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UV irradiation-assisted grafting of poly(ethylene terephthalate) fabrics

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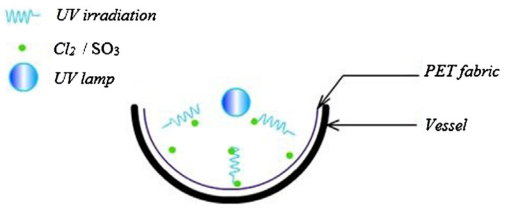
HIGHLIGHTS

- Efficient UV-assisted (254 nm) grafting of PET textile fabrics.
- UV-irradiation a stream of gaseous Cl_2 produces chlorinated PET surface.
- Easy handling, low-cost, solvent-free and continuous process UV irradiation.
- Maintaining of PET fabrics bulk properties while drastically changing their surface.
- Improved dying (with cationic dyes) of the modified surface of PET fabrics.

GRAPHICAL ABSTRACT



UV treatment of PET

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ABSTRACT

This paper reports the functionalisation of a poly(ethylene terephthalate) (PET) surface using an irradiation method under a stream of reactive gas (chlorine). The polyester textile fabric was directly exposed to UVC irradiation (wavelength of approximately 254 nm) under a continuous flow of gaseous chlorine in a solvent-free process. Different amounts of chlorine atoms were fixed to the surface of the fabric based on the experimental conditions. The amount of chlorine on the treated fabric was as much as 4.6% (w/w, oven dried material). First, the modified and virgin fabrics were thoroughly extracted to remove the physically adsorbed molecules. Then, these fabrics were characterised via several techniques including SEM, FTIR-ATR, DSC and XPS. The grafting was confirmed by analysing the fabric surface using MEB (EDS) and XPS (the presence of chlorine atoms). However, the bulk properties remained unchanged. The modified surface was more easily dyed with a cationic dye.

1. Introduction

One of the most commonly used polymers for textile applications is poly(ethylene terephthalate) (PET). With more than 18.2 million tonnes in 2010 [1], the use of PET represents 72% of the worldwide consumption of synthetic fibres. The polyester fibres have interesting physical, mechanical and chemical properties [2]. Therefore, PET is used in several applications, such as durable press, easy-care and wash-and-wear garments. However, the major problems associated with PET are related to its hydrophobic character, low moisture regain and lack of softness [3–6].

Copolymerisation or grafting techniques can improve the performance of PET. In fact, copolymerisation has been the preferred method [7–9] despite difficulty controlling the copolymer arrangement. Chemical modification using UV irradiation is an easy process that can also be used as a suitable alternative due to its low cost and efficiency for the modification and control of new PET derivatives [4,10–13]. UV irradiation has been previously applied to PET surfaces. In 1950, Oster and Shibata [12,14] published the first report on photografting polymerisation using UV. Since that time, more

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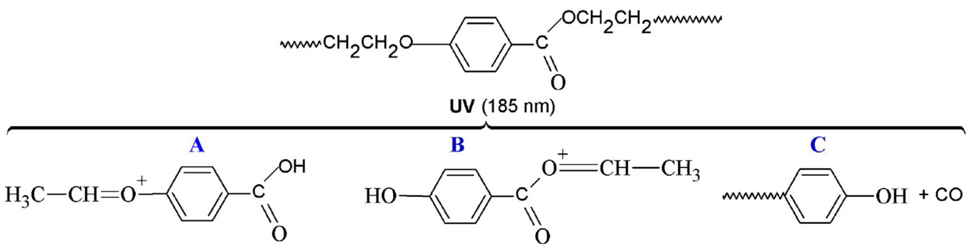

Fig. 1. Effect of UV irradiation (185 nm) on the PET surface [18].

research studies and applications using UV irradiation have been reported [12,13] and have focused on confirming the surface photografting phenomenon [12,13]. Then, Oster and Shibata published the results from studies that were aimed at improving surface modification in the liquid and vapour phases.

For some substrates containing carbonyl or ester groups, such as PET, photografting polymerisation can occur smoothly even without a photoinitiator, as reported, for example, by Denga et al. [12]. Shokrieh and Bayat [15] proved that the stress/strain properties of PET fabrics exposed to 800 W m^{-2} UV lights for 40 h did not decrease. However, after 100 h of UV irradiation with a lamp intensity of 800 W m^{-2}, the PET fabric lost 34.8% of its tensile strength and 15.2% of its failure strain [15]. In the same context, Day and Wiles [16] showed that the effect of irradiation by UVC light on the PET resulted in a slight discolouration of the polyester and the possibility of a photo-oxidation reaction (hydroperoxide formation) based on the irradiation atmosphere (i.e., in vacuum or in the presence of nitrogen, under oxidising or non-oxidising conditions). UV irradiation of PET can eliminate CO and the production of carboxylic acid (Norrish type I). Using wavelengths less than 185 nm, decarbonylation and the formation of an acid group (Fig. 1) can occur (Norrish type II) [17].

