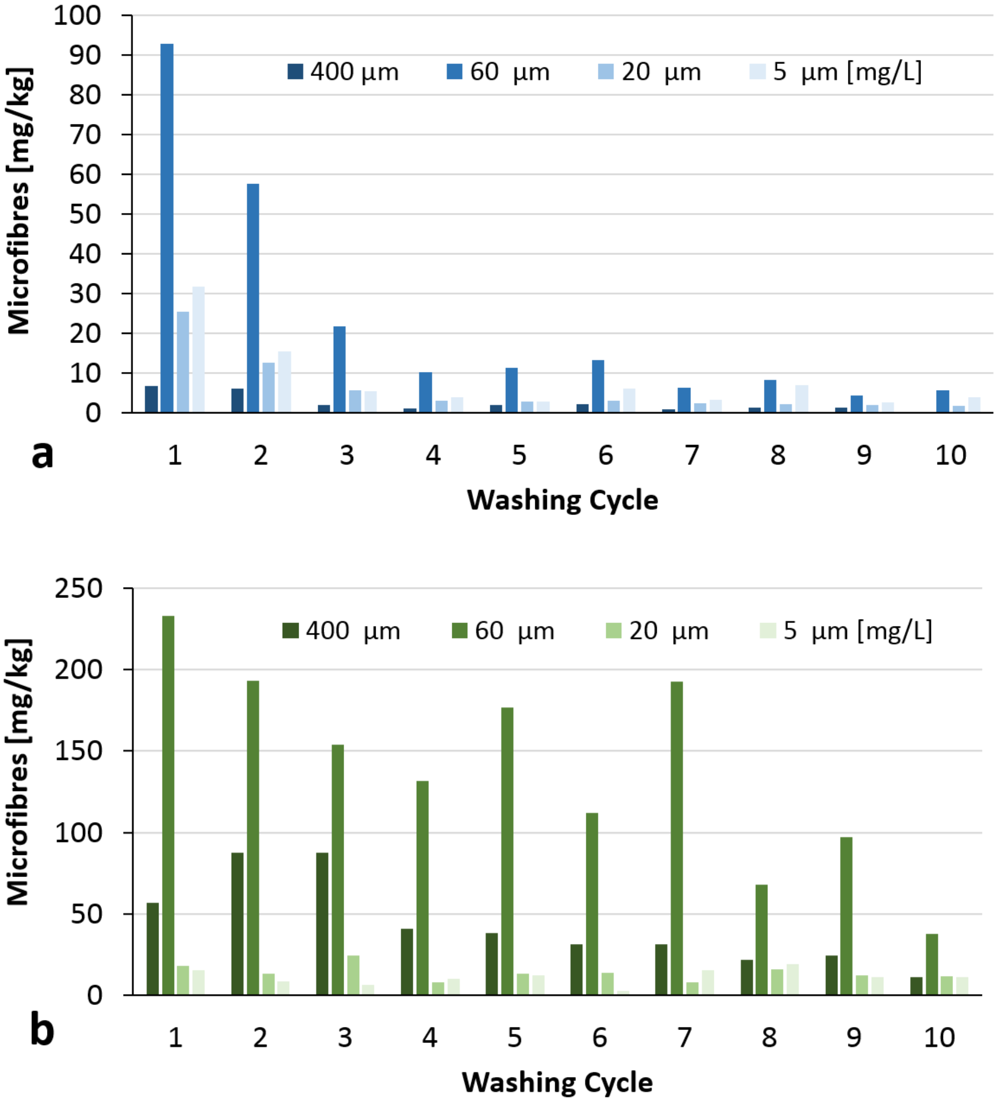

Figure 2.15. Aliquots of microfibres recovered on 400, 60 and 20 µm filters (expressed in mg/kg), and on 5 µm filter (expressed in mg/L), from blue t-shirts (BT) and green tops (GT) during 10 washing cycles.

The thermogravimetric curves reported in Figure 2.16, showed that compared to the thermal degradation of fibres from the 1st wash, previously described, both aliquots from the 5th and 10th wash have a single step degradation, with a close T_{max} (353° C for the 5th, 354 for 10th). This result seems to indicate that microfibres released during the 5th and 10th wash were mainly released from the cotton/modal back part.

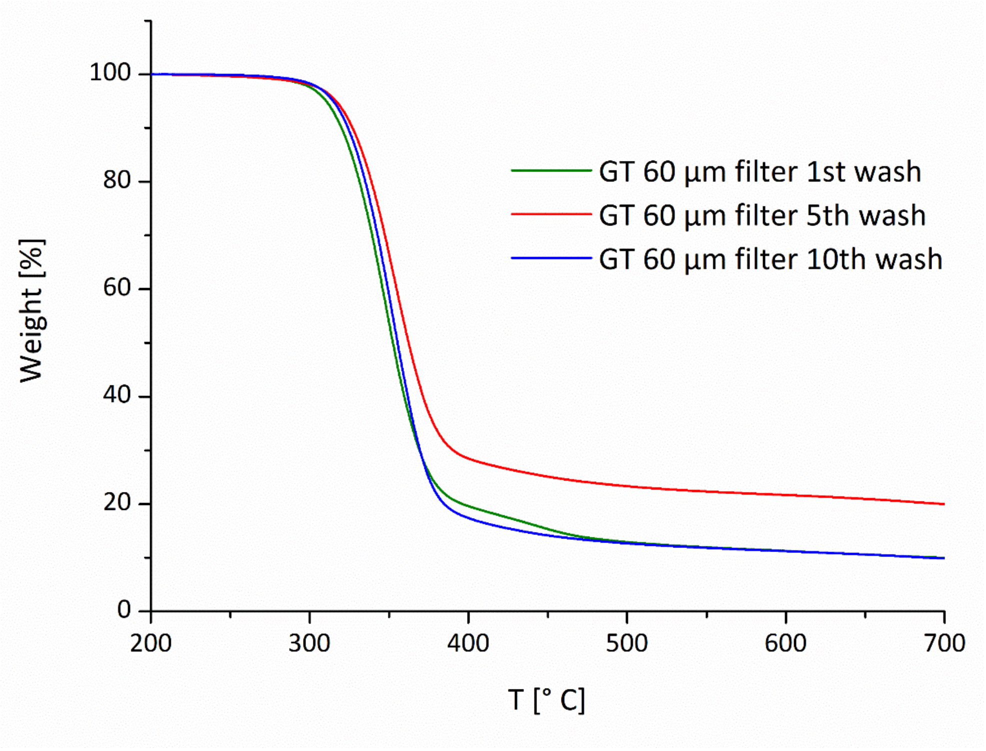

Figure 2.16. Thermogravimetric curves of the aliquots of microfibres recovered from

The comparison of the releases of microfibres herein reported with data obtained from other studies, is not immediate due to the different washing conditions and quantification methods used. However, the release of BT and RT (125.0 ± 32.1 mg/kg and 124.1 ± 12.4 mg/kg, respectively) were much lower than those reported by Pirc et al., that tested polyester fleece blankets whose multifilament structure released more easily microfibres.[5] Sillampää et al.[7]

reported a range of microfibres released from cotton and polyester clothes that is 0.12÷0.33 % w/w, which is instead much greater than the amounts reported in the present work, even considering GT. The decreasing trend in microplastic release after consecutive washings recorded for BT, seems to be in line with results from other works.[5,6,7] Concerning the type of textile, the greatest amounts released by GT, a blend of polyester/cotton/modal, is in contrast with the low quantities recorded by Napper et al.[6] Neverthless, the observations on the yarn characteristics are in agreement with the work of Carney Almoroth et al.8, concluding that yarns made of filament fibres with high twist could contribute to the reduction of microplastics released during washing processes of synthetic clothes. Moreover, the fact that the most abundant fraction of microfibres was recovered on a filter of 60 µm pore size, indicate that the dimension of these microfibres is compatible with those of microplastics found in water effluents coming from WWTPs,[29,30,31] and of microfibres found in marine sediments and ingested by fauna.[1,21,22]

2.3.3 Conclusions

Compared to the other available published works on the topic, this experimental study introduces three important simultaneous novelties:

- All the wastewater coming from the washing machine was filtered;
- Real washing conditions were tested washing more garments together, using a commercial detergent and a real washing program for synthetic clothes;
- 4 different filter pore sizes were used in a multistep filtration procedure that allow to have information on the dimensions of released microfibres.

The multistep filtration procedure proved to be an effective method to quantify the amount of microfibres released form washing tests in real household washing machines. Quantities of microfibres released range from 124 to 308 mg for kg of washed fabrics. Results allowed to identify some parameters that could decrease the release of microfibres: yarns made of continuous filaments, high twist and low hairiness. Blends of polyester with artificial or natural fibres tend to release more but mainly fibres of cellulosic nature. After subsequent washing tests up to 10 washes, the release of microfibres decreases and reach a plateau in the case of 100% polyester garments. The most abundant fraction of microfibre shed is retained by 60 µm filters, indicating dimensions that could could pass through WWTPs and pose a threat for marine organisms.

2.4 Quantification of microfibres released during washing of synthetic clothes in real conditions and at lab scale[d]

In this paragraph, a systematic study aimed at comparing the quantity of microfibres released from synthetic fabrics during washing performed by using a household washing machine and by using a lab scale Gyrowash system, a laboratory simulator of a real washing machine, is reported. The fibres extracted from wastewater recovered from both tests were examined to determine their dimensions, and to quantify the overall fibre shedding effect. The obtained results allow to conclude that the washing tests performed at lab scale are an effective analytical procedure to perform a low time/low cost estimation of microfibre release from synthetic fabrics.

2.4.1 Materials and Methods

Materials

The commercial clothes selected were blue t-shirts made of 100% polyester. The fabric nature was confirmed by Fourier transform infrared spectroscopy (FTIR), using a Perkin Elmer spectrum 100. The fabric characteristics were analyzed by means of Leica M80 optical microscope.

The commercial liquid detergent used for the washing tests had the following composition: 5-15% of anionic and non ionic surfactants; < 5% of soap and phosphonates; optical whitening agents; enzymes and perfume.

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[d] The work presented in this paragraph has been published as: De Falco, F., Gentile, G., Di Pace, E., Avella, M., Cocca, M., 2018. Quantification of microfibres released during washing of synthetic clothes in real conditions and at lab scale. The European Physical Journal Plus 133:257. DOI: 10.1140/epjp/i2018-12123-x

Washing tests

Two type of washing tests were carried out: in real conditions and at lab scale.

- **Real scale tests**

A Bosch washing machine serie 4 varioperfect WLG24225 was used to launder about 2.5 kg of polyester blue t-shirts. The washings were performed using the program for synthetic clothes at 40°C and 1200 rpm. A commercial liquid detergent was used in the dose recommended by the manufacturer. The wastewater coming directly form the drain pipe of the washing machine, underwent three subsequent filtrations by using three different pore size filters:

- 400 µm pore size sieve with a diameter of 8 cm;
- 60 µm pore size nylon filter (Merck Millipore) with a diameter of 4.7 cm;
- 20 µm pore size nylon filter (Merck Millipore) with a diameter of 4.7 cm.

After each filtration, about 1 liter of milli-Q water at 70°C was fluxed through the filter to remove the excess of detergent. All the filters were dried at 105°C for 30 minutes and weighted before and after the filtration in order to evaluate the amount in grams of microfibers released.

Two washings were performed of two different loads (each of about 2.5 kg), using each time new identical blue T-shirts.

- **Lab scale tests**

9 × 9 cm^2 squares were cut from a blue t-shirt and the edges were thermo-sealed in order to avoid the release of fibres from the cut edges. The washing tests at lab scale were performed by using a standard washing laundering machine Gyrowash (James H. Heal & Co, UK). The fabric specimens were placed in the steel containers of Gyrowash, along with 10 steel balls, and washed for 45 min at 40 °C using milli-Q water plus the dose of liquid detergent suggested by the manufacturer. The liquor ratio (liquor:specimen) was 150:1 vol/wt, corresponding to 150 mL of liquor, i. e. the solution composed by milli-Q water

plus the dose of detergent, per gram of fabric. Three replicate tests were performed with this procedure.

The washing water, obtained from the wash tests, was filtered by means of a peristaltic pump (Velp Scientifica flow rate 100 mL/min) connected with Tygon tubes, throughout polyvinylidene fluoride (PVDF) filters (Durapore®, Merck Millipore), with an average pore width of 5 µm and a diameter of 4.7 cm. Then, 400 mL of Milli-Q water at 70 °C were fluxed in the filtration system, since such amount of water was found optimal to avoid an excess of detergent on the filter surface. The filters were dried at 105 °C for 30 min.

Evaluation of released microfibres

The quantity of microfibers released during the washing tests in real conditions was gravimetrically determined. All the filters were weighted before and after the filtration in order to evaluate the amount in grams of microfibres released. Mean microfibre dimensions (length L and diameter D) were determined by using a Leica M80 optical microscope and the public domain software ImageJ (release 1.43u), analyzing a sample of microfibres recovered from the three filtrations.

According to Napper et al.[6] the number of microfibres released in the wastewater from each wash, N, was estimated from their weight, M_{tot}, using equation 5 and assuming that the fibres were of cylindrical shape:

$$N = \frac{\frac{M_{tot}}{\rho}}{\pi \cdot \frac{D^2}{4} \cdot L} \qquad \text{Equation 5}$$

Where ρ is the density of the material. This allow the determination of an approximate number of fibres released in the effluent per kg of washed clothes. The filters recovered from the lab scale tests were analyzed by using a scanning electron microscopy, SEM Quanta 200 FEG (FEI, The Netherlands).

SEM observations were performed in low vacuum mode (PH_2O = 0.7 torr), with a large field detector (LFD) and an accelerating voltage of 30 kV. The number of microfibres released was calculated following the procedure reported in paragraph 2. In brief, according to such procedure, 21 SEM images per filter were acquired along two orthogonal diameters of the circular filter. The number of microfibres per image was determined by visual observation and the value averaged over 21 images, was divided for the filter area in order to obtain the total number of microfibres per filter. Three filters were analysed for the lab scale test, obtaining the average N value among the three filters (N_a) and the related standard deviation (SD). Moreover, the length, L, and diameter, D, of the released microfibres was measured by the SEM micrographs using the public domain software ImageJ (release 1.43u). The weight in gram of microfibres released per kg of fabric washed, was estimated from the average number of microfibres released, Na, assuming the fibres were of cylindrical shape, following equation 6.

Microfibers (mg/Kg) = $N_a \cdot \left(\pi \cdot \frac{D^2}{4} \cdot L\right)\rho$ Equation 6

Where ρ is the density of the material.

2.4.2 Results and discussion

Polyester is the most used fiber in the textiles industry due to its physical properties, including good resistance to strain and deformation, lower price, versatility, and recyclability.[32] In 2015 the polyester consumption was more than double that of cotton.[33] Previous research has even reported that polyester fabrics release the highest amount of microfibers during a wash compared to polyester-cotton blend and acrilic fabrics[6] and polypropylene (see paragraph 2). It is reported in literature that the fibre loss from a textile, and particularly for polyester fabric, is due to pilling, which consists in fibre entanglement on the textile surface and thus in the formation of fibre balls or pills during processes like washing or wearing.[34] In order to evaluate the characteristics of the fabric constituting the t-shirts, an optical microscopy analysis was carried out on the fabric surface and on untwisted yarns, removed from a t-shirt. As shown in Figure 2.17a and b, the t-shirt is made of knitted polyester and is characterized by low hairiness, that consists of small fibres that protrude from the main yarn core.[12] The yarn appears to be made of continuous filaments with a very low twist as showed in Figure 2.17c.

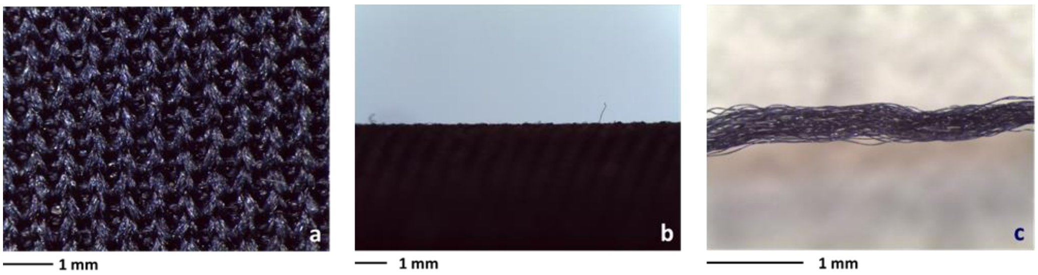

Figure 2.17. Optical micrographs of: a) t-shirts plane surface; b) t-shirt surface; c) untwisted yarn.

The wastewater recovered from the washing of polyester t-shirts using a householding washing machine contains an impressive amount of microfibers. The fibers were confirmed to be the material type labeled on the t-shirts, polyester, by Fourier transform infrared spectroscopy.

The total amount of microfibers released during the washes performed in a household washing machine was calculated to be 125 ± 32 mg per kg of washed fabric. The released microfibers were observed by using an optical microscope in order to determine their average dimensions that were found to be 645 ± 408 µm in length (L) and 18 ± 1 µm. Some of the acquired images are reported in Figure 2.18. These data were used to determine the number of microfibers released during the performed washings using equation 5. The results indicate that 549,913 microfibers are released by 1 kg of washed fabric.

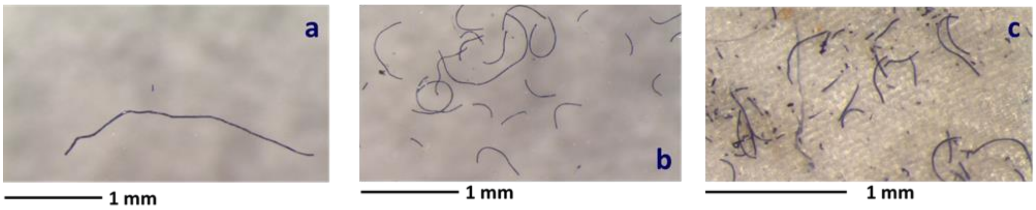

Figure 2.18. Optical micrographs of the fibers recovered on: a) 400 µm pore size sieve; b) 60 µm pore size nylon filter; c) 20 µm pore size nylon filter.

The wastewater recovered in the washing at lab scale was filtered on 5 µm pore size PVDF filters and the number of microfibres per gram of washed fabric was determined by using a counting method already reported in paragraph 2. A SEM micrograph of the filter surface is reported in Figure 2.19.

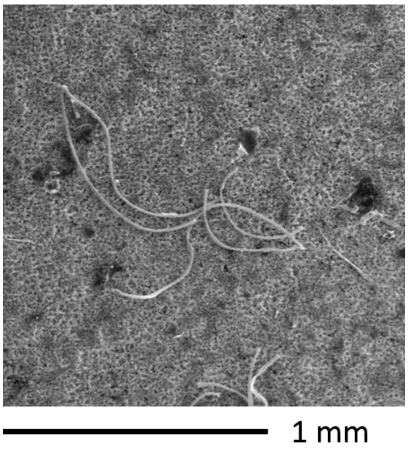

Figure 2.19. SEM micrograph of the surface of a 5 µm pore size PVDF filter containing microfibers.

The total number of microfibers, N_a, released during the washes performed at lab scale, was calculated to be 1733 ± 428 per g of washed fabric, i.e. about

1.733.000 microfibers per kg of washed fabric. Using equation 2 and the microfiber dimensions (L = 376 ± 82 µm and D = 18 ± 4 µm), calculated by SEM micrographs, the amount of microfibers released per Kg of washed fabric was calculated to be 219 mg.

