Eco-sustainable Functionalization of Polyamide Fabrics to Mitigate Microplastic Release

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Abstract The global textile production is mainly based on synthetic fibres like polyester, polyamide, polyacrylic and polypropylene. Recently, the washing process of synthetic clothes has been identified as a source of microplastics, plastic fragments smaller than 5 mm, that pollute marine ecosystems. In fact, the mechanical stresses and the friction of the detergent cause the detachment of microfibres from the yarns. In such scenario, the aim of this work is to develop functional finishing treatments that can protect the fabric during the washing, preventing in this way the release of microplastics. As alternative to synthetic polymers, pectin, a natural polysaccharide, was used to create a coating on polyamide fabrics. Pectin was chemically modified by the reaction with glycidyl methacrylate (GMA), whose vinyl groups were used to graft pectin on the surface of the fabric. A key point was the realization of a homogeneous coating, that did not modify the hand of the textile. For this aim, different ratios of pectin:GMA were tested and the treated fabrics were analysed by scanning electron microscopy (SEM), solid state nuclear magnetic resonance spectroscopy (NMR) and Attenuated Total Reflectance (ATR) Fourier Transform InfraRed (FT-IR) spectroscopy, in order to evaluate the effectiveness of the finishing treatments.

Keywords: microplastic, functionalization, finishing treatment, polyamide, pectin

1. Introduction

In the last years, a growing concern has been arising about the contamination of marine ecosystems by a new kind of pollutants named "microplastics", defined as plastic fragments smaller than 5 mm. Their impact on the environment is unpredictable and quite dangerous since they can adsorb organic pollutants and be ingested by marine organisms, potentially reaching the human food chain. Different sources of microplastics have been identified by several studies: deterioration of scraps of large dimensions, abrasives, cosmetics and lately, the washing processes of synthetic clothes. Due to the mechanical and chemical stresses that fabrics undergo during a washing process in a laundry machine, microfibres detach from the yarn and, through the wastewater, end up in marine environment. Sampling of marine sediments showed that polyester, acrylic, polypropylene, polyethylene, and polyamide fibres contaminate shores on a global-scale.

Proposed solutions to mitigate the release of microplastics from synthetic clothes, involve the production of special filters for washing machines or of advanced wastewater treatment plants. However, a different approach could be the development of functional finishing treatments of fabrics, which can protect clothes during washing processes, reducing the amount of microfibres released. Of course, from an environmentally friendly point of view, the materials selected for these treatments should also be biocompatible and not harmful to the environment. For such reason, natural polymers represent an interesting alternative to traditional chemical finishes. In particular, this work focuses on the use of pectin, a natural polysaccharide with a structure similar to other polymers, abundantly used for natural and synthetic textile treatments, such as tragacanth, chitosan, and alginate.

Pectin is a mainly linear polysaccharide, whose main chemical unit is D-galacturonic acid monomer, occasionally alternated to L-rhaminose units or other monomers. It is mainly found in cell walls of several vegetal species, where it is responsible for maintaining plant structure and support. Commercially available pectin is mainly extracted from suitable agro-by-products like citrus peel and apple pomace, and used in the food industry as natural ingredient for its gelling, thickening, and stabilizing properties. However, the greatest problem for the use of pectin in such application, is related to its solubility in aqueous medium, which would cause the loss of the functional treatment during the washing of garments.

Therefore, the aim of this study was to develop a pectin based finishing treatment of polyamide fabrics, through chemical modification of pectin by reaction with glycidyl methacrylate (GMA). Such monomer introduced vinyl groups in the polysaccharide structure, which were exploited to graft the pectin on the surface of polyamide fabric by crosslinking reaction.

2. Materials and methods

a. Finishing treatment of polyamide fabric

The synthetic route used to functionalize polyamide 6.6 fabric, was a two steps procedure.

During the first step, pectin-GMA was synthetized by stirring pectin and GMA for 24 hours under nitrogen atmosphere at 50°C, in different ratios.