The treatment of alkane groups with chlorine as a reagent or in the presence of visible or UV light resulted in chlorination. These reactions require a radical chain initiator, light, and higher temperatures. The reaction can also be applied to alkyl chains containing many functional groups [18].

To the best of our knowledge, several studies that involve UV irradiation in the modification of PET without the chlorination step are available in the literature [11–13,15,16,19]. The new technique proposed in this work employs UV radiation to activate polyester materials. The UV lamp emits intense and nearly monochromatic light to functionalise the PET surface prior to attachment of the chlorine compound. In addition, several techniques were employed to characterise the untreated and modified PET fabric and to demonstrate the modification ability.

2. Experimental

2.1. Materials

- Scoured PET jersey knitted fabric with weight of 140 g m^{-2} was purchased from SOBOLUX Company in Ksar Hellal, Tunisia. Prior to use, the fabric was washed in a solution containing 2 g L^{-1} of a non-ionic detergent at 60 °C for 1 h to remove the impurities and waxes from the fabric. Then, the clean fabric was dried overnight at 40 °C.
- The elemental chlorine used for chlorination was extracted from 12% sodium hypochlorite. The preparation of Cl_2 was achieved by adding hydrogen chloride to a solution of sodium hypochlorite.
- A Philips UVC lamp (G13 TL 25 W) with a high voltage power supply (220 V, 50 Hz) was used to functionalise the PET fabric.

2.2. Chlorination process of PET

UVC irradiation was employed to activate the polyester fabric under a stream of gaseous Cl_2. As shown in Fig. 2, a flow of air and Cl_2 cross over the vessel between the UVC lamp and fabric, as we previously reported [20]. The UVC lamp emits intense and nearly monochromatic light (254 nm) to functionalise the PET surface.

The UVC lamp used in this work emits energy of 512 KJ mol^{-1} per photon, which is sufficient to modify the PET surface [21]. Table 1 summarises the rupture energy of the chemical bonds present on PET macromolecules, and these results indicate that the chlorination reaction will most likely occur without damaging the PET macromolecular chains. Therefore, the UV irradiation treatment has been employed to modify the surface properties of several polymer surfaces without altering their bulk properties [11–13,21].

Several conditions were examined, as summarised in Table 2. After the chlorination step, the obtained samples were washed extensively with distilled water and an anti-chlorine bath to remove all of the residual chlorine. Finally, the prepared samples were dried for 48 h at room temperature. All of the prepared and modified fabrics were repeated at least five times.

2.3. Dyeing process

The dyeing was performed in a laboratory dyeing machine (Ahiba Datacolor International, USA). The fabrics were dyed at a liquor ratio of 40:1 using RED Maxilon GRL GR 200 (cationic dye, Fig. 3a). This chemical was purchased from Ciba. Fig. 3b shows the

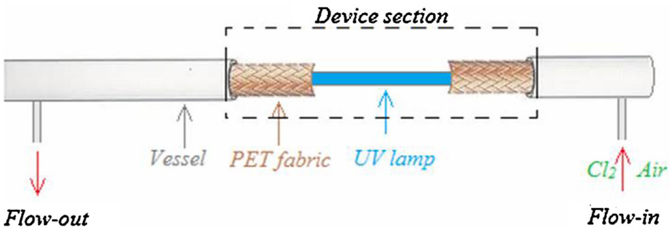

Fig. 2. UV treatment reactor.

Table 1
Rupture energies of the chemical links present in the PET macromolecules.

Chemical bond	C—H	H—C_6H_5	C—C	C—O	Cl—Cl
Fracture Energy (KJ mol^{-1})	337.2	461	607 ± 21	1076.5 ± 0.4	243

Table 2
Experimental conditions used to treat the PET specimens.

	Treatment time, h	Treatment atmosphere
PET-UV_{30}	30	Air
PET-UV-Cl_4	4	Cl_2
PET-UV-Cl_{12}	12	Cl_2
PET-UV-Cl_{30}	30	Cl_2