2.4.3 Conclusions

The large number of microfibres released during real and labscale washing tests of polyester t-shirts confirms that the washing of clothes made of synthetic fabric represents an important source of microplastic pollution in the environment. Comparing the amount of microfibres released per kg of washed fabric from the two approaches adopted, lab scale tests produce more microfibers than those released in real condition tests. This result is due not only to the difference between lab scale and real washings, but also to the different filtration procedure, since filtration performed at lab scale takes into account also the smallest microfibrers that are not collected in real washing tests. Moreover, the test at lab scale is likely to simulate more than 1 washing cycle in real condition. Considering that only few data are at the moment available on the number of microfibers produced with tests at lab scale, and a standard method for the simulation of the release of microfibres is still missed, it is possible to conclude that the experiments performed through lab scale approach allow to perform a low time/low cost estimation of the microfiber release from synthetic fabrics, since the amount of water used and filtered during the simulated test is very low. In conclusion, this approach could be adopted as an effective analytical procedure to perform comparative experiments and studies on the microplastic release as well as on mitigation solutions.

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Chapter 3 - Microplastic release from synthetic clothes to air[e]

3.1 Introduction

Microplastic pollution came up as a threat for marine environment, in fact most of the literature produced is focused on occurrence and fate of these tiny particles in freshwater, seas and oceans. Nevertheless, recently, an unexpected turn took place when scientists have started to talk about the possibility of microplastic pollution in the air. Airborne microplastic contamination, particularly fibres from clothing, is a well known problem of research activities that deal with microplastic sampling and analysis, leading to the development and adoption of appropriate protocols.[1,2,3,4]

Dris et al. were the first to identify the presence of microfibres in the atmospheric fallout of Paris, estimating that between 3 and 10 tons of fibers are deposited by atmospheric fallout every year.[4,5] They monitored two different sites: a dense urban area for one year and a sub-urban zone for around six months. Microplastics were collected using a stainless steel funnel, followed by filtration and observation with a stereomicroscope. Results showed an atmospheric fallout between 2 and 355 particles/m^2/day, with higher fluxes in the urban site and during wet periods. 29% of these fibres were all synthetic or a mixture of natural and synthetic material, and the most

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[e] The study here presented was partly performed at the University of Plymouth (UK), in collaboration with prof. Richard C. Thompson.

abundant length dimensions were 200-600 µm while the diameter had a range of 7-15 µm.[5]

Another study by Dehghani et al. investigated the presence, characteristics, and potential health risks of microplastic dust ingestion. They collected ten street dusts from the central area of Tehran, finding a range of 88-605 microplastics per 30 g of dry dust, whose 33.7% had a size range of 250-500 µm. Fibrous and granule microplastics were the most abundant shape collected. Starting from these findings, they calculated that, considering exposure during outdoor activities and workspaces, a mean of 3223 and 1063 microplastic particles per year could be ingested by children and adults, respectively.[7]

Following their first outcomes, Dris et al. investigated the presence of fibres in indoor and outdoor air.[8] They selected three sites for the indoor monitoring, two private apartments and one office, and the roof of the office building as outdoor site. Samplings took place in different period of the year to cover seasonal variations. The indoor monitoring was carried out by using a pump that sampled 8 L/min of indoor air onto quartz filters (1.6 mm pore size), and by using passive dust collector and vacuum cleaner. For the outdoor sampling, a pump was also used. In the case of the indoor sampling, concentration were found to be in the range 1.0-60.0 fibres/m^3, whereas lower values ranging from 0.3 to 1.5 fibers/m^3 where reported for outdoor sampling. Moreover, the indoor deposition rate of fibres ranged from 1586 to 11,130 fibres/day/m^2, and the fibres accumulated in the settled dust were 190-670 fibres/mg. The fibres collected indoor were further analysed, finding that the majority (67%) were natural fibres, mainly cellulosic, and the rest was of synthetic nature, mostly polypropylene. Regarding the size of the collected fibres, most of the fibres found in indoor, outdoor and dust fall were in the range of 50-850 µm, with maximum length of 4650-4850 µm found in dust fall, 3250 µm indoor and 1650 µm outdoor.

The obvious consequence of such findings is whether the occurrence of microfibres in the air could be dangerous for human health. The possibility for human fibres to enter into human respiratory system mainly depend on their size. There is a difference between the terms inhalable and respirable: the first are particles and fibres that can enter the nose and mouth and deposit in the upper airway; the latter are fibres that once entered, are able to reach and deposit in the deep lung.[9] Once they enter the respiratory tract, most fibres are likely to be trapped by the lung lining fluid but some of them may avoid the mucociliary clearance mechanisms of the lung, especially in individuals whose clearance mechanisms have been impaired, and accumulate and persist in the lungs.[9,10] Preliminary information of the consequences of inhaled fibres on human health can be derived from studies on the workers of synthetic textile and flock industries. Information are controversial since some studies have found increased cancer risk related to exposure to synthetic fiber dust, evident after 10-20 years, others did not find any association.[10] Also investigations on nylon flock workers found no evidence of increased cancer risk.[11] However, both synthetic flock and textile workers have been found positive to the following symptoms: interstitial lung disease, reduced lung capacity, coughing, dyspnea, wheezing, increased phlegm production, allergic reactions, asthma.[10] Other aspects to take into account are the toxicity of synthetic fibres that in certain doses can lead to inflammation, the possibility to transfer pollutants adsorbed from the environment due to their hydrophobic nature, and leaching of unreacted monomers, additives or dyes.[9] The potential harmful effect of airborne microfibres on humans mainly depends on the concentration of such pollutants in the environment and on the possibility of exposure to them. In a recent study, Catarino et al. compared the risk for humans of exposure to microplastics between two pathways: ingestion via consumption of mussels and exposure via household fibres fallout during a meal. To collect the data of dust fallout, they exposed petri dishes with adhesive tape during cooking and meal time. They evaluated a microplastic ingestion by humans via consumption of mussels that ranges between 123 particles/year/capita in the UK and 4620 particles/years/capita in countries with a higher shellfish consumption. Instead, the risk of fibre exposure during a meal via dust fallout in a household was found to be much bigger, with 13,731-68,415 particles/years/capita. [12]

The research activities carried out up to now on the occurrence of such pollutants in indoor and outdoor environments and of the possible health risks to humans, are still in a preliminary stage and have not provided a full and clear picture of the entity of the problem yet. Considering the state of the art, Gasperi et al. have highlighted the need to clarify the following points:

- assessment on the real risk of exposure to fibrous microplastics, in term of how and in what concentrations these pollutants can be considered a real risk;
- evaluation of data on the impact of fibrous microplastics on human health.

In particular, the dimensions of the microfibres are of striking importance since diameter is crucial to respirability, whilst length plays an important role in persistence and toxicity. The full spectrum of fibers (natural, artificial and synthetic) must also be considered.[9]

In such scenario, the work here reported is mainly aimed to evaluate and collect systematic data on the release rate of microfibres from clothes during wearing. Moreover, the identification of textile parameters that could influence the release of microfibers form clothes to air was assessed. For these objectives, experimental tests were carried out in a clean environment where the only potential input of microfibres came from selected garments, with a determined structure and nature. The analysis of the microfibres released in the clean environment was performed and related to the wearing of garments in order to study the effect that daily wearing of garments and real movements can have on microfibre release to air. The effects of textile parameters on the release were singled out by testing only polyester garments with different textile structures and characteristics. The same type of garments also underwent washing tests in a real household washing machine, in order to evaluate the release of microfibres to water and possible influences of the textile parameters on the release. Finally, results coming from both analyses, in air and in water, were compared.

3.2 Materials & Methods

Materials

Four commercial polyester garments were selected and tested: a blue T-shirt (100% polyester, code Blue), a green blouse (100% polyester, code Green), a pink sweatshirt (50% polyester, 50% cotton, code Pink), a black dress (100% polyester, code Black). For each type, eight identical garments were purchased. The identity of each fabric type was confirmed by Fourier transform infra-red (FTIR) spectroscopy, using a Hyperion 1000 microscope (Bruker) coupled to an IFS 66 spectrometer (Bruker). The spectra obtained were compared to a spectral database of synthetic polymers (Bruker I26933 Synthetic fibres ATRlibrary). The fabric structure and geometry of the selected garments were analysed by using a Leica M205 FA light microscope and a field-emission scanning electron microscope (FESEM, QUANTA 200, FEI, The Netherlands). Before the SEM analysis the samples were sputter-coated with gold–palladium. A commercial liquid laundry detergent was used in the washing tests, whose composition is: 5-15% of anionic and non ionic surfactants; < 5% of soap and phosphonates; optical whitening agents; enzymes and perfume.

Prewashing

A prewashing of the selected garments was performed. The eight items of each garment type were pre-washed all together using a Whirlpool WWDC6400 washing machine at 40°C, 1400 rpm for 1÷2 hours depending on the washing load. All washings were performed using the liquid laundry detergent in the dose recommended by the manufacturer. Cross-contamination of fibres between washes was prevented by running two consecutive empty washing cycles, the first at 60 °C, 1400 rpm for 1h 10 min, the second at 40° C, 1400 rpm and 45 min. Cotton lab coats and nitrile gloves were worn during all the experimental work.

Release of microfibres from synthetic clothes to air

The release of microfibres from selected garments to air was analysed in a closed room of 4 m^2, with no windows or ventilation. The carpet floor was covered using cardboard and paper tape. Before testing, the room was deeply cleaned using liquid soap, water and a handheld vacuum cleaner, cotton cloths were used during the cleaning of the room. The room has a desk with a height of 85 cm. A drawing of the room is reported in the Supporting Information (SI), Figure S3.1. All the operators involved in the cleaning and tests, wore boilersuits and shoe covers to avoid any fibre contaminations. To assess the absence of fibres in the room after the cleaning, 8 Petri dishes (diameter of 9 cm) were left in the room (4 on the desk, 4 on the floor) for 10 days, following a procedure reported elsewhere.[3] After 10 days, the Petri were observed under the Leica M205 FA light microscope. The observation revealed the presence of only one fibre in one of the Petri recovered from the desk, so the room was considered cleaned.

4 volunteers were involved in the experiments to evaluate the release of microfibres to air. Each volunteer tested, one per time, all the four type of garments. A total of 16 tests were conducted. One volunteer per time wore the garment to be tested, entering barefoot inside the testing room. In the tests with the Blue, Pink and Green clothes, the volunteers wore white leggings made of 100% cotton.

In the cleaned room, each volunteer performed a specific sequence of movements, that lasted 20 minutes. The sequence of movements was the following:

- 2 min and 30 sec: lateral opening and closing of arms and legs;
- 1 min: steady oscillation near the desk, gently shaking the garment;
- 1 min: steady with hands leaning against the desk;
- 1 min: walking, gently shaking the garment;
- 1 min 30 sec: walking opening and closing the arms laterally.
- 1 min: steady oscillation near the desk, gently shaking the garment;
- 1 min: steady with hands leaning against the desk;

This sequence, with a duration of 10 min, was performed twice to reach an overall testing time of 20 min. To determine fibres falling during the test, 8 petri dishes (9 cm of diameter) were left during the testing time, 4 on the desk and 4 on the floor, placed around the space within the volunteer moved (the scheme of the position of the petri dishes is reported in the SI, Figures S3.1 and S3.2). The Petri dishes contained dampened filter papers (Whatman n. 1) in order to capture microfibres released to air.

Prior to testing the selected garments, 4 tests were performed with a volunteer wearing 100% cotton t-shirt and leggings and doing the same sequence of movements, as reported above. Such type of tests was performed either to evaluate if the movements of a person in the room could lead to airborne contaminations caused by fibres already present in the room, double checking the cleaning of the room, either to assess possible airborne fibre contaminations due to the 100% cotton leggings worn also in the tests with the selected garments. Results showed that an average of 2÷3 fibres per petri dish can be found, so this contamination was considered neglectable. In fact, analysis of these fibres with both optical microscopy and FTIR spectroscopy revealed that they were all natural and well discernible from the fibres that composed the garments to test.

To avoid cross-contamination between two consecutive tests, the room was cleaned by an operator wearing 100% cotton clothes under a boilersuit, and by using a handheld vacuum cleaner.

The fibres on the surface of the paper filters were observed and counted by using a Leica M205 FA light microscope and analysed by Image J to measure their dimensions. A mean size was calculated for length and width based on the observation of 100 fibres for Blue, Pink and Black, 10 fibres in the case of Green. Additional analyses of the collected fibres were carried out by FTIR spectroscopy, using a Hyperion 1000 microscope (Bruker) coupled to an IFS 66 spectrometer (Bruker), in order to confirm their composition.

The number of fibres released by garments to air, during the 16 tests performed in the cleaned room, and recovered on the Petri dishes and was visually determined by analyzing the petri surfaces under an optical microscope. For each test, the average number of fibres per petri dish and per gram of worn garment, N_t, was calculated by using Equation 1:

$$N_t = \frac{\sum_{i=1}^{8} N_i}{8} / W_t \qquad t=1,2,....16 \qquad \text{Equation 1}$$

with N_i the number of fibres counted in each petri dish, W_t the weight in grams of the garment worn in each of the 16 tests.

Then, the average number of fibres released by each type of garment per gram of worn fabric, m^2 and hour, N_a, was obtained averaging the 4 N_t obtained from the 4 replicate tests of each type of garment, and normalizing for the area of the petri dish (A) and the time duration of the test (t), according to Equation 2.

$$N_a = \frac{\sum_{t=1}^{4} N_t}{4} \Big/ (A \cdot t) \qquad \text{Equation 2}$$

The standard deviation (SD) of N_a among the 4 replicate tests per each type of garment was also evaluated.

The mean dimensions, length (L) and diameter (D), of the fibres released by each type of garment, were used to convert the number of microfibres released in grams assuming that the fibers are of cylindrical shape, according to Equation 3, already used in Chapter 2, and reported below.

$$\text{Grams of microfibre/kg fabrics} = 1000 \cdot N_a \cdot \left(\pi \cdot \frac{D^2}{4} \cdot L\right) \cdot \rho \qquad \text{Equation 3}$$

Where ρ is the density of the material.

Release of microfibres from synthetic clothes to water

The release of microfibres from the selected garments due to laundering was evaluated. Washing tests were performed using a Bosch washing machine serie 4 varioperfect WLG24225it with the following program for synthetics at 40°C, 1 h 47 min and 1200 rpm. A commercial liquid detergent was used in the dose recommended by the supplier. Each garment was washed alone, and four washing replicates for each garment type were performed. A total of 16 washing trials were performed. Cross-contamination of fibres between washes was prevented by running two consecutive empty washing cycles, both at 40 °C, 1200 rpm for 30 min each.

The analytical procedure adopted to determine the amount of the released microfibres consisted in the filtration of the wastewater, coming directly form the drainpipe of the washing machine, with a 400 μm pore size mesh. The wastewater was recovered in tanks and filtered by means of a peristaltic pump (SP 311/60 Velp Scientifica) connected with Tygon tubes, throughout a nylon net filter with a 60.0 μm pore size (Merck) and then through a nylon net filter with a 20.0 μm pore size. Finally, 300 ml of the filtered wastewater was further filtered on a Durapore PVDF membrane a 5 μm pore size. At the end of each tank, 1L of distilled water was poured into, the tank was shaken, and the water filtered. Such procedure was carried out twice for each tank to collect possible fibres that remained attached on the surface of the tanks. Finally, 1L of distilled water at 70 °C was fluxed in the filtration system to clean the filters from excess of detergent. All the filters were dried in oven at 105° for 1 h and then weighted. They were weighted before and after the filtration in order to evaluate the amount in grams of microfibres released, that was normalized for the washing load, obtaining W_t. The average amount of fibres per gram of washed fabric for each type of garment, W_a, and the standard deviation (SD), were calculated considering the 4 W_t obtained from the 4 replicate washing tests of each type of garment.

To avoid cross contamination of fibres among the different filtrations, tygon tubes, filter holders and tanks were cleaned with distilled water and with a jet of compressed air. Cotton lab coats and nitrile gloves were worn during all the experimental work.

Statistics

Statistical analysis of the number and the amount of microfibres released to air and water, respectively, was carried out by using OriginPro 8.5 software. Since the data resulted to be normally distributed (Kolmogorov-Smirnov and Shapiro-Wilk normality tests), One-way Analysis of Variance (ANOVA) with Tukey's post-hoc test was performed to assess significant differences among the types of garments. A 5% significance level was used for all statistical tests; p values <0.05 indicate significant difference among the data.

3.3 Results and discussion

A protocol to collect and evaluate the number of microfibres released to air from synthetic clothes was developed. Starting from the approach used to collect dust, and taking into account some recent works on airborne contamination, petri dishes with dampened filters papers were placed in the room. [3,8,12,13] The number of petri dishes was set to 8, to have a statistically representative sampling of the surfaces of both desk and floor of the room. Dampened filter papers were preferred to adhesive tape, to not affect the FTIR analysis.[3,12] The 8 petri dishes were placed in the room around the volunteer trying to minimize the space among the petri and the person, in order to collect a significant number of microfibres. The type of movements was selected to simulate a mix of real-life activities. The duration of the movements performed by volunteers was set to 20 min as a compromise between a reasonable time to allow microfibres to deposit and acceptable time for the volunteers that had to move in a close room without ventilation or any air input. Concerning the analysis of filter surfaces, they were observed through optical microscopy to allow a quick evaluation of the fibres present, as already reported in other works.[3,8,12] For fibre identification, different criteria suggested elsewhere were taken into account, but basically the recognition occurred considering the colour and shape of the original fibres from the garments.[8,14]

All the four garments were initially observed under optical microscope for two purposes: to evaluate textile structure and geometry, and to evaluate fibre morphological features. Figure 3.1 shows optical micrographs acquired of the surfaces of the selected garments and of the yarns constituting the fabric. The blue t-shirt has a knitted structure (Figure 3.1a), a yarn made of continuous filaments (Figure 3.1b) and very low hairiness (Figure 3.1c). The black dress and the pink sweatshirt have similar characteristics since they present a knitted structure (Figures 3.1d and 3.1g), yarns made of short staple fibres (Figures 3.1e and 3.1h), and a very high hairiness (Figure 3.1f and 3.1i). Nevertheless, Pink is not composed by 100% polyester like Black, but is made of a blend of 50% polyester and 50% cotton. Pink fabric was analysed also by SEM to understand how cotton and polyester fibres were combined together in the yarns. In Figure 3.2 SEM micrographs of Pink sample are reported. From this figure, it is clearly detectable the presence in the yarn of cotton fibres, with the typical twisted ribbon form, and of polyester fibres with a cylindrical and smooth surface.[14] The two kinds of fibres are mixed together to assembly the yarns. Another difference between cotton and polyester is the length of the staple fibres. The staple length of a synthetic fibre is controlled by the manufacturer, so they may be all the same length, or they consist of a mixture of fibres of different lengths blended in known proportions. In the case of a natural fibre, staple length is a much less easily defined characteristic of any batch of fibre, which basically consist of fibres varying in length over a wide range.[15] Finally, the Green fabric is characterized by a woven structure with very low hairiness, as observable from Figures 3.1l and 3.1o. In this case, there are two types of yarn, the warp and the weft (Figures 3.1m and 3.1n), both made of continuous filaments and with very high twist.