In the second step, pectin-GMA was grafted on polyamide; the fabric was dipped in the pectin-GMA solution in presence of sodium persulfate as catalyst.

2.2 Characterization techniques

The pectin-GMA-polyamide textiles were characterized by using a field-emission scanning electron microscope (SEM), Attenuated Total Reflectance (ATR) Fourier Transform InfraRed (FT-IR) spectroscopy, Solid-state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy; Thermogravimetric Analysis (TGA).

3. Results

With the aim to graft pectin on polyamide 6.6, pectin was modified with GMA. The epoxide group of GMA reacted with a carboxyl group of the pectin monomer, through a nucleophilic substitution reaction. In this way, pectin-GMA had a reduced water solubility with respect to neat pectin. Moreover, the vinyl units of the pectin-GMA structure represented the attaching sites for polyamide. The grafting reaction of pectin-GMA on the textile surface occurred through a free radical polymerization method, using sodium persulfate as common redox initiator system.

The SEM investigation showed good perspectives for pectin application in the textile finishing field, since it displayed the efficacy of the coating treatment (**Figure 1**). The ATR FT-IR analysis corroborated the presence of the pectin-GMA coating on the polyamide fabric. In fact, the ATR FT-IR spectrum of the treated fabric showed the presence of absorbance bands due to the vibrations of functional groups of pectin-GMA.

A similar analysis was carried out on the same samples, using solid state NMR spectroscopy. The treated polyamide fabrics presented the signals corresponded to the carbons of the main chain of pectin.

Finally, thermal stability of the polyamide textiles treated with pectin-GMA, was evaluated by means of TGA in comparison with neat polyamide. The degradation of neat and treated polyamide fabrics started at around 380 °C and 340 °C respectively. Despite the closeness of these two temperatures, the kinetic of the degradation process was different since it occurred faster for the treated fabric due to the presence of the grafted Pectin-GMA.

4. Conclusions

The results herein reported highlighted good perspectives for pectin application in textile finishing. Pectin was successfully modified by reaction with GMA and a homogenous coating was obtained on polyamide fabrics, as confirmed by several characterization techniques.

Future steps will involve washing tests of the treated fabrics, in order to evaluate the amount of microfibres released.

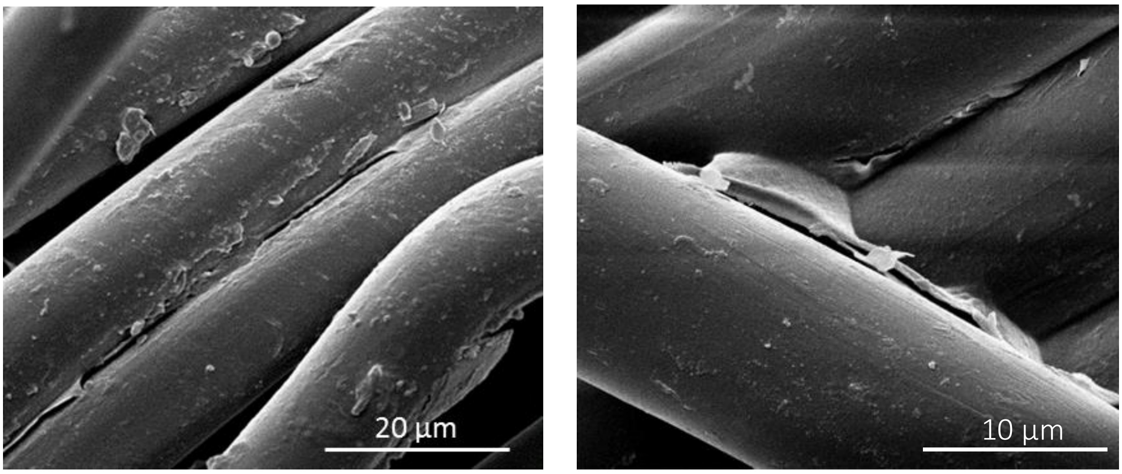

Figure 1. SEM micrographs of polyamide treated with pectin-GMA

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