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# An innovative method to functionalize textiles for the remediation of polluted media

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ABSTRACT

A new, efficient and fast process was developed to coat poly(ethylene terephthalate) (PET) fabrics with acrylic acid (AA) and this novel eco-friendly material was designed to be used as a filtration medium for complexing heavy metals from aqueous media. PET is impregnated with acrylic acid, and directly polymerized using a KrF excimer laser. The conditions of irradiation were optimized using the experimental design technique: a 40 mm × 3.5 mm surface was irradiated per pulse, and 24 mJ/cm$^2$ and 700 pulses were necessary to obtain a good coating without degrading the textile structure. For industrial purpose, these conditions were extended to treat larger surfaces (40 mm × 11.5 mm pulse) using a fluence of 24 mJ/cm$^2$ and 700 pulses. Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) were carried out to characterize the functionalized surfaces. A thick coating, resistant to low-temperature-washing was obtained. Finally, the efficiency of this coated textile was evaluated with copper sulfate solutions: 0.131 mg copper was trapped per cm$^2$ of PET, which is a promising result.



## 1. Introduction

Many harmful components contaminate the environment due to human activity. Indeed, the high concentration of heavy metals such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn in a geographic area leads to famous catastrophic events [1,2]. One potential solution to this problem would consist in the filtration of wastewater containing these hazardous components using functionalized geotextiles. Geotextiles are well-known for their permeable structures providing filtration and draining properties. The grafting of molecules, such as acrylic acid [3,4] or maleic anhydride [5] at the surface of a geotextile leads to a material possessing interesting depolluting properties towards heavy metals. Acrylic acid grafting has already been realized in our laboratory on polypropylene nonwoven [6] and polyethylene terephthalate [7] using a low pressure cold plasma process. However, this process requires many steps: (1) activation of the textile sample by low pressure argon cold plasma process; (2) immersion in an acrylic acid solution; and (3) graft-polymerization of the acrylic acid by low pressure cold plasma again. Moreover, this method is difficult to transfer to industrial scale due to the grafting conditions at low pressure.

The novel idea in this paper is to use the high potential of UV laser to quickly modify PET surfaces. Indeed, the UV excimer laser is one of the most precise industrial processing tools and has many applications like eye surgery and semiconductor lithography [8]. Moreover, modifications induced on PET surfaces by UV lasers have been extensively studied [9] and major changes such as: surface amorphization [10]; roughness evolution [11–13]; chemical modifications [14–16]; and increased wettability [17] are well-known consequences of the laser irradiation. Studies show that Laser Induced Periodic Surface Structures (LIPSSs) are formed on fibers using a 248 nm excimer laser with a fluence below the ablation threshold of the material [13]. LIPSSs depend on the irradiation conditions as well as on the material properties [18]. It is mostly accepted that these LIPSSs are due to interference phenomena between the incident pulse and a secondary surface electromagnetic wave generated by scattering of laser radiation [19,20]. Another study reveals that, in the case of metallic surface irradiated with ultrafast laser-induced ripples, the Surface Plasmon Polaritons (SPPs) are involved in the LIPSSs [18]. Laser treatment on PET leads, for example, to the enhancement of cell proliferation

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and cell adhesion, improving the biocompatibility of an implant [21]. Moreover, it was shown that photons allow the grafting of some organic molecules, like the 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone onto a poly(ethylene glycol)-based matrix [22]. Thus, effects of excimer laser treatment on PET fabrics are known, but the use of such a technique for the grafting of molecules on PET knitted fabrics is emerging.

Praschak et al. showed that radicals can be generated on PET surfaces thanks to an irradiation with a KrCl excimer laser [23]. These radicals play an important role in the *in situ* grafting with air molecules. Thus, in order to avoid this phenomenon, the PET sample must be in close contact with the molecule to graft. For example, alginic acid in aqueous solution was successfully immobilized by chemical bonds on a polyurethane film previously irradiated with a XeCl excimer laser [24].

Based on this literature review, the goal of this study is to functionalize a geotextile with a specific precursor, using a quick and simple process easy to upscale, *i.e.* excimer laser treatment, in order to decontaminate fluvial or marine sediments. In this paper, an innovative method was developed using KrF excimer irradiation in ambient air conditions to graft acrylic acid onto PET knitted fabrics (Fig. 1).

The acrylic acid coating can be carried out directly at atmospheric pressure without any activation step, to give the so-called PET-c-AA in abbreviated form. In this article, the experimental design technique is used to determine the irradiation conditions allowing obtaining the best acrylic acid coating: the highest amount of acrylic acid while keeping a regular coating. The optimized PET-c-AA will be characterized using various techniques (SEM and XPS) and the efficiency of the coated geotextile will be evaluated using artificially polluted solutions containing copper sulfate.