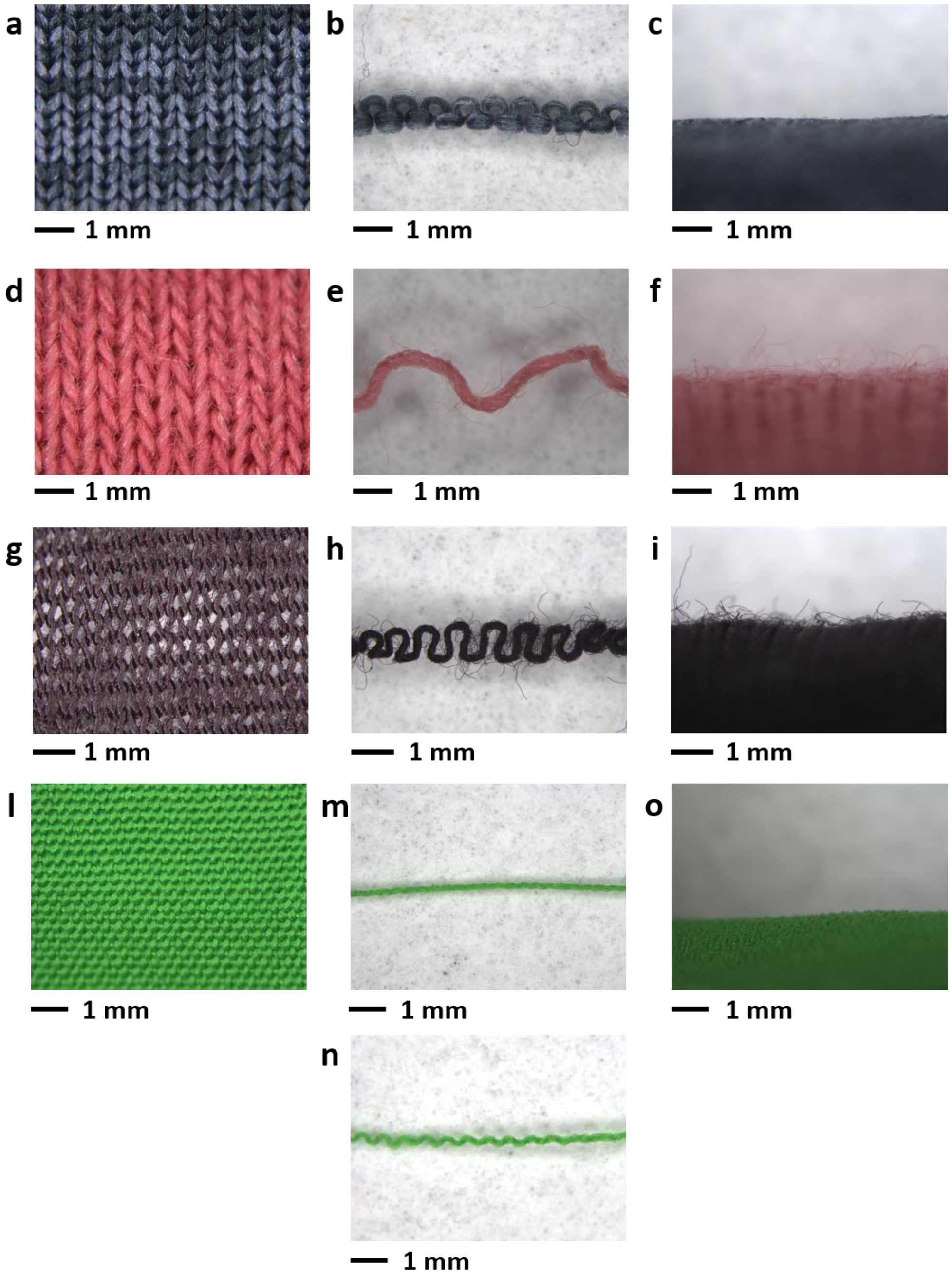

Figure 3.1. Optical micrographs of: Blue fabric a) plane surface, b) yarn, c) surface; Pink d) plane surface, e) yarn, e) surface; Black g) plane surface, h) yarn, i) surface; Green fabric l) plane surface, m) warp yarn, n) weft yarn, o) surface.

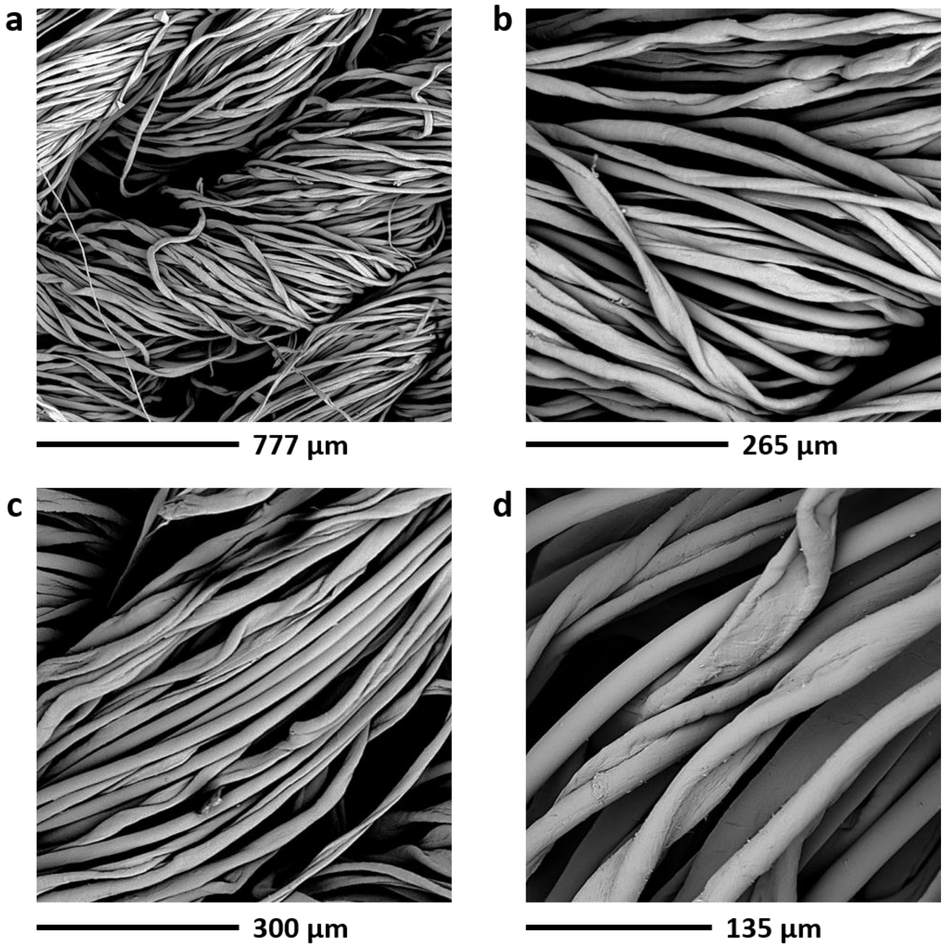

Figure 3.2. SEM micrographs of Pink fabric at different magnification

The number of fibres released by garments to air, during the 16 tests performed in the cleaned room, and recovered on the Petri dishes, was visually determined by analyzing the petri surfaces under an optical microscope. To confirm the nature of the counted fibres, FTIR spectroscopy was used to analyse subsamples of the fibres collected in the petri dishes after testing of each garment. The obtained spectra were compared with the FTIR library created with the FTIR spectra of all the tested garments. 16 fibres randomly selected were analysed for both Blue and Green tests, confirming that they were all polyesters. The same result came out for 4 fibres collected during the Green tests, such smaller number was analysed due to the overall low amount of fibres released by Green garments. Since for Pink tests fibres could be of double nature, cotton or polyester, 32 fibres randomly selected among the 8 petri dishes were analysed. Only 1 fibre was polyester, whereas the others were all cotton. Such result was foreseen during the inspection of filters under light microscope since the pink fibres observed had all the characteristics of cotton fibres.[14] The results as N_a (Number of fibres/g/m^2/h) for each kind of tested garment are reported in Figure 3.3, together with the standard deviation (SD).

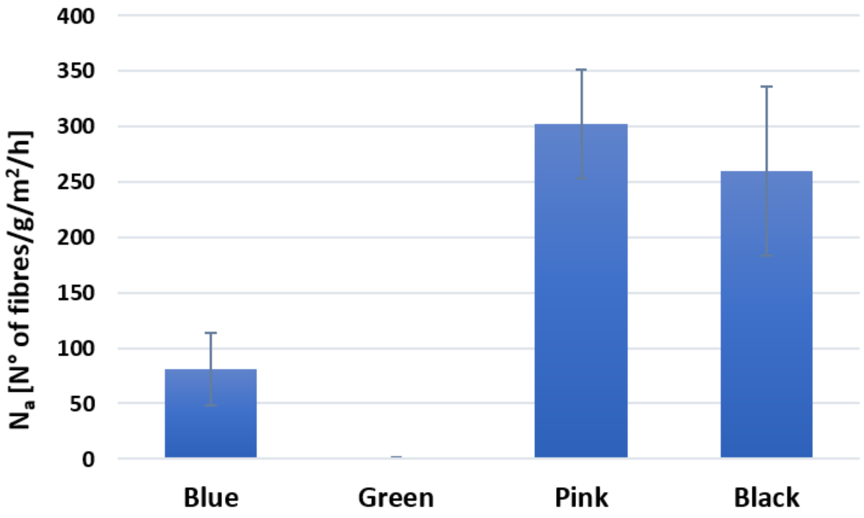

Figure 3.3. Number of fibres per gram of fabric, per m2 and hour (Na ± SD) released to air by wearing the blue t-shirt (Blue), the green blouse (Green), the pink sweatshirt (Pink) and the black dress (Black).

From this figure it is possible to highlight that the release to air due to the wearing is function of the garment type. In fact, the pink sweatshirt, made of a knitted fabric composed by a blend 50% polyester and 50% cotton, released the highest amount of microfibres that is 302 ± 49 fibers/g/m^2/h. The black dress, made of knitted polyester fabric released a lower value, compared to that released by Pink, of 260 ± 76 fibres/g/m^2/h. The lower number of microfibers was released by the green blouse, made of a woven polyester fabric (1 ± 1 fibre/g/m^2/h), while the blue t-shirt made of knitted polyester fabric released 81 ± 33 fibre/g/m^2/h.

The statistical analysis performed on N_a confirmed that the amount of microfibres released to air during the wearing of the garments differs significantly depending on the type of garment ($p=0.00$). Tukey post-hoc test revealed that the average number of microfibers, Na, released from Pink and Black garments were significantly higher than those of Green and Blue ($p=0.00$ in all cases). No significant differences were found between values of Pink and Black ($p=0.61$) and between Blue and Green ($p=0.14$). These results may be explained taking into account the different textile structure and yarn characteristics of the fabrics constituting the garments. In fact, both Pink and Black have similar textile characteristics since are made with a knitted fabric and their yarns are composed with short staple fibres and present a very high hairiness. As reported in Chapter 2 for the release to water, the presence of short staple fibres and high hairiness are responsible of a greater release of microfibres since short fibres can more easily slip away do to the mechanical actions of wearing and moving. Moreover, it should be also considered that Pink is made of a blend of 50% polyester and 50% cotton that could be responsible for the higher release of microfibres obtained with this garment, as founded for the release to water for similar garments (see Chapter 2 – paragraph 2.2). Another worsen effect in the case of Pink, could be pilling, that is reported as a major problem in polyester cotton blends.[16] Instead, both Blue and Green have continuous filaments constituting the yarns, with very low hairiness. That results in a more compact structure maybe less sensible to wearing stresses. In particular, the almost inexistent release of microfibres from Green could be also due to its woven structure that requires yarns denser than those made for knit fabrics, resulting in a higher twist that produce stronger yarns. Instead, yarns made for knit products are typically softer and more flexible.[17]

Mean fibre dimensions, length and diameter, were calculated analyzing the optical micrographs of the microfibres recovered in the petri dishes. As for the FTIR analysis, the number of microfibers analysed released by the Green fibres was much smaller than those for the other garments. Blue, Pink and Black fibres had similar dimensions, in fact, microfibres released by Blue were characterized by a length of 1036 ± 393 µm and diameter of 18 ± 4 µm; the dimension of microfibres released by Pink were 1024 ± 1008 µm in length and 21 ± 6 µm in diameter; microfibres released by Black had a length of 1023 ± 467 µm and a diameter of 18 ± 3 µm. Instead, microfibres released by Green had smaller dimensions, length of 494 ± 15 µm and diameter of 15 ± 4 µm. It is interesting to note that microfibres released by both Blue and Black have similar dimensions even if the release for the latter is significantly higher. The high standard deviation of the length of Pink microfibres, is in line with the wider length range of short staple fibres accounted to the cotton fibres as previously mentioned. The evaluated average dimensions were used to convert the number of microfibres released in grams. The amount of microfibres released by Blue was esteemed to be 0.031 mg per kg of fabric worn, per m^2 and per hour; 0.116 µg per kg of fabric worn, per m^2 and per hour of microfibres were released by Green; the release from Pink was of 0.152 mg of microfibres per kg of fabric worn, per m^2 and per hour; finally black released a quantity of microfibres of 0.094 mg per kg of fabric worn, per m^2 and per hour. The obtained results allow to indicate a clear trend in the release of microfibers to air from the wearing of the garments that was Pink>Black>Blue>Green.

Comparing these results with the findings of Dris et al., the number of fibres released daily per m^2 found in the work here reported range from 4,244 to 1,907,655 fibre/day/m^2, values much higher than those calculated by Dris et al., that are between 1586 and 11,130 fibres/day/m^2. Nevertheless, there is an agreement for the dimension range of the released microfibers observed in the present and Drias works.[8] It is to be highlighted that the results obtained indicate a release to air of microfibres with length ranging from 100 to 200 µm, that can represent a risk for inhalation since microfibres with a similar dimension have been found in human lungs.[18]

The release of microfibres from the selected garments was also tested in water during laundering. For this purpose, each type of garment was washed alone in a real washing machine, replicating the tests. The wastewater was filtered, using the procedure detailed in the materials and methods section, trough filters with different pore size. The amount of fibres released during the washing tests was determined gravimetrically, weighting the filters before and after the filtration. Results of the amount in grams of microfibres released normalized for the weight of the washed fabric, W_a, are reported in Figure 3.4 for each tested garment, along with the SD.

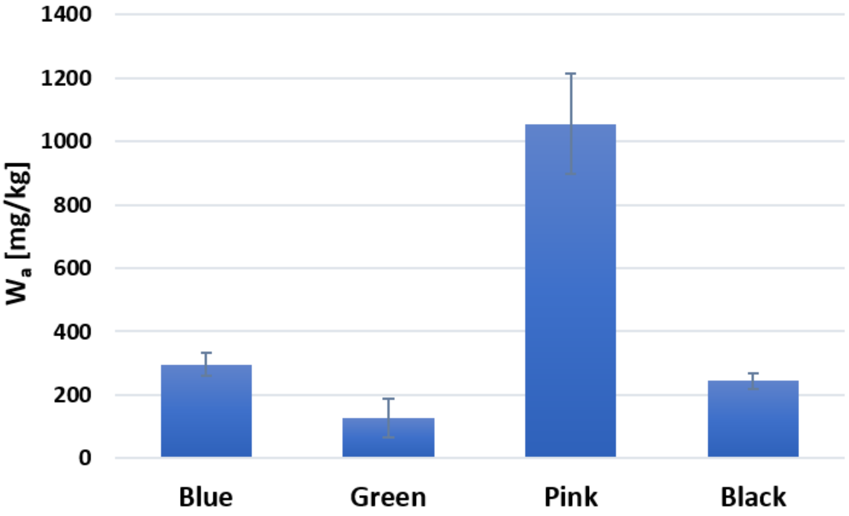

Figure 3.4. Mg of fibres released per kg of washed fabric (Wa ± SD) of blue t-shirt (Blue), the green blouse (Green), the pink sweatshirt (Pink) and the black dress (Black).

It is clearly observable that the garment that releases more microfibres, 1054 ± 158 mg/kg, is Pink. Blue and Black released a close quantity of microfibers, 296 ± 36 mg/kg and 244 ± 25 mg/kg, respectively. The lowest quantity of microfibres, 128 ± 62 mg/kg, was released by Green. Nevertheless, the statistical analysis performed on the quantities of microfibres released with ANOVA Tukey's post-hoc test detected a significant difference in the quantities released only between Pink and the rest of clothes (p=0.00 in all cases, Pink-Blue, Pink-Green, Pink-Black). No significant difference was found among the releases from Blue, Green and Black (Blue-Green: p=0.08; Blue-Black: p=0.83; Green-Black: p=0.29). Blue, Green and Black clothes did not show a significant pattern in the release to water. Blue and Black, which have the same knitted structure, released similar quantities but no effects of the different length of the fibres constituting the yarns was observed. Comparing these results with those reported in Chapter 2 – paragraph 2.2, the overall quantities of microfibres released during these washing tests are much higher. A possible explanation could be that washing tests carried out with only one garment saw a greater wettability of the fabric that could enhance the mobility of fibres that detach from the yarns. The blue t-shirt, which had a textile structure similar to those of blue and red t-shirts of Chapter 2, released more than the double in the tests herein reported. However, the textile characteristics of Green, woven structure combined with yarns made of filaments, confirmed to be responsible of the smallest release even if no significant difference was found with the other garments.

Figures 3.5 amd 3.6 report the amounts of microfibres recovered on filters of 400 µm, 60 µm, 20 µm and 5 µm pore sizes, for each garment type. The largest amounts of microfibres were recorded on filters with 60 µm pore size for all garments except Green. The statistical analysis indicated that only Blue reported a significant difference among the amounts collected on the 60 µm filter and all the other filters (p=0.00 in all cases), whereas Pink and Black had the 60 µm aliquot significantly greater than those of 20 and 5 µm (p=0.00 in all cases) but no difference was found with 400 µm (Pink: p=0.54, Black: p=0.10). For Green, who reported the smallest quantities, the greatest aliquot was recovered on the 20 µm filter that was significantly greater than those collected on 400 and 5 µm (p=0.01 and p=0.00, respectively) but statistically equivalent to 60 µm (p=0.60). The closeness reported for the quantities of fibres recovered on 400 and 60 µm filters seem to indicate a release of bigger fibres compared to those released during a greater load of clothes (see chapter 2 – paragraph 2.2). This behavior could be due to a less mechanical action, friction in particular, that occurs on a single washed garment, compared to the simultaneous washing of more clothes together.

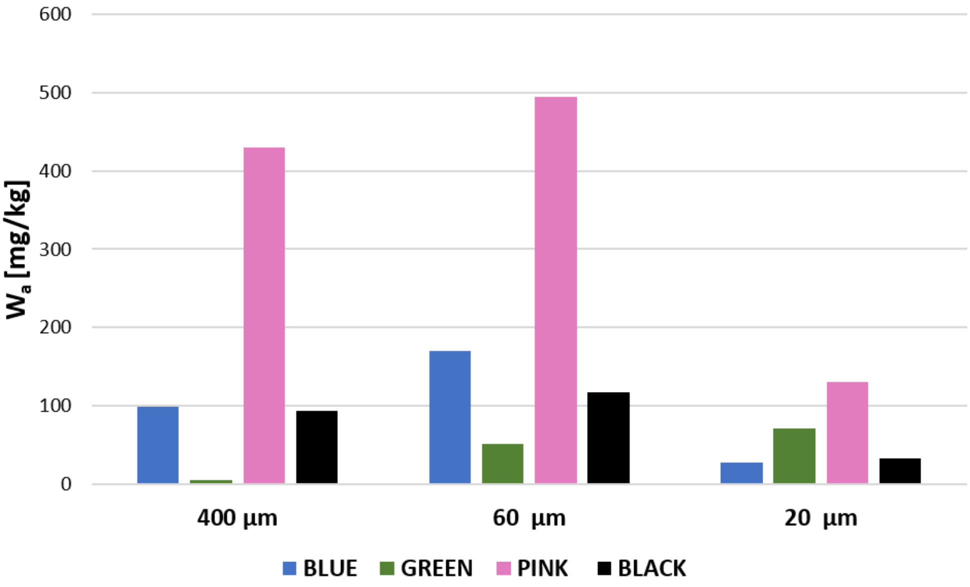

Figure 3.5. Aliquots of microfibres recovered on 400, 60 and 20 µm filters, Wa, from the blue t-shirt (Blue), the green blouse (Green), the pink sweatshirt (Pink) and the black dress (Black).

