



Pectin based finishing to mitigate the impact of microplastics released by polyamide fabrics

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ABSTRACT

Washing processes of synthetic clothes have been identified as the main source of microplastic pollution in marine ecosystems. Textile microfibres have been found in marine sediments and organisms, posing a real threat for the environment. The development of mitigation approaches is strongly needed to prevent the impact of microplastics. In this work, an innovative finishing treatment of polyamide fabrics is proposed to mitigate the microplastic impact, by preventing the damage of fabrics during washings. The treatment is based on the use of pectin, a natural polysaccharide present in the cell walls of plants. To functionalize the fabric, pectin was firstly modified with glycidyl methacrylate (GMA) and then grafted on polyamide. Washing tests of treated fabrics showed the effectiveness of the treatment in reducing of about 90% the amount of microfibres released by untreated fabrics. Post-wash analysis of the treated fabrics revealed a promising resistance to the washing process.

1. Introduction

In the last years, a source of microplastic pollution in marine environment has been identified in the washing processes of synthetic clothes (Browne et al., 2011; Cesa, Turra, & Baruque-Ramos, 2017; Thompson et al., 2004). During washing, fabrics undergo mechanical and chemical stresses that damage the yarns, leading to the release of “microplastics”, plastic fragments smaller than 5 mm (Arthur, Baker, & Bamford, 2009; Costa et al., 2010), that remain in the wastewater reaching marine ecosystems (Magnusson & Wahlberg, 2014; Mintenig, Int-Veen, Löder, Primpke, & Gerdt, 2017; Sutton et al., 2016; Talvitie et al., 2015; Ziajahromi, Neale, Rintoul, & Leusch, 2017). A recent study (Boucher & Friot, 2017) has estimated that the release of microfibres from washing 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. Several scientific papers have pointed out the interaction of microplastics with marine fauna (Wright, Thompson, & Galloway, 2013), such as ingestion by plankton (Cole et al., 2013), adsorption and further transfer of organic pollutants to marine organisms (Bakir, Rowland, & Thompson, 2014; Rochman, Hoh, Kurobe, & Teh, 2013). In particular, studies on microplastics from synthetic textiles have revealed that polyethylene terephthalate (PET) microfibres have deadly effects on the zooplankton crustacean *Daphnia*

magna (Jemec, Horvat, Kunej, Bele, & Kržan, 2016), and that microfibres have been found in fish and shellfish on sale for human consumption (Rochman et al., 2015). These findings put a question mark over the possible implications these pollutants may have on human health, urging immediate action to prevent the increase of their concentration in marine ecosystems.

In this work, an innovative finishing treatment was developed with the aim to create a protective coating on the surface of synthetic fabrics, which reduces the amount of microfibres shed during a washing process and thus mitigates the environmental impact of microplastics. The key-factor of such treatment is its eco sustainability as the process avoids the introduction of other polluting agents that could jeopardize the final mitigation purpose. In fact, the functionalization treatment 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 (Voragen, Coenen, Verhoef, & Schols, 2009). 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 (Voragen et al., 2009). The pectin heterogeneous and complex chemical structure is rich of ester, carboxyl and hydroxyl

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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 (Nešić et al., 2017). A possible solution to reduce the high solubility of polysaccharides is to mask its polar groups, such as carboxyl and hydroxyl, through their conversion into ester units (Maiores, Reis, Muniz, & Cavalcanti, 2008).

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 cross-linking reaction. The effectiveness of the treatment in reducing the microfibre release from the synthetic fabric was tested and confirmed through washing trials simulations at laboratory scale, followed by the analysis of the number and size of microplastics released.

2. Experimental

2.1. Materials

The raw 100% polyamide-6,6 woven fabric (PA, code 361, weight 130 g/m²) was purchased by Ausilari Tessili S.r.l. (Italy). Citrus Pectin Classic CU 701 (PEC) 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 (Na₂S₂O₈, ≥98%) were acquired from Sigma–Aldrich. Distilled water was used for the functionalization of polyamide fabrics.

2.2. 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 h in nitrogen atmosphere at 50 °C. For PEC:GMA molar ratio and pectin concentration in water (wt/v%), refer to Table 1.

2.3. Grafting of PEC-GMA on PA

1 g of polyamide fabric (PA), cut in square of about 9 cm × 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 h 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 h 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 h.

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

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

where W₀ and W_g are the weights of the fabric sample before and after

Table 1
PEC:GMA molar ratios and concentrations of pectin in water.

Sample	PEC:GMA (moles)	PEC/H ₂ O 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

grafting, respectively.

2.4. 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 ¹³C 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 ¹³C π/2 pulse width of 3.6 μs and a repetition time of 40 s.

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.

2.5. Washing tests

Wash trials were performed in Linitest apparatus (URAI S.p.A., Assago, Italy), a laboratory simulator of real washing machines, 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 × 9 cm², 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 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 °C for 30 min.

2.6. 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

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