## 2. Experimental

### 2.1. Experimental materials

Polyethylene terephthalate E1931 (150 g/m$^2$) was provided by DYLCO, France. Acrylic acid (purity 99.5%) was purchased from Acros. Sulfuric acid (purity of 95%) and hydrochloric acid (purity of 37%) were purchased from VWR. Coating experiments were carried out using a roll-padder (KMS Colortech Service Co., Ltd), a KrF excimer laser (Lambda Physik, model Compex 205), and an optic bench possessing a rectangular aperture which allows to obtain a uniform rectangular beam, a set of a convergent cylindrical lens ($f_1$ = 300 mm) and a divergent spherical lens ($f_2$ = −100 mm) allowing to adapt the size of the beam according to the sample. The sample is maintained on a mobile motorized support perpendicular to the beam whose displacement speed can be adjusted to control the irradiation conditions. For the copper sorption tests, a solution was prepared by diluting 158 mL of $CuSO_4$ at 0.1 M (purchased from Sigma–Aldrich) in distilled water (conductivity 0.2 μS/cm) in a 1 L-volumetric flask: the obtained solution contains 1000 mg/L Cu and has a pH of 4.3. Analyses by flame atomic absorption were carried out using a Thermo Solaar S4 AA Spectrometer, Thermo S Series, with a multi-elements combined coded hollow-cathode lamp for Cr–Cu–Mn–Ni, from Thermo Scientific.

### 2.2. Preparation of the samples

Squares (5 cm × 5 cm) were cut from PET. The samples were first washed in an ultrasonic bath for 1 h in ethanol and for 1 h in distilled water, and then dried under vacuum before use (at room temperature for 16 h). After washing and drying, the size of the sample was 4.5 cm × 4.5 cm.

### 2.3. Coating of acrylic acid by excimer laser treatment

The PET samples were first immersed and stirred in a solution containing 20% of acrylic acid in distilled water and then padded one time using a roll-padder at 0.2 MPa to impregnate the fibers and remove the excess solution. Then, the KrF excimer laser was used to irradiate 40 mm × 3.5 mm area of PET samples at a scanning speed of 0.05 mm/s. The PET samples were placed on a *X*–*Y* motorized table and the knitted fabrics were scanned by the laser beam. The irradiation was carried out with the experimental conditions given in Table 1. Finally, samples were washed in ultrasonic bath for 1 h with distilled water and then dried under vacuum. For this study, the varying parameters were the laser fluence and the number of pulses. The other parameters, *i.e.* frequency and the surface irradiated per pulse, remained unchanged.

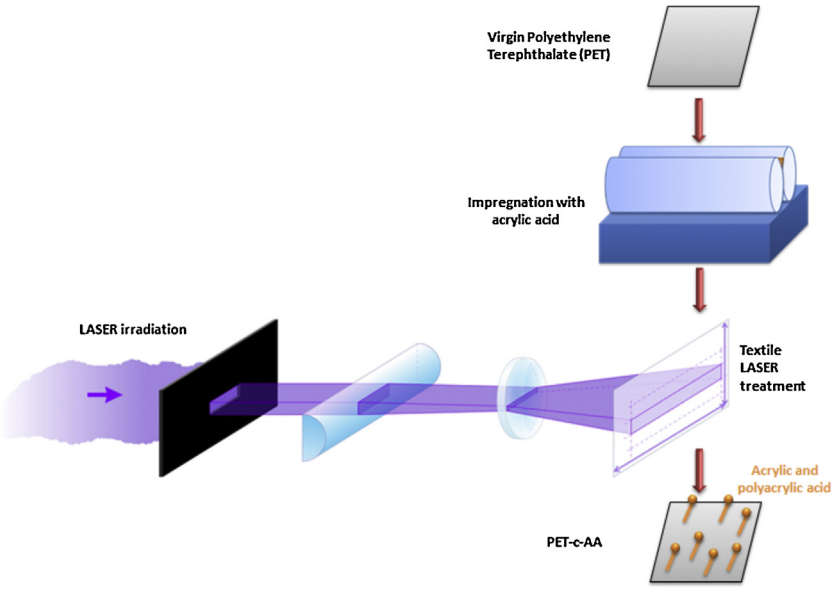


**Fig. 1.** Schematic illustration of the preparation of the PET-c-AA from virgin PET which was first impregnated with acrylic acid and then irradiated with a KrF laser. The size of the beam was adapted to the sample using an optical bench composed of a rectangular aperture, and a set of a convergent cylindrical lens ($f_1$ = 300 mm) and a divergent spherical lens ($f_2$ = −100 mm).