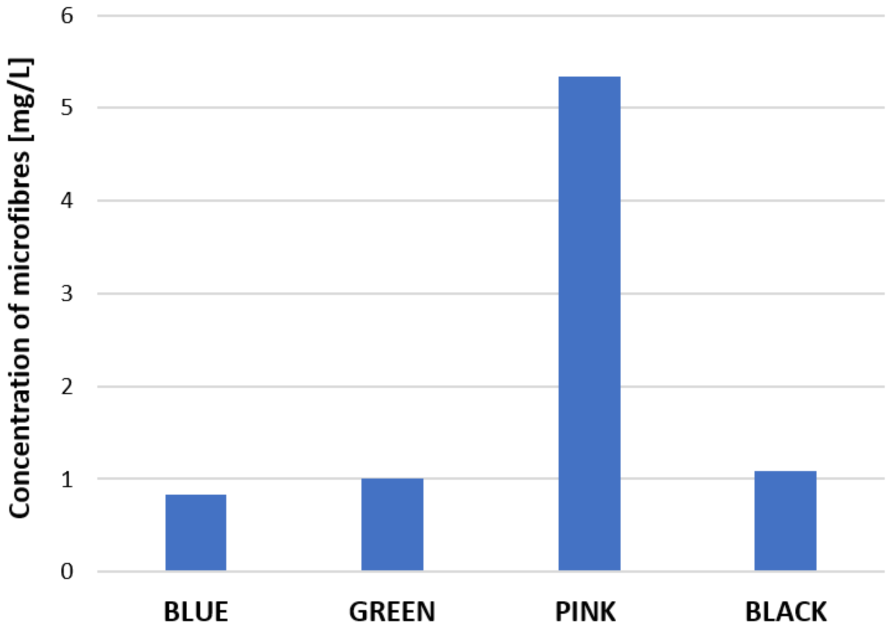

Figure 3.6. Aliquots of microfibres recovered on 5 µm filters (expressed in mg/L), from the blue t-shirt (Blue), the green blouse (Green), the pink sweatshirt (Pink) and the black dress (Black).

The overall results obtained for the release of microfibres from the selected garments either to air due to the wearing and to water due to laundering, confirmed that the cotton/polyester blend garment was responsible for the greatest release of microfibres, both to air and water. FTIR and optical microscopy analyses of microfibres collected on Petri dishes during the tests performed in the cleaned room, pointed out that almost all the fibres released were of cotton nature. In order to understand the composition of the microfibres recovered during the filtration of the wastewater in the washing tests, a thermogravimetrical investigation was carried out on microfibres accumulated on 400 and 60 µm pore size filters. The thermogravimetric curves reported in Figure 3.7, show that all three samples present a twostep thermal degradation, starting from 200° C. Pink fabric has a weight loss of around 51% during the first step, corresponding to a temperature of max weight loss (T_{max})

of 402° C; the weight loss in the second step is of around 41% at a T_{max} of 468° C. These values are perfectly in line with the composition of the fabric that is 50% polyester and 50% cotton. In fact, the first step correspond to the degradation of the cotton part, which usually involves the decomposition of the glycosyl units to char at lower temperatures and the depolymerization of such units to volatile products containing levoglucosan at higher temperatures.[19] The second step corresponds to the further degradation of polyester, due to the decomposition of the main chain.[20] The aliquots of fibres recovered from both 400 and 60 µm pore size filters, presented similar behaviors, with a weight loss of 84% and 80% respectively during the first step (400 µm: T_{max}=346° C; 60 µm T_{max} =353° C), and of 10 % for both of them in the second step (400 µm: T_{max}=435° C; 60 µm T_{max} =429°). Such findings indicate that around the 80% of the fibres released from Pink to air are cotton, a result that is in line with what observed in the investigation reported in Chapter 2 – paragraph 2.2, and also on what observed in the tests to assess the release of microfibres to air.

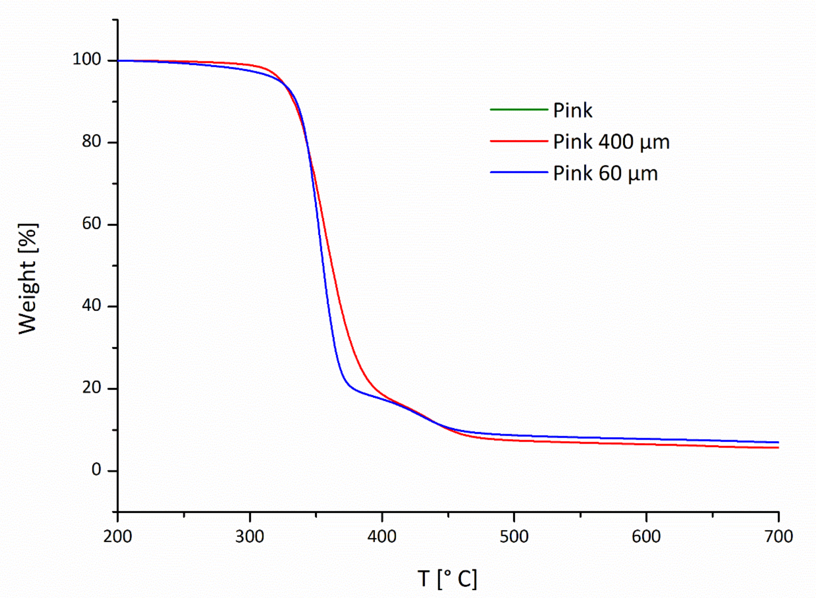

Figure 3.7. Thermogravimetric curves of Pink fabric, Pink fibres recovered form 400 and 60 µm filters.

3.4 Conclusions

The investigation here reported has developed an effective method to quantify the release of microfibres from synthetic clothes to air. Results have shown how one person wearing 1kg of polyester clothes and doing common movements could release from 971 to 302,230 fibres/m^2 per hour, with a length ranging from 100 to 200 µm, that could potentially be inhalated with still unknown consequence on human health. Through the test of polyester garments with different textile characteristics, it was possible to observe that more compact structures like woven and the use of continuous filaments instead of short staple fibres, have a decreasing effect on the release of microfibres to air. Knitted structures are also preferable with yarns made of continuous filaments than short staple fibres. Blends of cotton/polyester release a huge amount of fibres but most of them are cotton. The further investigation on microfibre release to water from the same garments, reported amounts of fibres released to water per kg of washed fabric that range from 128 to 1054 mg/kg but did not provide such clear picture about the possible influence of textile parameters, suggesting more complex mechanisms of release to water than to air. Nevertheless, it confirmed that woven structure with yarns made of continuous filaments induce a lower release of microfibres both to air and water, and that polyester/cotton blend fabrics release a massive quantity of microfibres, majorly of cotton.

3.5 Supporting Information

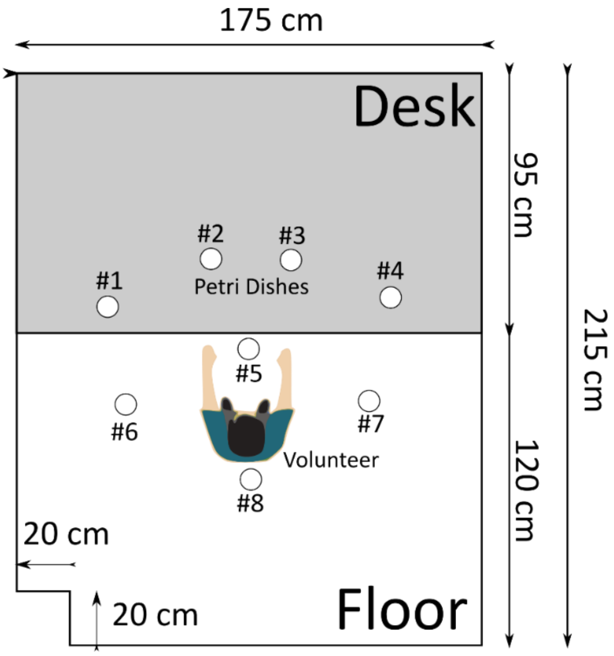

Figure S3.1. Drawing of the test room.

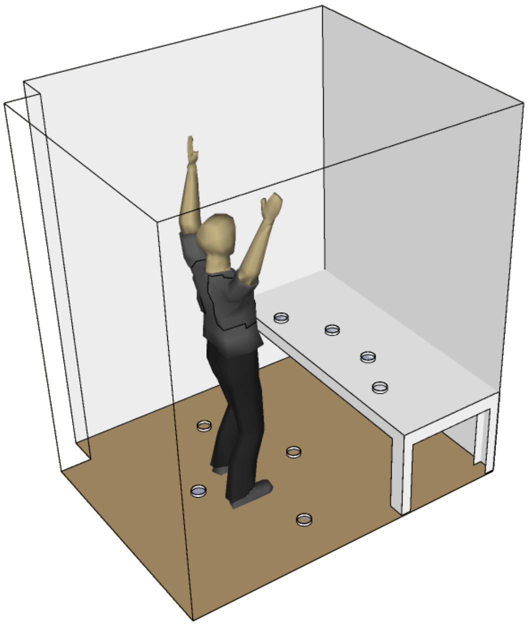

Figure S3.2. 3D model of the test room.

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Chapter 4 - Mitigation actions: development of innovative finishing treatments

4.1 Introduction

In 1974, one of the first studies on the occurrence of microplastic particles in Northwestern Atlantic, already called for prevention measures to tackle the problem of plastic pollution in marine environment. They suggested: the development of water-soluble and photodegradable polymers; the development of efficient, non-atmospheric polluting incinerators to replace open dumping and sanitary landfill; increased effort in the technological development of plastic reclamation systems; increased efforts in plastic recycling.[1] Since then, plastic global production has been constantly increasing, reaching the current massive level of use of plastic in the most various items. At the same time, plastic pollution has worsened year after year, adding the discovery of microplastics, leading to an urgent need for remediation, mitigation and prevention actions. Wu et al.[2] summarized possible solutions to tackle the problem of microplastic pollution, highlighting the following issues:

- removing plastic microbeads from personal care products;
- use of biodegradable materials;
- improved reuse, recycle and recovery of plastics;
- development of clean-up and bioremediation technologies;

- improved separation efficiency of wastewater treatment plants (WWTPs).

Legislation at national level have already been working on banning the use of microbreads in cosmetics and other products.[3] The European Commission has decided to tackle marine plastic pollution with new and strong actions. In January 2018, the "European Strategy for Plastics in a Circular Economy" was launched with the aim to change how plastic products are designed, produced, used and recycled.[4] In addition, in May 2018, the EC proposed new rules to tackle 10 single-use plastic products, which resulted to be the most present on European beaches and in seas.[5] Targeted policies on the use and consume of plastic materials and on the industry that produces them, could contribute to speed up the process of finding and developing solutions to plastic pollution.

For example, biodegradable polymers can replace traditional plastics for many applications, especially for single-use plastic items, and be a potential solution for plastic pollution also in marine environment. In fact, any product discarded into the sea is a potential "stressor" and, since the environmental risk depends on the concentration of the "stressor" and on its residence time in the environment, biodegradability reduces the residence time thus reducing the risk.[6] Biodegradable polymers are designed to degrade during their disposal, thanks to the enzymatic action of microorganisms (i.e. bacteria, algae and fungi), or to nonenzymatic processes (i.e. chemical hydrolysis). Their market ranges from packaging, disposable nonwovens, hygiene products to consumer goods and agricultural tools.[7] However, up to now biodegradable polymers have been designed to degrade in soil, but the environment they found in water is totally different, with salt that acts as a preservation agent, and thus the bacteria that thrive in this ecosystem have life conditions that are completely different from soil.[8] Then, more studies are needed to assess the degradation rate of biodegradable polymers in water and to develop water-degradable polymers.[9]

Concerning the role of WWTPs as barriers for the entrance of microplastics in aquatic environments, Talvitie et al. have proved the efficiency of WWTPs that use different advances final stage treatment technologies such as disc filter, rapid sand filtration, dissolved air flotation and membrane bioreactor.[10] Then, the use of WWTPs that have pre, primary, secondary and advanced tertiary treatment processes could reduce the release of microplastics, particularly of microfibres coming from the washing of synthetic clothes. But besides the intervention at the final stage of the entrance route of microplastics, it is also important to act at the very beginning of this source of pollution that is during the washing of synthetic garments.

Filters for washing machines have been proposed but they are not of easy design since they must be able to retain fibres of micro dimensions, without blocking the flux of water. The Canadian company Environmental Enhancements is selling the Lint LUV-R Washing Machine Discharge Filter as device capable of screening out synthetic microplastic particulates but no studies on its actual efficiencies are available.[11] Another company that is working with research centres on filtration systems for washing machines, is the Slovenian Planet Care. They have developed an external filtration system with a layered filter structure designed to distribute fibre capture through the entire depth of the filter, preventing in this way clogging and prolonging the lifetime of the filter. Final data of the efficiency of their filter are not yet available but the preliminary results are interesting.[12]

Other solutions involve the use of microfibres catching devices to insert into the washing machine: Cora Ball[13] and the Guppyfriend washing bag[14]. The first is a ball whose design is inspired by the structure of corals, which should collect entangled fibres, catching about a third of the microfibres per load from washing downstream. The latter is a polyamide 6.6 bag that enclose the clothes to be washed, retaining the microfibres released. No information on efficiency tests on Cora ball are available, whereas the Guppyfriend bag have been tested by some research institutes, claiming to be able to reduce by 86% the amount of shed fibres, but no more data on the tests carried out have been disclosed.

All these type of solutions, particularly advanced WWTPs and filters for washing machines, could contribute to the overall reduction of microplastic shedding during washing of synthetic clothes, but one important concurrent factor of this scenario also need to be taken into account: the synthetic textiles themselves. Microfibres detach from the yarns that constitute the textile structure because either they are damaged, either they just slip away from the yarn. By treatment of the textile surface, it could be possible to prevent the shedding of microfibres during washing. In fact, the approach presented in this chapter is based on the idea of developing a protective coating on the surface of the fabric, that could protect it from chemical and stresses inside a washing machine, mitigating in this way the overall microplastic release to wastewater. Protective coatings have been already developed during the Life+ MERMAIDS project but they were based on commercial textile auxiliaries all of synthetic nature (i.e. silicone emulsions, acrylic resins, etc.).[15] Instead, the following paragraphs will present two innovative finishing treatments, both based on natural or biodegradable polymers, which preserve the eco-sustainability of the process avoiding the introduction of other polluting agents that could jeopardize the final mitigation purpose. The first treatment is based on the chemical grafting of a natural polysaccharide, pectin, on the surface of polyamide 6.6 fabrics. The second one applies a layer of two different biodegradable polymers, polylactic acid (PLA) or polybutylene succinate adipate (PBSA), on polyamide 6.6 fabrics, by using a non-conventional electrofluidodynamic (EFD) process. Both treatments were developed at laboratory scale, trying to maintain unaltered key properties of the fabrics for their commercial applications (i.e. the hand of the textile). Preliminary tests on the treated fabrics showed very promising results for the application of these innovative treatments as mitigation actions for microplastic pollution from washing of synthetic clothes. Moreover, considering the results of chapter 3, such protective coatings could also prevent the release of microfibres from synthetic clothes to air.

4.2 Pectin based finishing to mitigate the impact of microplastics released by polyamide fabrics[f]

The innovative finishing treatment herein proposed is based on the use of pectin, a natural polysaccharide that represents an interesting product since cheap and abundantly available, being a waste product of fruit juice, sunflower oil, and sugar manufacture. Pectin is extracted from suitable agro-by-products like citrus peel and apple pomace.[16] Pectin is defined as a hetero-polysaccharide predominantly containing galacturonic acid residues, in which varying proportions of the acid groups are present as methoxyl esters, while a certain amount of neutral sugars might be present as side chains.[16] The pectin heterogeneous and complex chemical structure is rich of ester, carboxyl and hydroxyl groups, responsible for its peculiar high reactivity. However, pectin is soluble in aqueous medium, limiting its application in sectors where the contact with water can induce an undesirable solubilization of the polysaccharide.[17] A possible solution to reduce the high solubility of polysaccharides is to mask its

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[f] The work presented in this paragraph has been published as: De Falco, F., Gentile, G., Avolio, R., Errico, M. E., Di Pace, E., Ambrogi, V., Avella, M., Cocca, 2018. Pectin based finishing to mitigate the impact of microplastics released by polyamide fabrics. Carbohydrate Polymers 198, 175-180. DOI: 10.1016/j.carbpol.2018.06.062

polar groups, such as carboxyl and hydroxyl, through their conversion into ester units.[18] In this study, the surface functionalization of polyamide fabrics was performed, firstly modifying pectin with glycidyl methacrylate (GMA), which was then grafted on the surface of polyamide fabric by crosslinking reaction. The effectiveness of the treatment in reducing microfibre release from synthetic fabrics was tested and confirmed through washing trials simulations at laboratory scale, followed by the analysis of the number and size of microplastics released and of the effect on textile properties of the fabric.

4.2.1 Materials and Methods

Materials

The raw 100% polyamide-6,6 woven fabric (code 361, weight 130 g/m^2) was purchased by Testfabrics Inc. (USA). Citrus Pectin Classic CU 701 was kindly supplied by Herbstreit & Fox (Germany), with a degree of esterification of 34% and a galacturonic acid content of 86 %. Glycidyl methacrylate (GMA, 97%) and sodium persulfate ($Na_2S_2O_8$, ≥ 98%) were acquired from Sigma–Aldrich. Distilled water was used for the functionalization of the polyamide.

Synthesis of PEC-GMA

Pectin was dissolved in distilled water and the solution was stirred at 300 rpm with a magnetic stirrer. Then, GMA was added to the pectin solution and the mixture was stirred for 24 hours in nitrogen atmosphere at 50°C. For PEC:GMA molar ratio and pectin concentration in water (wt/v%), refer to Table 4.1.

Grafting of PEC-GMA on PA

1 g of polyamide fabric, cut in square of about 9 cm x 9 cm and previously wetted with distilled water, was dipped into the solution in order to favour the adsorption of the PEC-GMA product and mildly stirred at 100 rpm for 1 hour at 50°C. Then, the fabric was removed from the solution and sodium persulfate

(13.5% wt with respect to PA) was added, as initiator. Once the sodium persulfate was completely dissolved, the fabric was dipped again and the mixture was kept under continuous magnetic stirring for 1 hour in nitrogen atmosphere at 60°C, temperature sufficient to initiate the reaction. Then, the polyamide fabric was removed from the mixture, manually squeezed with a poly(tetrafluoroethylene) (PTFE) roll to remove the excess of material, and dried in oven at 70°C for 24 hours.

The grafting percentage (% G) was calculated using the following equation:

$$\% \, G = \frac{(W_g - W_0)}{W_0}$$

where W_0 and W_g are the weights of the fabric sample before and after grafting, respectively.

Characterization techniques

The morphological characterization of the PEC-GMA-PA textiles was performed by using a field-emission scanning electron microscope (FESEM, QUANTA 200, FEI, The Netherlands), before the SEM analysis the samples were sputter-coated with gold–palladium.

Fourier Transform InfraRed (FTIR) spectra of PEC, of PEC-GMA film and PEC-GMA-PA textile samples were acquired with a Perkin Elmer Spectrum One FTIR spectrometer, equipped with the Universal ATR accessory, using 16 scans and a resolution of 4 cm^{-1}, over the range 4000–400 cm^{-1}.

Solid-state ^{13}C magic angle spinning (MAS) spectra were collected on a Bruker Avance II 400 spectrometer operating at a static field of 9.4 T, equipped with a 4 mm MAS probe. Finely ground samples were packed into 4 mm zirconia rotors sealed with Kel-F caps and spun at a spinning speed ranging between 10 and 12 kHz. All spectra were referenced to external adamantane (CH signal at 38.48 ppm downfield of tetramethylsilane (TMS), set at 0.0 ppm). On PA and PEC-

GMA-PA samples, cross-polarization (CP) spectra were recorded with a variable spin-lock sequence (ramp CP-MAS), using a ^1H π/2 pulse width of 3.6 μs, a contact time of 2 ms and a repetition time of 4 s. On PEC and PEC-GMA samples, direct polarization (SP) spectra were recorded. SP spectra were recorded using a ^{13}C π/2 pulse width of 3.6 μs and a repetition time of 40s.

Thermal stabilities of PA and PEC-GMA-PA samples were evaluated with a Perkin Elmer Pyris Diamond TG/DTA thermogravimetric analyser. A small piece of each sample was placed in a platinum open pan and heated from 30 to 850 °C at 10 °C/min. High purity nitrogen was fluxed through the furnace at a flow rate of 50 mL/min.

The tearing strengths of PA and PEC-GMA-PA samples were measured by using an Instron 5564 tensile testing machine following the ASTM D2261.

Washing tests

Wash trials were performed in Linitest apparatus (URAI S.p.A., Assago, Italy), a laboratory simulator of real washing machine, according to the ISO 105-C06:2010 standard method used for testing the color fastness of textiles to domestic and commercial laundering. The trials were conducted on fabric samples of about 9 x 9 cm^2, thermo-sealed at the edges to prevent fibre shedding. Milli-q water was used as medium, in the ratio (water:fabric specimen)150:1 vol/wt, corresponding to 150 ml of water per 1 g of fabric. The selected detergent was a commercial one (detailed composition in Table S4.1 in the SI) used in the dose recommended by the manufacturer. The fabric samples were placed in the steel containers of Linitest, containing 10 steel balls, and washed for 45 min at 40˚C. Each washing test was conducted in triplicate for statistical reason. The washing effluents, obtained from each wash test, were filtered by means of a peristaltic pump (Mettler Toledo, flow rate 100 ml/min) connected with Tygon tubes, throughout polyvinylidene fluoride (PVDF) filters

(Durapore®, Merck Millipore), with an average pore width of 5 µm and a diameter of 4.7 cm. Then, 400 ml of Milli-Q water at 70°C were fluxed in the filtration system, since such amount of water was found optimal to avoid an excess of detergent on the filter surface. The filters were dried at 105 ºC for 30 min.

Microfibre counting procedure

The filter surfaces were analysed using a scanning electron microscope, SEM, Quanta 200 FEG (FEI, The Netherlands). SEM observations were performed in low vacuum mode (P_{H2O} = 0.7 torr), using a large field detector (LFD) and an accelerating voltage of 30 kV. The observations were conducted on filters mounted on a circular sample stage (diameter 7 cm) by using adhesive tape. Since the low vacuum conditions prevent charging effects on non-electrically conductive samples, the filter surfaces were not pre-treated or coated with any kind of metal layer. The quantitative determination of the amount of microfibres released and the microfibre sizing and weight estimation was performed using the method described in Chapter 2 – paragraph 2.1.2.

4.2.2 Results and Discussion

The finishing treatment of polyamide fabric (PA), based on the use of pectin (PEC), was performed through a two-step process: 1) synthesis of PEC-GMA and 2) grafting of PEC-GMA on the fabric (PEC-GMA-PA). In the first step, pectin was chemically modified by reaction with GMA; the reaction responsible for the formation of the PEC-GMA product is in charge of the epoxide group of GMA, whose three-membered ring opens and reacts with a carboxyl group of the pectin monomer through a nucleophilic substitution reaction, see Figure 4.1a.[18] Such reaction, hiding the highly polar carboxyl groups, reduce the water solubility of pectin, in view of textile finishing applications. Moreover, the modification of pectin with GMA allows the introduction of vinyl groups in the polysaccharide structure, representing the reactive site for the grafting to polyamide during the second step. The grafting reaction occurs through a free radical polymerization, using sodium persulfate as initiator. The reaction mechanism between modified pectin and polyamide involves the removal of a hydrogen atom from the polyamide backbone by the radical initiator, with consecutive formation of free radical active centres on the textile surface. Such sites are responsible for the addition to the double bond of PEC-GMA, with formation of a new bond between the nitrogen atom of the amide group of the fabric and the carbon atom derived from the GMA double bond, see Figure 4.1b.[19]

Different molar ratios between pectin and GMA and different pectin concentrations were tested according to Table 4.1, in order to optimise the synthesis of PEC-GMA, the grafting reaction and to obtain the formation of a homogeneous and regular coating on the fabric surface, without altering the hand of the fabric. The latter is a textile characteristic related to the perception of fabric surface by fingers and palm skin. In order to evaluate this feature, the treated fabrics were analysed by holding them in comparison with non-treated polyamide.[20] This parameter is of key importance in the textile industry, so it was taken into account in the perspective of future applications at industrial scale. The analysis of the different samples pointed out that the most promising results were obtained by using PEC:GMA molar ratio 1:1 and 0.5 wt/v% of pectin in water (sample 5). The results of the characterizations performed on this sample are reported in Figure 4.2, while those obtained analyzing the other samples are reported in the Supporting Information, SI, Figures S4.1-5. SEM micrographs of sample 5 (Figure 2.2a) allow to observe the presence of a thin film covering the surface of neighbouring fibres in the fabric. The morphologies of the coatings obtained in the other samples were indeed quite different, since the coating was too irregular and abundant in samples 1, 2 and 3 (Figures S4.1, S4.2, S4.3), or insufficient in the case of samples 4 and 6 (Figures S4.4, S4.5).

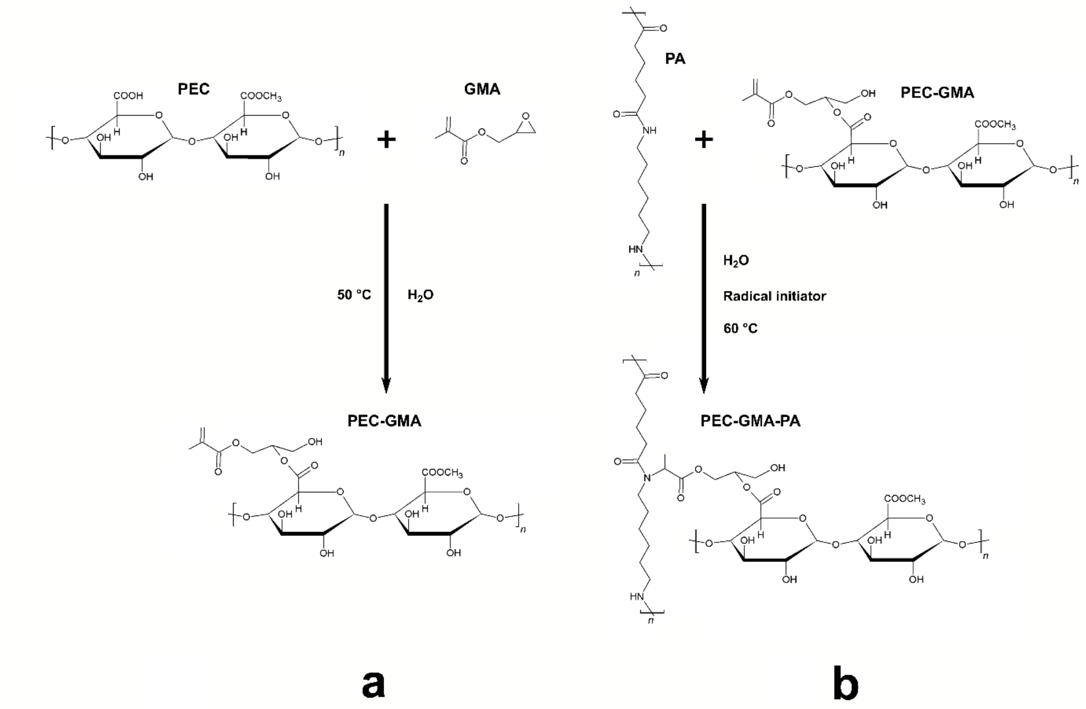

Figure 4.1. Reaction schemes: (a) synthesis of PEC-GMA, (b) grafting of PEC-GMA on PA.

Table 4.1. PEC:GMA molar ratios and concentrations of pectin in water.

Sample	PEC:GMA (moles)	PEC/H_2O wt/v%
1	1:1	2
2	1:2	1
3	1:1	1
4	2:1	1
5	1:1	0.5
6	2:1	0.5

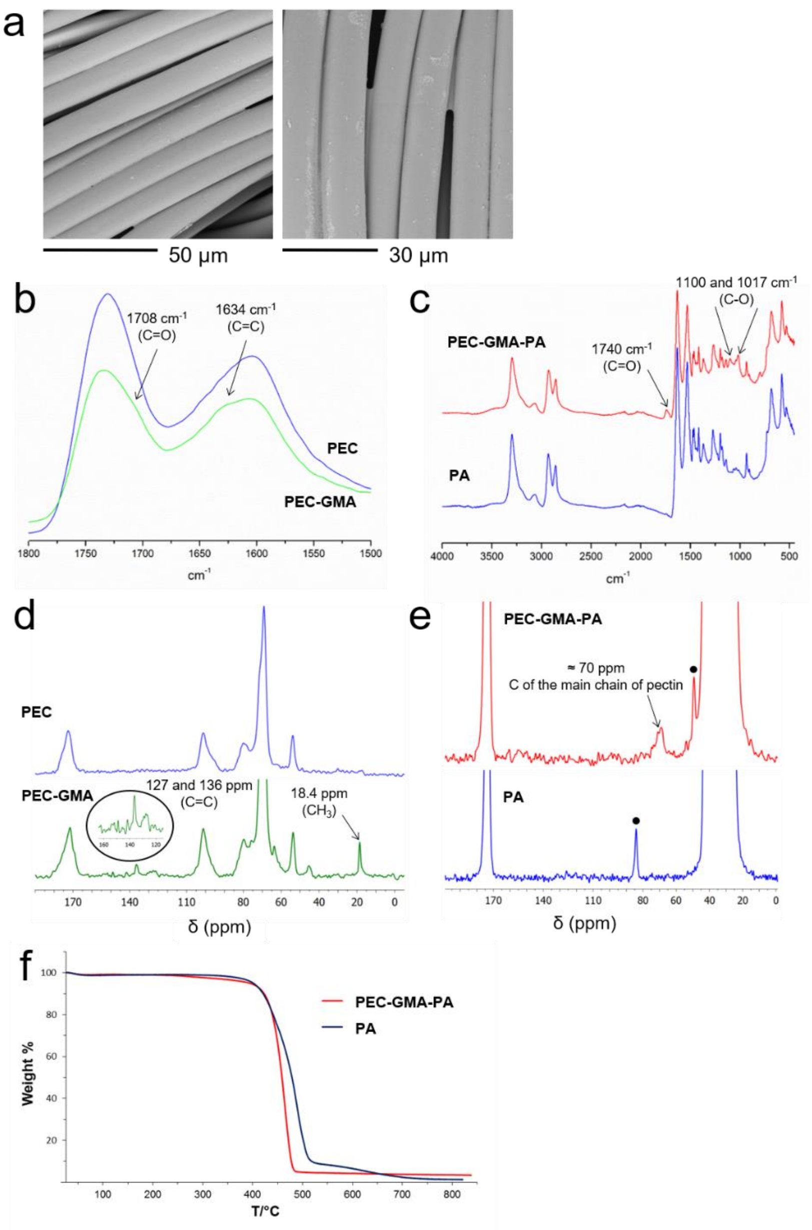

Figure 4.2. Characterizations of sample n. 5: **(**a) SEM micrographs of polyamide treated with PEC-GMA; (b) ATR FTIR spectra of PEC and PEC-GMA recovered from the 1st reaction step; (c) ATR FTIR spectra of PA and PEC-GMA-PA; (d) solid state ^{13}C NMR, direct excitation spectra of PEC and PEC-GMA with a magnification of the signals attributed to the unsaturated carbons of GMA; (e) solid state ^{13}C NMR, cross-polarization spectra of PA and PEC-GMA-PA, spinning sidebands are marked by a dot; (f) TGA thermograms of PA and PEC-GMA-PA.

In order to have a better understanding of the chemistry of the reaction, an ATR FTIR spectrum was acquired on some PEC-GMA recovered after the 1st reaction step (Figure 4.2b). The PEC-GMA spectrum shows two shoulders at 1708 cm^{-1} and 1634 cm^{-1}, attributed respectively to the axial deformation of C=O conjugated ester groups from GMA and to (C=C) vibrations of the GMA vinyl groups.[18] The ATR FTIR analysis corroborated the grafting of PEC-GMA coating on polyamide. In fact, in the ATR FTIR spectrum of PEC-GMA-PA, see Figure 4.2c, it is possible to observe an absorption band centered at 1740 cm^{-1}, due to the C=O stretching vibration of PEC-GMA, and two absorption bands at 1017 cm^{-1} and 1100 cm^{-1}, attributed to the stretching vibration of the ester C-O-C of pectin-GMA.[19]

On the same samples solid state nuclear magnetic resonance spectra (13C NMR) were also acquired. ^{13}C NMR spectroscopy confirms the effectiveness of the synthesis of PEC-GMA during the reaction first step, detecting the vinyl groups (C═C) of GMA attached to the polysaccharide backbone. In fact, the ^{13}C NMR spectrum of PEC-GMA, reported in Figure 4.2d, presents vinyl-carbon signals corresponding to the methacryloyl groups attached onto the polysaccharide. The signal at 18.4 ppm was assigned to the methyl groups ($-CH_3$) of GMA, and the signals that appears in the magnification are attributed to the unsaturated carbons of GMA (C=C). Moreover, the ^{13}C NMR spectrum acquired on treated polyamide indicates the presence of pectin on the fabric since the signal at around 70 ppm in the spectrum of PEC-GMA-PA, reported in Figure 4.2e, corresponds to the carbons of the main chain of pectin.[21]

Thermal stability of the polyamide fabrics treated with PEC-GMA, was evaluated by means of thermogravimetric analysis in comparison with neat polyamide (Figure 4.2f). PA presents a characteristic two-steps thermal degradation. The first step occurs at around 380 °C and is generally assigned to main-chain breakdown, releasing water, NH_3, CO_2, hydrocarbon fragments and

CO; the second weight loss step starts around 450 °C and is attributed to the thermal degradation of the residue.[22] PEC-GMA-PA presents a similar thermal behaviour in comparison to the untreated fabric PA. However, treated polyamide shows degradation steps shifted to lower temperatures, which can be due to the decomposition of the grafted PEC-GMA.[18,19] Moreover, PEC-GMA-PA exhibits a much higher residual weight than the untreated PA.

The grafting percentage for sample 5, calculated as reported in the materials and methods section, was 1.25 %. Assuming the formation of a uniform coating on the polyamide surface, the grafting percentage allows to determine that the amount of the PEC-GMA layer is 0.154 mg for 1 cm^2 of polyamide.

The layer of PEC-GMA on PA surface unalters the PA surface morphology and roughness, as observable from Figure 2.3, where SEM micrographs of PA are compared to those of PEC-GMA-PA sample.

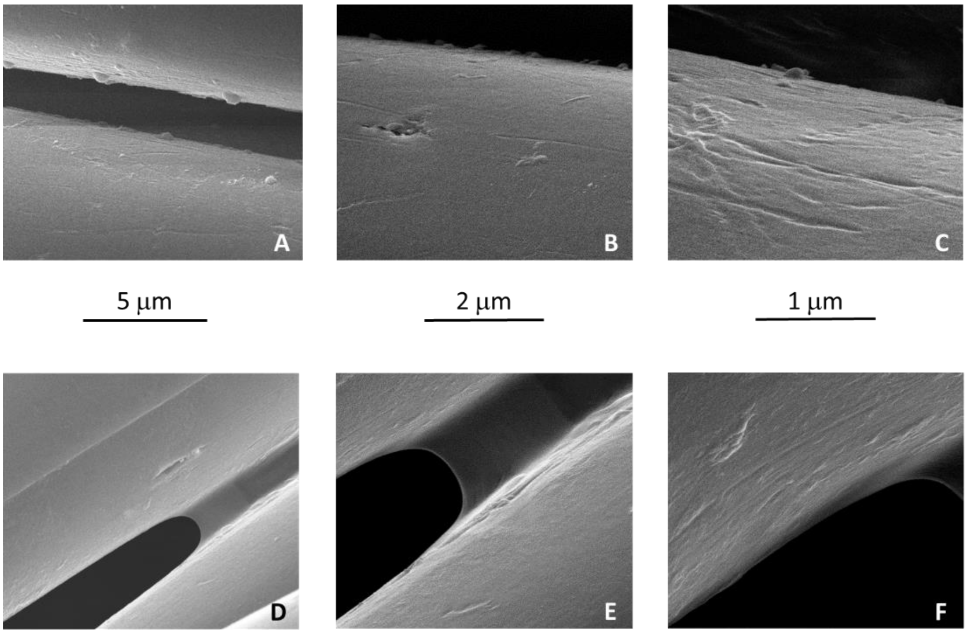

Figure 4.3. SEM micrographs of A-C) PA surface and D-F) PEC-GMA-PA surface.

The finishing treatment slightly increase the tear strength of polyamide fabric. In fact, the average tear strength of PEC-GMA-PA was 68.4 ± 1.6 N, to be compared with the value of 64.6 ± 1.0 N, recorded for PA.

Polyamide fabric samples treated with pectin (according to the ratios and concentrations of sample 5), underwent simulated washing tests to evaluate the effectiveness of the finishing treatment in preventing the release of microplastics during washing processes. For comparison, also neat polyamide fabric samples were tested. Each washing test was performed in triplicate, and the outcomes are reported in Figure 4.4, as average number of fibres released among the triplicates of each washing test (N_a) ± the standard deviation (SD), following the procedure previously reported in Chapter 2 – paragraph 2.2. It was found that the reduction induced by the pectin based treatment is about 90% with respect to the amount of fibers released by untreated polyamide. The washed fabric samples were then analysed by SEM and ATR FTIR to investigate the resistance of the treatment to the washing process. Results are reported in Figures 2.5. The morphological features of the fabric sample after washing revealed that the coating was still present, as also confirmed by ATR FTIR spectroscopy. SEM analysis of the microfibres released from the washing tests permits to conclude that the biobased coating reduces the fragmentation of the polyamide fabric during washings. Indeed, microfibres released by neat polyamide had a mean length of 312 ± 222 μm and a mean diameter of 18 ± 3 μm, leading to a weight estimation of 0.359 g of shed microplastics per kg of washed fabric. On the other hand, in the case of the pectin-treated fabrics, the average length and diameter were 550 ± 384 μm and 16 ± 4 μm, respectively. Then, the approximated amount of microfibres released per kg of fabric was of 0.058 g, only the 16% of the quantity released by the untreated polyamide.

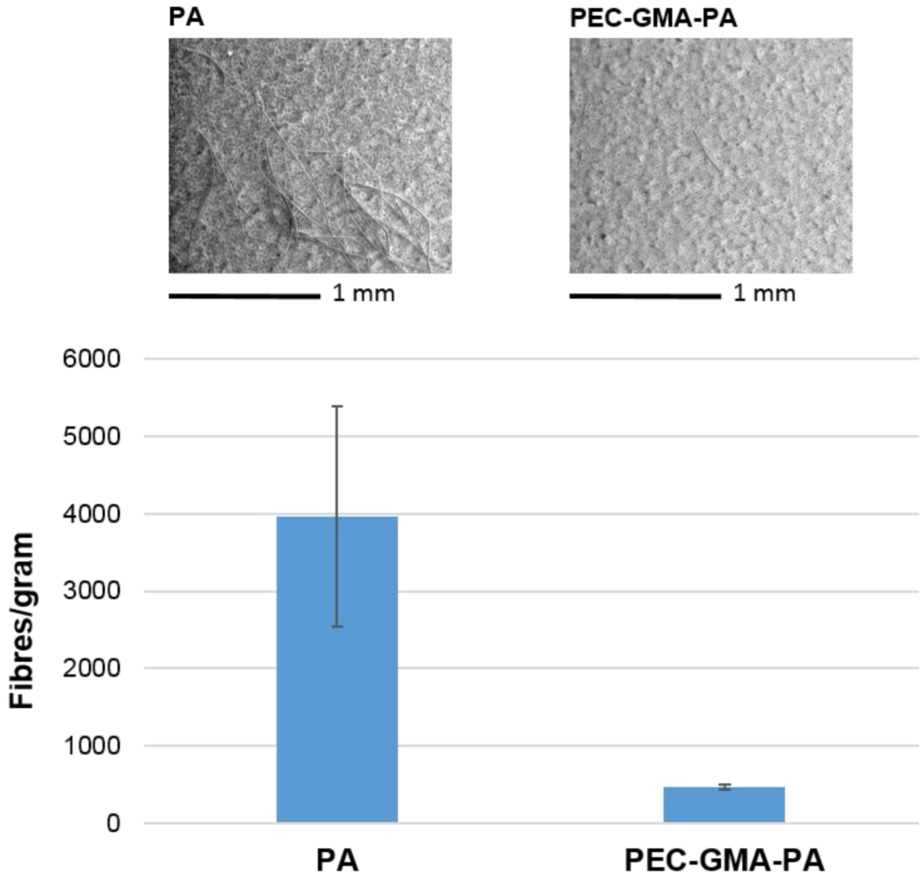

Figure 4.4. Evaluation of the amount of microfibres released: Number of fibres per gram of fabric (Na ± SD) released by neat polyamide (PA) and pectin treated polyamide (PEC-GMA-PA).

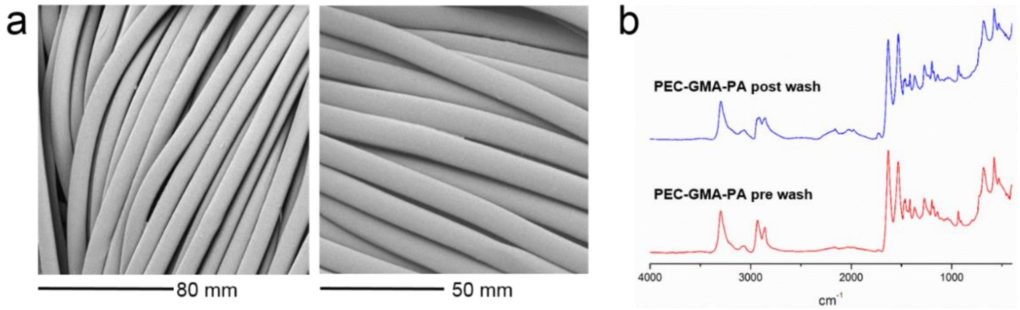

Figure 4.5. Characterizations of washed treated polyamide: (a) SEM micrographs of washed PEC-GMA-PA samples. (b) ATR FTIR spectra of PEC-GMA-PA pre and post washing.

These results allow to conclude that passing from the lab scale to a real household washing process, if we consider an average washing load of 5 kg, the number of microfibres released by neat polyamide is around 20,000,000 corresponding to about 1.79 g, an impressive number that could be reduced to about 2,000,000 (0.29 g) by applying the pectin-based finishing treatment. The order of magnitude of such values is in line with the study reported in Chapter 2 – paragraph 2, and with another recent work that has investigated the amount of microfibres shed during washing, even though polyamide was not among the type of textiles tested in both cases.[23]

4.2.3 Conclusions

In this study, we have successfully developed an innovative eco-sustainable finishing treatment of polyamide textiles. The ratios and concentrations of pectin and GMA were optimized to realise a thin continuous coating that preserve the hand of the fabric. Washing tests of the treated fabrics revealed how the treatment can reduce by almost 90% the number of microplastics released by the untreated polyamide. The finishing treatment developed on polyamide fabrics is compatible with common padding processes already used in textile industry, with the benefit of applying a natural material obtained from food waste. In fact, polyamide fabric was immersed in the reactive solution and then squeezed with a roll, simulating a padding process which consists of two steps: 1) the fabric is immersed in the liquor to achieve a good impregnation and 2) it is passed between two rollers to squeeze it. The overall results point out that the pectin-based treatment can pave the way to a novel approach in the mitigation of microplastic pollution caused by washing processes of synthetic clothes.

4.2.4 Supporting information

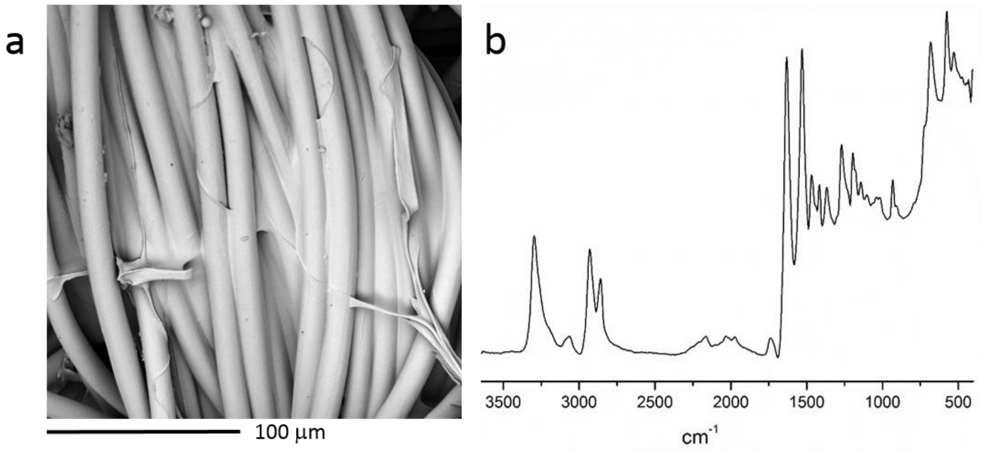

Figure S4.1. Sample 1: (a) SEM micrograph and (b) ATR FTIR spectrum

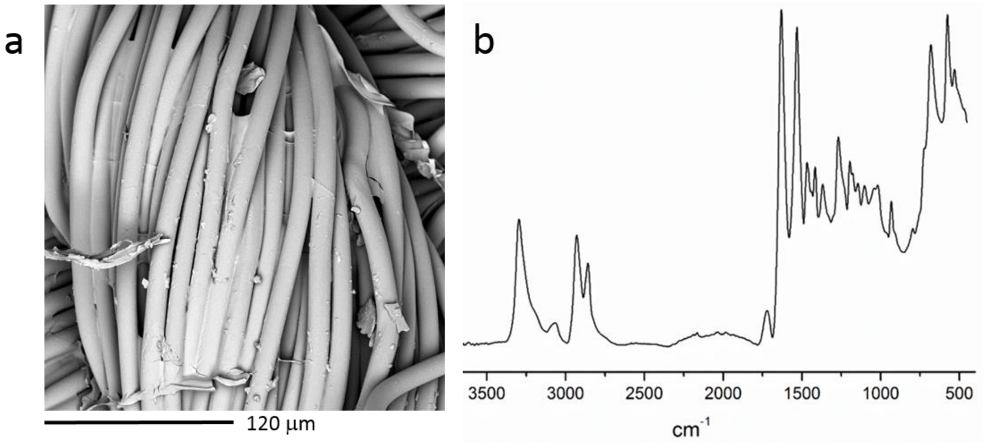

Figure S4.2. Sample 2: (a) SEM micrograph and (b) ATR FTIR spectrum.

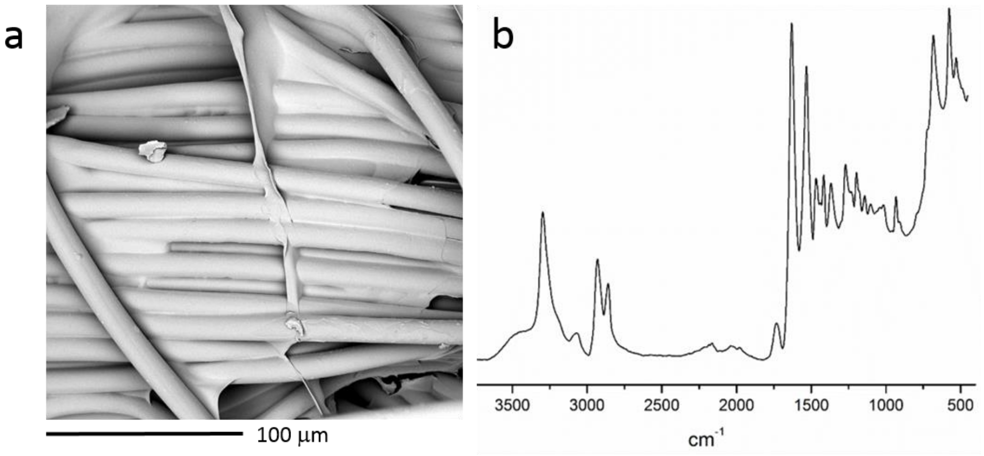

Figure S4.3. Sample 3: (a) SEM micrograph and (b) ATR FTIR spectrum.

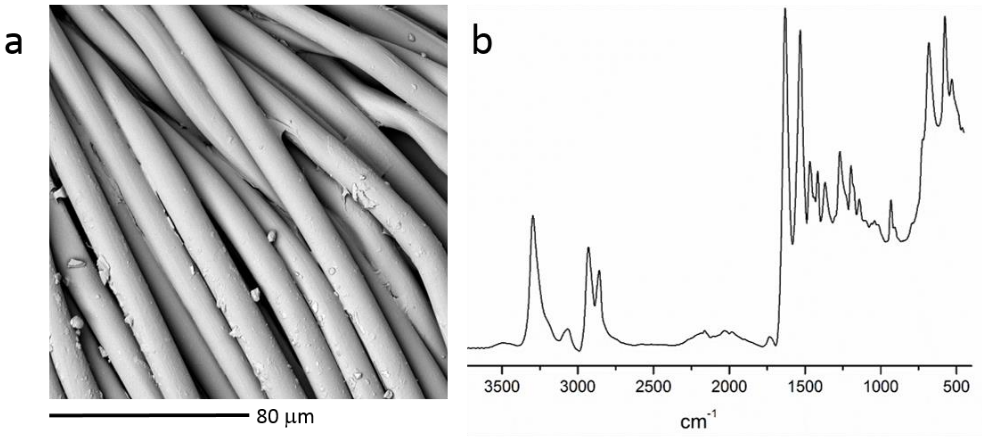

Figure S4.4. Sample 4: (a) SEM micrograph and (b) ATR FTIR spectrum.

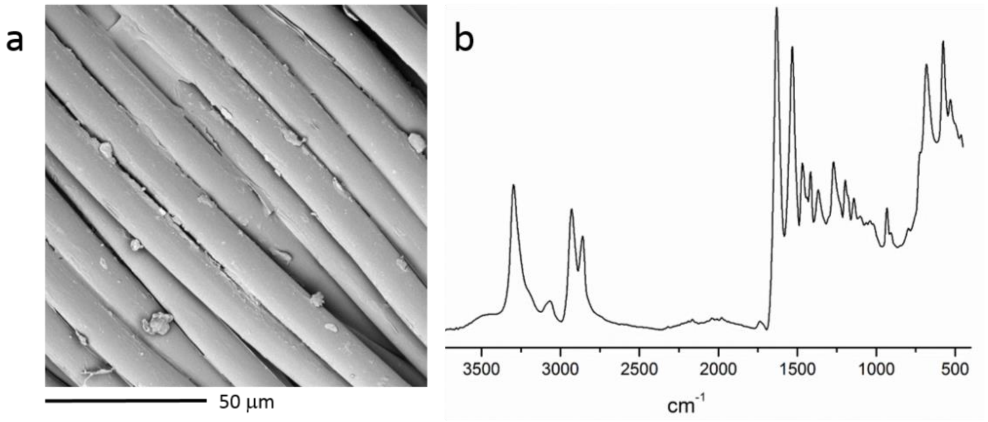

Figure S4.5. Sample 6: (a) SEM micrograph and (b) ATR FTIR spectrum.

Table S4.1. Detergent description

Component	**Function**
Aqua	Osmotic water microbiologically tested, acting as solvent
Sodium Laureth Sulfate	Plant-derived surfactant
Glycereth-6 Cocoate	Plant-derived surfactant
Sodium Chloride	Thickener
Potassium Cocoate	Plant-derived surfactant
Sodium Formate	Stabilizer
Sodium Lauryl Sulfate	Plant-derived surfactant
Phenoxyethanol	Preservative
Tridecyl Salicylate	Active ingredient
Parfum	Perfume with raw materials at least 90% biodegradable
Lauryl Polyglucose	Plant-derived surfactant
Decyl Octyl Polyglucose	Plant-derived surfactant
Sodium Carboxymethyl Inulin	Sequestrant / Dispersant
Citric Acid	Sequestrant and stabilizer
Polydimethylsiloxane	Additive

4.3 Novel finishing treatments of polyamide fabrics by electrofluidodynamic process to reduce microplastic release during washings

New finishing treatments of polyamide fabrics were performed by using a non-conventional electrofluidodynamic (EFD) method with the aim to reduce the amount of microfibres released during the washing. EFD represents a new highly versatile and cost-effective process to functionalize polymer based textile substrates.[24] Such emerging methodology is based on liquid atomization employing electrical forces. Due to these forces, the meniscus of a liquid flowing out a capillary nozzle elongates, forming a fine jet, which next is atomised into fine droplets. Depending on the flow rate and potential of the capillary, the droplets can be of submicron size, with narrow size distribution. Main applications of this technique are nanoparticle production, thin film deposition, functional layer formation.[25] In this work, EFD was used to apply a nano-coating on polyamide surface, with the aim to protect the fabric during the washing process and then reduce the release of microfibres. Due to the importance of the environmental impact of such textile treatment, two biodegradable polymers – i.e., poly(lactic acid) (PLA) and poly(butylene succinate-co-butylene adipate) (PBSA) – were used as finishing materials. PLA is a linear aliphatic thermoplastic polyester derived from renewable sources (mainly starch and sugar), and with lactic acid (2-hydroxy propionic acid) as building block.[26] PBSA is a random copolymer of poly(butylene succinate) (PBS), synthesized by polycondensation of 1, 4-butanediol with succinic and adipic acids and it is also obtained from renewable resources.[27] The EFD process was optimized to realize homogeneous coatings onto polyamide fabrics. Morphological, thermal and surface properties of fabrics coated with PLA or PBSA were investigated. Finally, washing tests of the coated textiles were performed to assess the effectiveness of the coating in reducing the amount of microplastics released.

4.3.1 Material and Methods

Materials

Raw 100% woven polyamide-6,6 fabric, PA, was purchased by Ausiliari Tessili, Italy. Poly(lactic acid), PLA 4032 D was provided by NatureWorks, USA. poly(butylene succinate-co-butylene adipate), Bionolle #3001, was supplied by Showa Denko, Japan. Chloroform (CHCl3) (⩾99%) was purchased from Sigma Aldrich (Milan, Italy) and used without further purification.

Coating deposition

PLA or PBSA pellets were dissolved in chloroform by magnetic stirring at room temperature, to yield a 2% w/v solution. The coating deposition was performed using the electrospinning system NANON-01A, Mecc, Japan. The polymer solution was placed in a 5 ml syringe (BD Plastipack, Italy), fixed on the pump system, and joined to a stainless-steel needle with an inner diameter of 0.8 mm, connected to the positive pole. Polyamide fabric samples (9 x 9 cm^2) were fixed on a drum collector covered by aluminum foil. Such configuration allowed the treatment of multiple fabric samples. All the process parameters were optimized in order to obtain a homogeneous and uniform coating on the surface of the fabric samples. Collector rotation speed and needle/collector gap were set at 50 rpm and 8 cm respectively. The syringe moved parallel to the axis of the drum, at a speed of 1 mm/s and for a length of 120 mm. Other parameters were set as follows: applied voltage (11 kV), feed rate (2.5 mL/h), deposition time (4h for each side of the fabric sample) and humidity degree (36% at 25°C). The amount of the coating deposited on the fabric was determined by measuring the weight difference between the polyamide fabrics before and after the EFD treatment. The amount of polyester coated on fabric surface (W%) was calculated using Equation 1:

$$W\% = \frac{W_1 - W_0}{W_0} \cdot 100 \qquad \text{Equation 1}$$

where W_0 is the weight of the fabric before the EFD treatment and W_1 is the weight after the deposition of the coating.

Characterization techniques

Coating morphology was analysed by using a field-emission scanning electron microscope (FESEM, QUANTA200, FEI, The Netherlands). Before the observation, about 1 cm^2 of treated and untreated fabrics were sputter-coated with gold–palladium alloy.

Fourier Transform Infrared (FTIR) spectra of neat and treated polyamide samples and of neat PLA and PBSA films, were acquired by means of a Perkin Elmer Spectrum One FTIR spectrometer, equipped with the Universal ATR accessory, using 16 scans and a resolution of 4 cm^{-1}, over the range 4000–400cm^{-1}.

Thermal stabilities of untreated and treated polyamide samples were evaluated with a Perkin Elmer Pyris Diamond TG/DTA thermogravimetric analyser. A small piece of each sample was placed in a platinum open pan and heated from 30 to 850 °C at 10 °C/min. High purity nitrogen was fluxed through the furnace at a flow rate of 50 mL/min.

Contact angle measurements were performed using an FTA-1000 B-class drop shape instrument (First Ten Angstroms, USA). 5 µl of Milli-q water were dispensed on the surface of the fabric, and the contact angle of the drop was analysed by FTA32 software. All measurements were performed 5 times for each fabric sample, the mean value and the standard deviation was calculated.

Washing tests

Washing tests were performed in Linitest apparatus (URAI S.p.A., Assago, Italy), a laboratory simulator of a real washing machine, following the ISO 105-C06:2010 standard method used for testing the color fastness of textiles to domestic and commercial laundering. A commercial bio-detergent was selected, composed by anionic and non-ionic surfactants, soap, phenohyethanol and perfume. The applied liquor ratio (liquor:specimen) was 150:1 vol/wt, where the liquor was a solution of Milli-q water plus the dose of detergent recommended by the manufacturer. Fabric samples, with a size of 9 x 9 cm2, were thermossealed at their cut edges, in order to prevent the release of fibres from them. Then, each fabric sample was placed in a steel container of the Linitest, along with the liquor and 10 steel balls, and washed for 45 min at 40˚C. Each washing test was performed in triplicates on three different samples in order to obtain data statistically analyzable. The washing effluents, obtained from each wash test, were filtered by means of a peristaltic pump (Mettler Toledo, flow rate 100 ml/min) connected with Tygon tubes, throughout polyvinylidene fluoride (PVDF) filters (Durapore®, Merck Millipore), with an average pore size of 5 µm and a diameter of 4.7 cm. Then, 400 ml of Milli-Q water at 70°C were fluxed in the filtration system, since such amount of water was found optimal to avoid an excess of detergent on the filter surface. The filters were dried at 105 ºC for 30 min. The number, size and weight of the microplastics released during the washing tests were determined according to the procedure described in Chapter 2 – paragraph 2.2. Briefly, such procedure involves the acquisition of 21 SEM micrographs along two diagonals of the filter surfaces, the determination of the number of microfibers per micrographs and of the average number of microfibers over 21 images. The total number of microfibers per filter, N, was calculated by dividing the average value of microfiber for the filter area. Three filters, were analysed for each sample and the average N value among the three filters (N_a) and the related standard deviation (SD) was determined. Since the weight of microfibres released per filter was not determinable by gravimetric method, microfibre dimensions were used to evaluate the weight in grams of microfibres released by 1 kg of fabrics, by applying the following Equation 2:

$$\text{Microfibers (mg/Kg)} = N_a \cdot \left(\pi \cdot \frac{D^2}{4} \cdot L\right) \rho \qquad \text{Equation 2}$$

where ρ is the density of the material.

4.3.2 Results and Discussion

PLA and PBSA were applied on polyamide substrate by an EFD method in order to obtain a thin, continuous and homogeneous coating, able to protect the fabric during washings and reduce the amount of microfibers shed. Process parameters such as applied voltage, feed rate, deposition time and distance needle-collector, were preliminarily screened to realize the deposition of a coating. The morphological analysis performed on the surfaces of PLA and PBSA coated polyamide samples (Figure 4.6) was essential to confirm the effective presence of homogeneous and uniform coatings that cover all the fibres of the yarn, for both the applied materials. The surface of the coatings appears smooth and thin. The amount of polyester coated on polyamide fabric, determined gravimetrically, was 4 wt% both in the case of PLA and PSA and, hypothesizing a uniform distribution of the material, it corresponds to 0.494 mg of PLA or PBSA per 1 cm^2 of treated polyamide. Such small quantities of coated polymers should leave unaltered the hand of the polyamide fabric. This feature is related to the perception of the thickness and surface of the textile by the fingers and palm skin and it is of crucial importance for the textiles industry.[20] For this purpose, the treated fabrics were analysed by holding them in comparison with non-treated polyamide. The result was that the PBSA coating unaffects the hand of the fabric, whereas the PLA coating was lightly perceptible. In light of these results, EFD could be an interesting alternative to conventional methods of finishing, such as pad-dry-cure, which are often accompanied by excessive weight add on, loss of feel and reduced comfort to the wearer.[28]

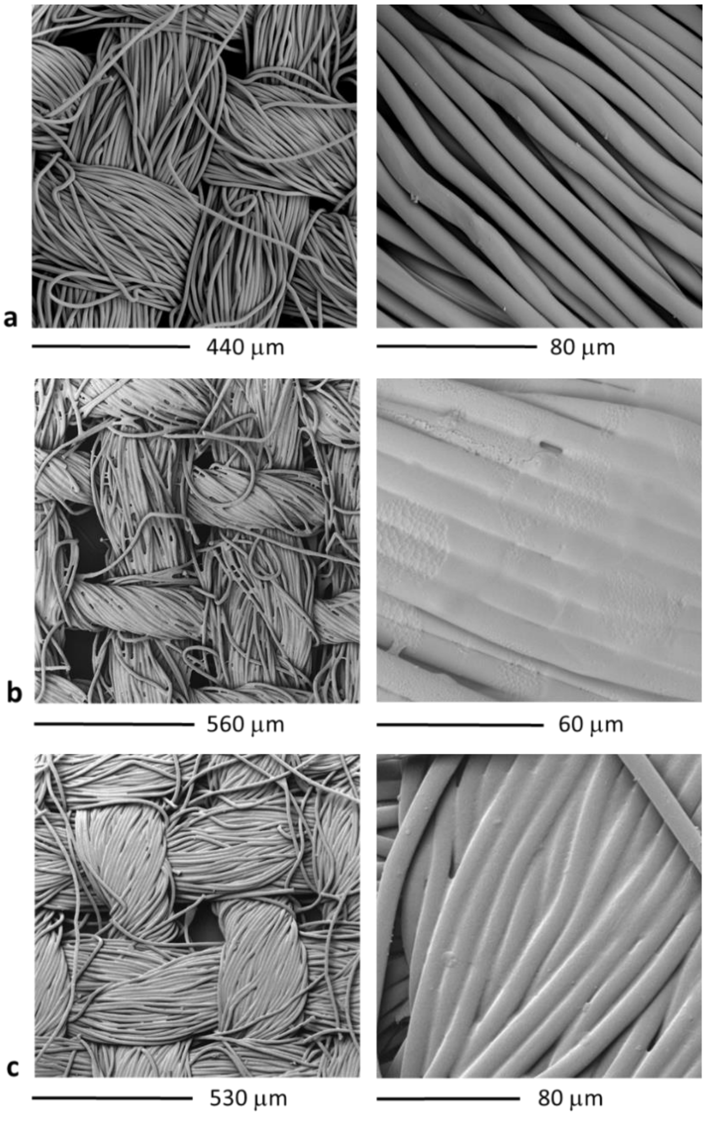

Figure 4.6. SEM micrographs of polyamide fabrics, PA, a) neat; b) coated with PLA, c) coated with PBSA.

FTIR analysis of the treated fabrics confirmed the nature of the coatings, as observable from the spectra reported in the Supporting Information (Figure S4.6). PLA and PBSA coated samples underwent thermogravimetric analysis to evaluate their thermal stability in comparison with neat polyamide (PA) and neat PLA and PBSA (Figure 4.7).

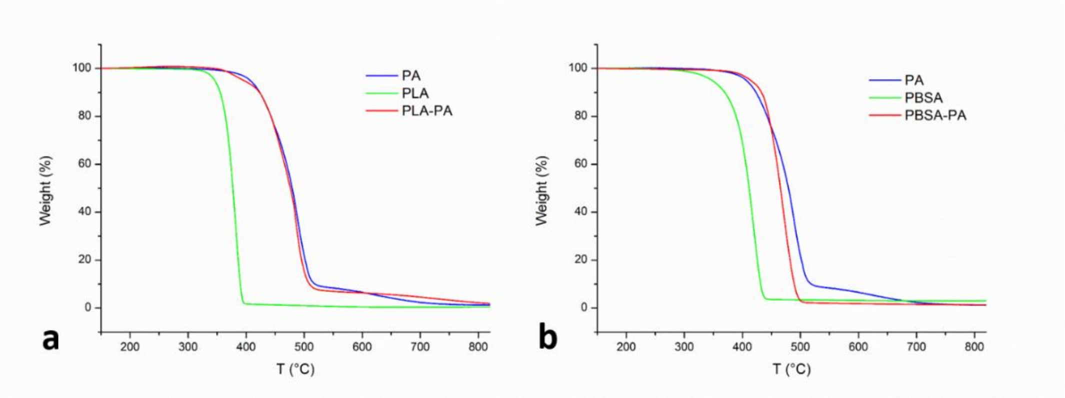

Figure 4.7. TGA thermograms of: a) PLA-coated PA (PLA-PA), neat PLA and neat PA; b) PBSA-coated polyamide (PBSA-PA), neat PBSA and neat PA.

Polyamide fabric showed a two step thermal degradation: the first step was at around 380° C and is attributed to the main-chain breakdown, releasing water, NH_3, CO_2, hydrocarbon fragments and CO; the second step occurred at around 450 °C and it is due to the thermal degradation of the residue.[22] The main degradation pathway of PLA is a non radical transesterifaction reaction involving –OH chain, which can produce lactide, oligomers or acetaldehyde plus carbon monoxide. The TGA curve of neat PLA samples showed a one-stage weight loss, with the onset temperature at around 330 °C and the degradation completed at around 400 °C.[29] Neat PBSA sample is also characterized by a one-step thermal degradation, starting at around 320 °C and ending at around 440 °C, and by a slower degradation kinetic with respect to PLA. PLA-PA samples showed a thermal behaviour very close to uncoated PA, whereas PBSA-PA samples had a different degradation kinetic with respect to neat PLA. This could be due to the decomposition of the PBSA coating that affect the PA behaviour. In fact, the onset temperature of PBSA-PA was around 390 °C but the degradation ended at around 500°C in one-step.

The influence of the coating on the wettability of neat polyamide was evaluated through water contact angle (WCA) measurements, reported in Figure 4.8. Neat polyamide showed a WCA of 137 ± 5º, a value in line with other studies, indicating a hydrophobic behavior.[30,31] WCA analyses of both PLA and PBSA coated fabrics reported no significant changes in the WCA value (131 ± 8º for PLA-PA, 132 ± 3º for PBSA-PA), highlighting that the treatments preserve the hydrophobic nature of the fabric.

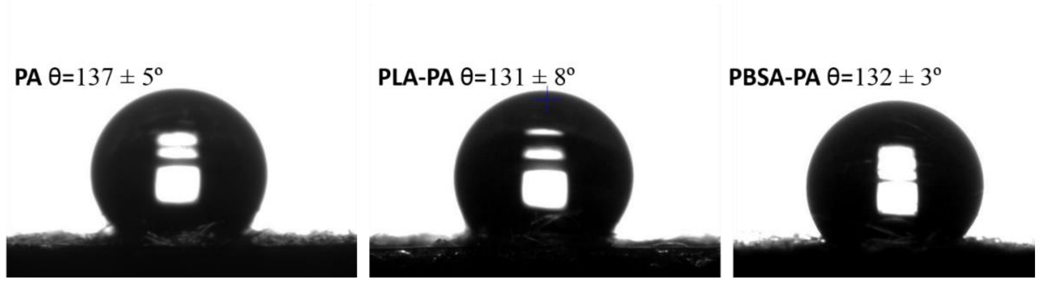

Figure 4.8. WCA images on neat PA (a), PLA-PA (b) and PBSA-PA.

Once that the nature and morphology of the coatings was assessed, the effectiveness of the finishing treatments in reducing the release of microfibres during washing, was tested. Laboratory simulations of real washing processes were performed on uncoated polyamide samples and on PLA and PBSA coated ones. The procedure previously reported in Chapter 2 – paragraph 2.1.4, was applied to evaluate the number of microfibres released during such washing tests. The outcomes are reported in Figure 4.9 as average number of fibres released among the triplicates of each washing test (N_a) ± the standard deviation. Neat polyamide samples released 3966 ± 1425 microfibres per gram of fabric, whereas PLA and PBSA coated samples released 428 ± 92 and 456 ± 120, respectively. Comparing the numbers of microfibres released, the reduction induced by EFD based treatments is about the 90% of the amount released by untreated polyamide.

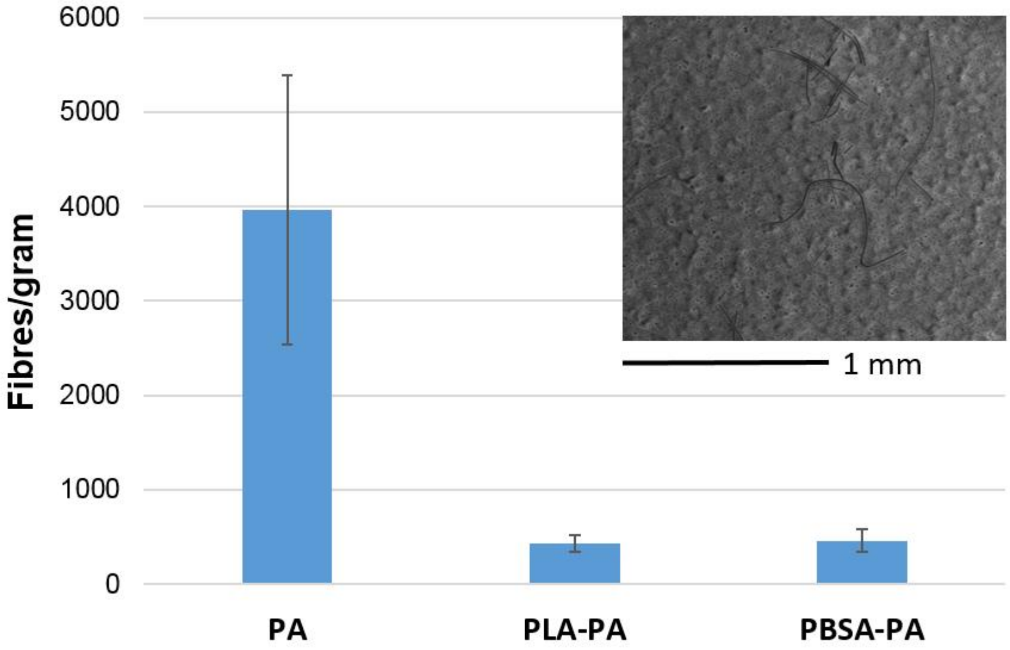

Figure 4.9. Number of fibres per gram of fabric (Na ± SD) released from neat polyamide fabric (PA), PLA coated polyamide fabric (PLA-PA), PBSA coated polyamide fabric (PBSA-PA). In the upper part of the figure, an example of a SEM image of the filters is reported.

The analysis of the dimensions of the microfibres released, led to the data reported in Table 4.2. In comparison to neat PA and PLA-PA, PBSA-PA samples seem to release longer fibres, possibly due to a protective effect of PBSA that, being more ductile than PLA, reduce fibre breakage phenomena. Such values were applied to convert the number of microfibres released to their amount in grams. In details, PA released 0,35 g/kg of microfibres, PLA-PA 0,033 g/kg, PBSA-PA 0,081 g/kg.

Table 4.2. Dimensions (mean ± standard deviation) of the microfibres released.

Sample	Length, L, [μm]	Diameter, D, [μm]
PA	312 ± 222	18 ± 3
PLA-PA	268 ± 190	18 ± 4
PBSA-PA	577 ± 410	19 ± 8

Transferring these data to the context of a real washing machine, considering a general load of 5 kg, the numbers of microplastic released is quite impressive. In fact, a 5 kg of neat polyamide textiles can release almost 20,000,000 microfibres, corresponding to 1,79 g per each wash. By using polyamide fabrics coated with either PLA or PBSA, the number of microfibres released could decrease to around 2,000,000, corresponding to 0,164 g of microfibres released in the case of PLA and to 0,405 g for PBSA. The comparison of such data with other works on the amount of microfibres released by synthetic textiles, is not straightforward since they did not analyse polyamide, and all used different methods and washing conditions.[32,33,34] Nevertheless, the values here reported are in line, as order of magnitude of amount of microfibres released, with those presented in other recent investigations and with those reported in Chapter 2 – paragraph 2.2.[23]

The washed fabric samples were then analysed by FTIR, SEM and TGA to investigate the durability of the treatments to washing process. Results are reported in Figure 4.10. SEM analysis revealed that after washing both the coatings were still present, almost unaltered in PLA coated samples, damaged in some parts in PBSA samples. FTIR investigation confirmed the presence of the coatings, detecting the same bands attributed to functional groups of PLA and PBSA previously detected. In fact, the spectra of PLA coated samples (Figure

4.10b) showed the peaks at about 1753 cm^{-1} and 1182 cm^{-1} which are attributed to C=O stretching and C–O–C stretching vibrations of PLA.[35] In the FTIR spectra of PBSA coated samples, the band attributed to C=O stretching vibrations of PBSA is clearly visible at 1716 cm^{-1} (Figure 4.10d).

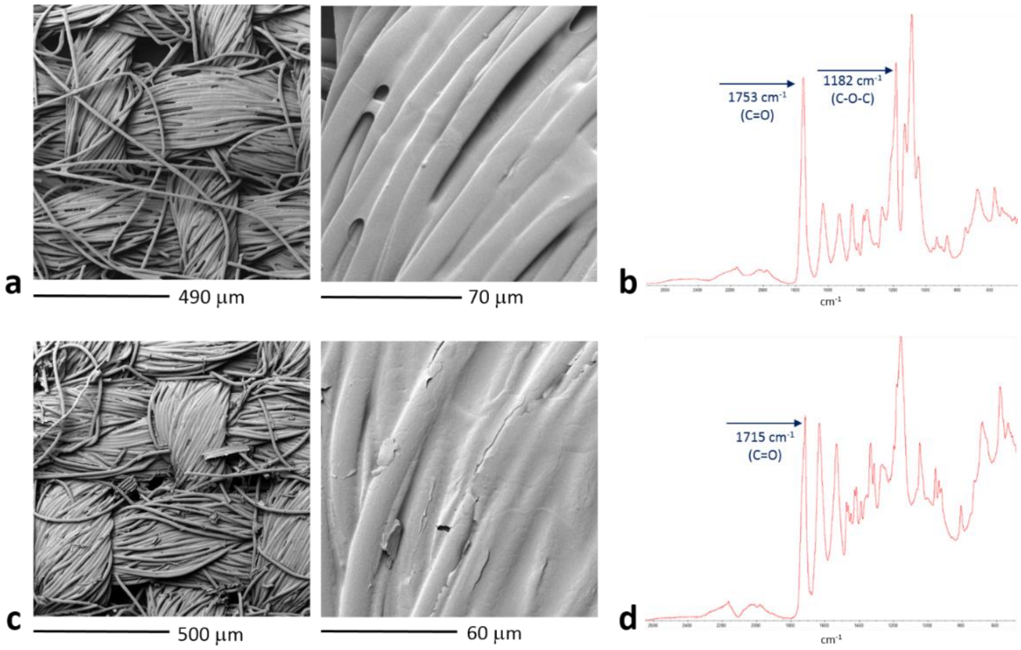

Figure 4.10. (a) SEM micrographs and (b) ATR FT-IR spectrum of PLA-PA post washing; (c) SEM micrographs and (d) ATR FT-IR spectrum of PBSA-PA post washing.

4.3.3 Conclusions

The general results of this study allow to validate the use of EFD surface treatment to reduce microplastic release during washings of polyamide textiles. The PLA and PBSA based coatings did not affect the hand and the wettability of polyamide 6.6 and were able to reduce dramatically the amount of microfibres released. In addition, the developed coatings proved to endure a washing cycle, showing a promising application as mitigation action of the environmental impact of synthetic textiles.

4.3.4 Supporting Information

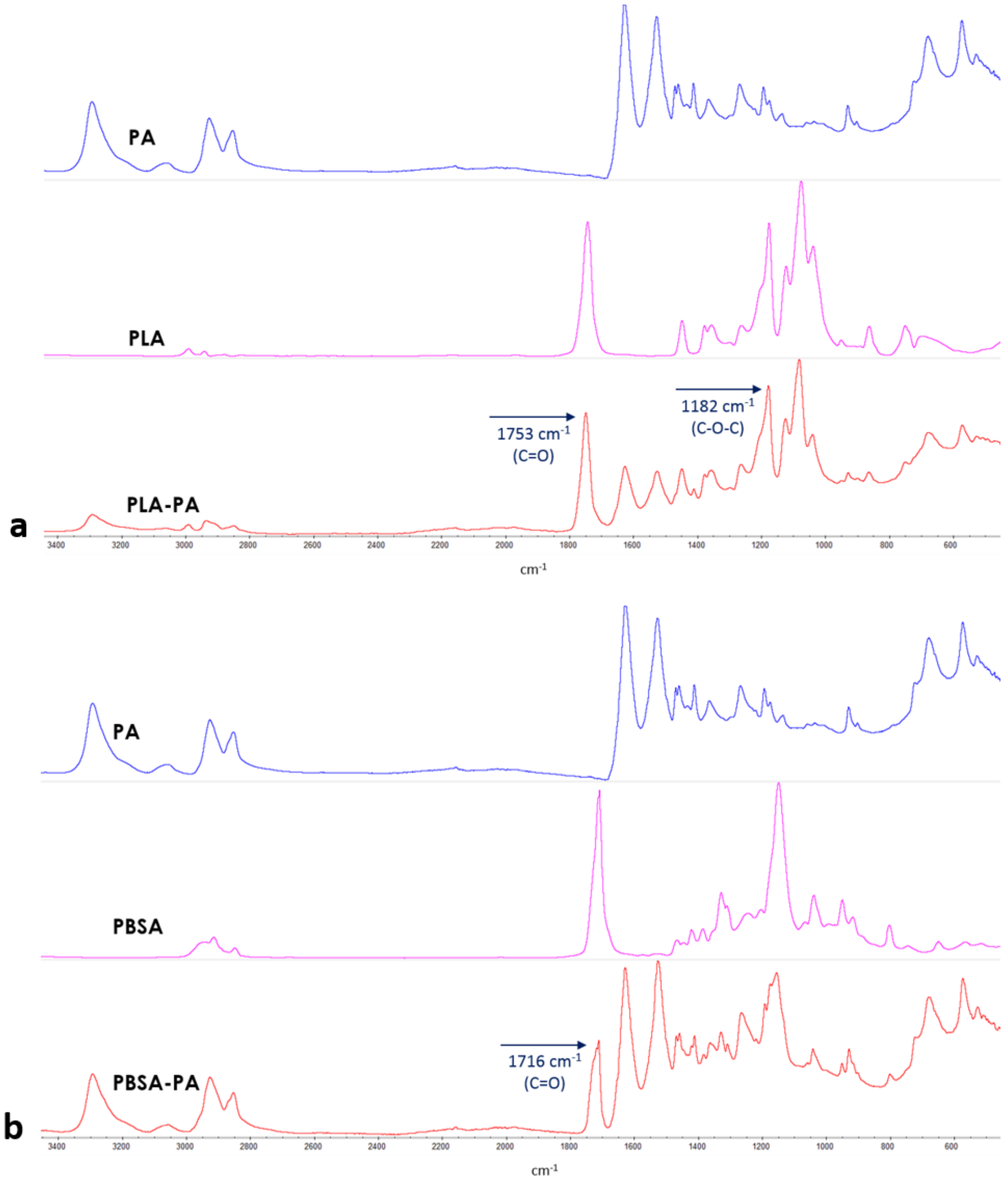

Figure S4.6. Absorbance FT-IR spectra of: a) neat polyamide fabric (PA), neat PLA film (PLA) and post-wash PLA coated polyamide fabric (PLA-PA); b) neat polyamide fabric (PA), neat PBSA film (PBSA) and post-wash PBSA coated polyamide fabric (PBSA-PA).

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Chapter 5 - Conclusions

The work here presented provides a comprehensive investigation of the release of microplastics from synthetic textiles, one of the most unexpected and still poorly understood sources of microplastics. After the development of quantification procedures at lab and real scale, of the release to water as well as to air, the influence of textile parameters on the release was assessed. Moreover, mitigation measure of the impact of such source of pollution were implemented and successfully demonstrated.

First of all, experimental procedures to evaluate microfibres released during washing processes of synthetic textiles were developed. An effective analytical protocol was developed to evaluate the microfibre release during wash trials from standard fabrics simulated at lab scale. Such procedure consisted in the filtration of washing waters and the analysis of the filter surface by scanning electron microscopy (SEM), followed by the application of a counting procedure to perform a direct quantification of the number and dimension of microfibres released. The adopted protocol proved to be a useful tool for the evaluation of the extent of the release from textiles, allowing the identification of specific trends in microplastic release, as a function of textile nature and geometry, different detergents and washing conditions. Among the tested fabrics, woven polyester released the highest number of microfibres with respect to knitted polyester and woven polypropylene during washing under domestic conditions, independently of the used detergent. Additional trials performed on woven polyester pointed out that the lowest release of microfibres was obtained by using a softener, due to its ability of reducing the friction among fibres. Regardless the type of fabric, results indicated that powder detergent, higher temperature, higher water hardness and mechanical action increased the microplastic release. The approximate number of microfibres released from a typical 5 kg wash load of polyester fabrics was calculated to be more than 6,000,000. Passing from lab to real scale, a quantification method was developed to estimate the amount of microfibres released during wash tests of commercial synthetic garments in a real household washing machine. A multistep filtration procedure, through filters of different pore size, of all the wastewater coming from the washing machine, allowed a reliable gravimetrical evaluation of the release, identifying also that the most abundant fraction of microfibres released are retained by the filter with 60 μm pore size. Quantities of microfibres released range from 124 to 308 mg for kg of washed fabric. Results allowed to identify some parameters that could decrease the release of microfibres from polyester clothes: yarns made of continuous filaments, high twist and low hairiness. Blends of polyester with artificial or natural fibres tend to release more but mainly fibres of cellulosic nature. After subsequent washing tests of polyester garments up to 10 washes, the release of microfibres decreases and reach a plateau. Compared to other available published works on the topic, this quantification method introduces important simultaneous novelties that support the effectiveness of the procedure. The two evaluation procedures developed at lab and real scale were also compared in a dedicated study, washing the same type of polyester fabric either in a laboratory simulator, either in a washing machine. Comparing the amount of microfibres released per kg of washed fabric from the two approaches adopted, lab scale tests produce more microfibres than those released in real condition tests, maybe due not only to the difference between lab scale and real washings, but also to the different filtration procedure, since filtration performed at lab scale takes into account also the smallest microfibres that are not collected in real washing tests. Moreover, the test at lab scale is likely to simulate more than 1 washing cycle in real conditions. Nevertheless, the experiments performed through the lab scale approach allowed a low time/low cost estimation of microfibre release from synthetic fabrics, since the amount of water used and filtered during the simulated test is very low. Considering the different efficiency of WWTPs and the amount and the dimensions of the microfibres collected in this part of the work, a significant fraction of them could potentially reach marine environment with negative effects on aquatic organisms.

Secondly, the release of microfibres to air from wearing of synthetic clothes was also investigated and compared with the release to water. Tests were designed to collect data on the amount of microfibres released to air and on the possible influence of textile properties on the release itself. The tests were performed in a clean room, minimizing every source of contamination, with volunteers wearing the garments to test and performing a sequence of movements to simulate daily activities. Released fibres were collected on petri dishes containing dampened filter papers and disposed around the volunteer. Optical microscopy analysis of the filters allowed the determination of the number and dimensions of microfibres released. Results showed that one person wearing 1kg of polyester clothes and doing common movements could release from 971 to 302,230 fibres/m^2 per hour, with a length ranging from 100 to 200 µm, that could potentially be inhaled with still unknown consequences on human health. Considering the different textile characteristics of the tested garments, the following consideration on their effect on the release can be drawn: more compact structures like woven and the use of continuous filaments instead of short staple fibres have a decreasing effect on the release of microfibres to air; blend of cotton/polyester release a huge amount of fibres but most of them are cotton ones. A further investigation of microfibre release to water from the same garments was performed through wash trials in a washing machine with the multistep filtration procedure. The amounts of microfibres released to water per kg of washed fabric ranged from 128 to 1054 mg/kg but did not provide such clear picture about the possible influence of textile parameters, suggesting more complex mechanisms of release to water than to air. Nevertheless, it confirmed that woven structure with yarns made of continuous filaments induce a lower release of microfibres both to air and water, and that polyester/cotton blend fabrics release a massive quantity of microfibres, majorly of cotton.

Finally, in the last part of this thesis, mitigation strategies were demonstrated, based on the idea of developing a protective coating on the surface of the fabric, that could protect it from chemical and mechanical stresses inside a washing machine, mitigating in this way the overall microplastic release to wastewater. For this purpose, finishing treatments of polyamide fabrics were developed by using natural or biodegradable finishing materials instead of conventional synthetic ones, in order to preserve ecosustainability, avoiding the introduction of other polluting agents that could jeopardize the final mitigation purpose. The first treatment is based on the chemical grafting of a natural polysaccharide, pectin, on the surface of polyamide 6.6 fabrics. Pectin, a waste product of the food industry, was first chemically modified by reaction with a monomer, glycidyl glycidyl methacrylate (GMA), in order to reduce its solubility in water, and then the new product Pectin-GMA was grafted on the surface of polyamide fabric. The ratios and concentrations of pectin and GMA were optimized to realise a thin continuous coating that preserve the hand of the fabric. Other possible effects on the treatment of the textile characteristics of the fabric were investigated by scanning electron microscopy and tearing strength tests. Washing tests of the treated fabrics revealed how the treatment can reduce by almost 90% the number of microplastics released by untreated polyamide. The finishing treatment developed on polyamide fabrics is compatible with common padding processes already used in textile industry, with the benefit of applying a natural material obtained from food waste. The second developed treatment applies a layer of two different biodegradable polymers, polylactic acid (PLA) or polybutylene succinate adipate (PBSA), on polyamide 6.6 fabrics, by using a non-conventional electrofluidodynamic (EFD) process. The EFD process was optimized to realize homogeneous coatings onto the polyamide fabrics. Morphological, thermal and surface properties of fabrics coated with PLA or PBSA were investigated, finding that both PLA and PBSA based coatings did not affect the hand and the wettability of polyamide 6.6. Washing tests performed on treated and untreated fabrics, showed that, also in this case, the treatments were able to reduce dramatically, of almost 90%, the amount of microfibres released by polyamide fabrics. Both types of finishing treatment developed showed very promising results, paving the way to a novel approach in the mitigation of microplastic pollution caused by synthetic textiles.

Appendix 1 – Papers published on ISI Journals

- Evaluation of microplastic release caused by textile washing processes of synthetic fabrics.
  F. De Falco, M. P. Gullo, G. Gentile, E. Di Pace, M. Cocca L. Gelabert, M. Brouta-Agnésa, A. Rovira, R. Escudero, R. Villalba, R. Mossotti, A. Montarsolo, S. Gavignano, C. Tonin, M. Avella.
  Environmental Pollution 236, 916-925 (2018).
  DOI: 10.1016/j.envpol.2017.10.057

- Pectin based finishing to mitigate the impact of microplastics released by polyamide fabrics.
  F. De Falco, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Avella, M. Cocca. Carbohydrate Polymers 198, 175-180 (2018)
  DOI: 10.1016/j.carbpol.2018.06.062

- Quantification of microfibres released during washing of synthetic clothes in real conditions and at lab scale.
  F. De Falco, G. Gentile, E. Di Pace, M. Avella, M. Cocca.
  The European Physical Journal Plus 133: 257 (2018).
  DOI: 10.1140/epjp/i2018-12123-x

Appendix 2 – Papers published in Conference Proceedings

- Microplastic pollution: impact and mitigation strategies
  M. Cocca, **F. De Falco**, G. Gentile, R. Avolio, M. E. Errico, V. Ambrogi, E. Di Pace, M. Avella
  Atti del XXIII Convegno Nazionale AIM, 9-12 settembre 2018 Catania, pp 128-129.
  ISBN: 978-88-7751-449-3

- Innovative Treatment Of Polyamide 6.6 Fabric To Mitigate Microplastic Release During Washing
  F. De Falco, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Cocca, M. Avella
  Atti del XXIII Convegno Nazionale AIM, 9-12 settembre 2018 Catania, pp 37-38.
  ISBN: 978-88-7751-449-3

- Eco-sustainable textile treatments to mitigate the release of microplastics in the wastewater of laundry processes
  F. De Falco, V. Guarino, G. Gentile, R. Avolio, M. E. Errico, V. Ambrogi, E. Di Pace, M. Avella, M. Cocca
  Proceedings of the fifth International conference on small and decentralized water and wastewater treatments plants (SWAT 2018), pp 375-377.
  ISBN: 978-960-243-710-0

- Degradation of Biodegradable Plastic Buried in Sand.

  M. Cocca, **F. De Falco**, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, M. Avella.

  Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea. Springer Water. Springer, Cham (2018)

  DOI: 10.1007/978-3-319-71279-6_28

  Online ISBN: 978-3-319-71279-6

  Print ISBN: 978-3-319-71278-9

- Eco-Sustainable Finishing Treatment of Polyamide Fabrics to Reduce the Release of Microplastics During Washing Processes.

  F. De Falco, M. P. Gullo, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Avella, M. Cocca

  Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea. Springer Water. Springer, Cham (2018)

  DOI: 10.1007/978-3-319-71279-6_30

  Online ISBN: 978-3-319-71279-6

  Print ISBN: 978-3-319-71278-9

- Microplastics from synthetic clothes: environmental impact and mitigation strategies

  M. Cocca, **F. De Falco**, M. P. Gullo, G. Gentile, E. Di Pace, L. Gelabert, M. Brouta-Agnésa, A. Rovira, R. Escudero, R. Villalba, R. Mossotti, A. Montarsolo, S. Gavignano, C. Tonin, M. Avella

  Proceedings of the 15th International Conference on Environmental Science and Technology, 31 August – 2 September 2017, Athens, Greece.

  ISBN: 978-960-7475-53-4

- Eco-sustainable Functionalization of Polyamide Fabrics to Mitigate Microplastic Release
  F. De Falco, M. P. Gullo, R. Avolio, M. E. Errico, E. Di Pace, G. Gentile, V. Ambrogi, M. Cocca, M. Avella.
  Proceedings of the 15th International Conference on Environmental Science and Technology, 31 August – 2 September 2017, Athens, Greece.
  ISBN: 978-960-7475-53-4

- Mitigation of microplastics release caused by textile washing processes: Life Mermaid Project
  S. Gavignano, A. Montarsolo, R. Mossotti, M. avella, M. Cocca, E. di Pace, **F. De Falco**, G. Gentile, M. P. Gullo, M. Brouta-Agnésa, R. Escudero, J. Lancharro, R. Nicolau, M. Westerbos, J. Dagevos.
  Proceedings 7th European Weathering Symposium on Natural and Artificial Ageing of Polymers, Napoli 16-19 settembre 2015.
  ISBN: 978-398-1628-66-1

Appendix 3 – Contributions at International Conferences

- Quantitative approaches to investigate the release of microfibres from washing processes of synthetic clothes
  F. De Falco, G. Gentile, E. Di Pace, M. Cocca, M. Avella
  Microplastics2018, 28-31 ottobre 2018 Ascona (Svizzera).
  Oral presentation

- Innovative Treatment Of Polyamide 6.6 Fabric To Mitigate Microplastic Release During Washing
  F. De Falco, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Cocca, M. Avella
  XXIII Convegno Nazionale AIM, 9-12 settembre 2018 Catania.
  Oral presentation

- Eco-sustainable textile treatments to mitigate the release of microplastics in the wastewater of laundry processes
  F. De Falco, V. Guarino, G. Gentile, R. Avolio, M. E. Errico, V. Ambrogi, E. Di Pace, M. Avella, M. Cocca
  5th SWAT International conference on small and decentralized water and wastewater treatments plants, Thessaloniki, 26-29 agosto 2018.
  Poster presentation

- Microplastics released from washings of synthetic fabrics: quantification and influencing parameters

M. Cocca, **F. De Falco**, G. Gentile, E. Di Pace, M. Avella
9th International Conference Times of Polymers (TOP) & Composites, Ischia, 17-21 giugno 2018
Poster presentation

- Biodegradable coatings of synthetic fabrics to retain microplastic release
  F. De Falco, M. Cocca, V. Guarino, G. Gentile, V. Ambrogi, L. Ambrosio, M. Avella
  International Conference on Microplastic Pollution in the Mediterranean Sea mMED2017, Capri 26-29 September 2017
  Poster presentation

- Eco-sustainable finishing treatment of polyamide fabrics to reduce the release of microplastics during washing processes
  F. De Falco, M. P. Gullo, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Avella, M. Cocca
  International Conference on Microplastic Pollution in the Mediterranean Sea mMED2017, Capri 26-29 September 2017
  Poster presentation

- Eco-sustainable functionalization of polyamide fabrics to mitigate microplastic release
  F. De Falco, M. P. Gullo, R. Avolio, M. E. Errico, E. Di Pace, G. Gentile, V. Ambrogi, M. Cocca, M. Avella.
  15th International Conference of Environmental Science and technology CEST 2017, Rhodes 31 August - 2 September 2017
  Poster presentation

- Microplastics from synthetic clothes: environmental impact and mitigation strategies

M. Cocca, **F. De Falco**, M. P. Gullo, G. Gentile, E. Di Pace, L. Gelabert, M. Brouta-Agnésa, A. Rovira, R. Escudero, R. Villalba, R. Mossotti, A. Montarsolo, S. Gavignano, C. Tonin, M. Avella 15th International Conference of Environmental Science and technology CEST 2017, Rhodes 31 August - 2 September 2017
Oral presentation

- Innovative functionalization of polyamide fabrics with a natural biopolymer
  F. De Falco, M. P. Gullo, R. Avolio, M. E. Errico, E. Di Pace, G. Gentile, V. Ambrogi, M. Cocca, M. Avella
  Materials.it 2016, Catania, 12-16 dicembre 2016
  Poster presentation

- Marine microplastics pollution from synthetic clothes: quantitative analysis and mitigation measures
  F. De Falco, M. Cocca, M.P. Gullo, E. Di Pace, G. Gentile, S. Gavignano, A. Montarsolo, R. Mossotti, M. Avella
  Materials.it 2016, Catania, 12-16 dicembre 2016
  Oral presentation

- Assessment and mitigation of the environmental impact of microplastics caused by textile washing processes
  De Falco F., M. Cocca, E. Di Pace, S. Gavignano, G. Gentile, M.P. Gullo, A. Montarsolo, R. Mossotti, M. Avella.
  The 9th International Conference on Modification, Degradation and Stabilization of Polymers, Krakow, Poland, 4-8 settembre 2016.
  Oral presentation

Appendix 4 – Awards and recognition

- The poster presentation "*Eco-sustainable Functionalization of Polyamide Fabrics to Mitigate Microplastic Release*, **F. De Falco**, M. P. Gullo, R. Avolio, M. E. Errico, E. Di Pace, G. Gentile, V. Ambrogi, M. Cocca, M. Avella" won the Best Poster Presentation Award at 15th International Conference of Environmental Science and technology CEST 2017.
- The article "*Pectin based finishing to mitigate the impact of microplastics released by polyamide fabrics*, **F. De Falco**, G. Gentile, R. Avolio, M. E. Errico, E. Di Pace, V. Ambrogi, M. Avella, M. Cocca. Carbohydrate Polymers 198, 175-180 (2018)" was selected as Research Hihlight by the journal Nature Sustainability in August 2018.

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