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Sulfonation of polyester fabrics by gaseous sulfur oxide activated by UV irradiation

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ABSTRACT

This paper describes an original technique aiming to improve the hydrophilic properties of polyester fibres. In this method, the sulfonation of the aromatic rings is carried out using gaseous sulfur trioxide activated by UV irradiations. Thus, exposing the polyester textile fabric to the UVC light (wavelength around 254 nm) under a stream of sulfur trioxide leads to the fixation of $-SO_3H$ groups. The amounts of the fixed sulfonate groups depended on the reaction conditions. Evidence of grafting deduced from the measurements of hygroscopic properties was carried out by contact angle measurement, moisture regain as well as by measuring the rate of retention. SEM and FT-IR analysis, DSC and DTA/TGA thermograms showed that no significant modifications have occurred in the bulk of the treated PET fabrics.

1. Introduction

One of the most used polymers for textile applications is originating from polyester family (polyethylene terephthalate). In fact, more than 30.3 million metric tons were consumed in 2008 with an increase of 22 million metric tons in the last 6 years [1,2]. In fact, these polyester fibres have interesting characteristics, namely: good mechanical behaviour and wrinkle recovery, low moisture uptake and release and good resistance to most of acid or basic agents, as well as towards organic solvents [2–4]. The surface of these fibres is generally hydrophobic because of their high crystalline degree and low content in polar groups [4,5].

However, in textile technology, the surface modification of these fibres is correlated to surface properties such as water repellence and adhesion [6–9]. Therefore, in the past years, there has been much interest in developing surface modification techniques to control the chemical and physical properties of polymer materials surfaces in order to develop new markets products.

Many researches have been undertaken to improve the wettability of polyester fibres with preserving their intrinsic bulk properties [6–9]. For this purpose, several surface modification methods are employed, namely: chemical, thermal, mechanical and electrical treatments [4]. Chemical methods include copolymerization approach (or segmented polymerization) and grafting-onto and grafting-from techniques [5,10–12]. The major drawback of the first chemical method is that it must be performed during the polymerization process itself. Therefore, it is difficult to control the co-polymer arrangement because of the reaction parameters complexity. The second method, presents some limitations such as heterogeneous surface grafting and irregular distribution of the grafted reactive sites. For the "grafting from" methods, a possible deterioration of the bulk properties of the materials could occur. Moreover, the modification effects could be effective only for a short period [12].

The UV photo-grafting treatment has been ahead recognition as a surface modification technique [4,13,14]. Compared with other methods, surface graft polymerizations induced by UV irradiation reveal some advantages: dry, low temperature, fast reaction rate, low cost of processing, simple equipment, and most importantly: the easy industrialization [4,12–14]. The distribution of the grafted chains is limited to a shallow region near to the surface without affecting the bulk of the fibres. Thus, surface photo-grafting polymerization offers the unique ability to tune the surface properties without damaging the bulk material properties. UV photochemical grafting is an easy process to modify and control new PET derivatives [12,14,15].

Usually, grafting reaction is carried out in aqueous or organic solvent, in the presence of the molecule to be grafted, under

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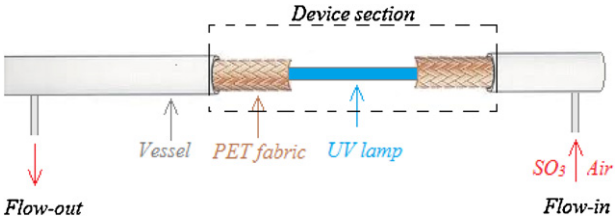

Fig. 1. UVC treatment device.

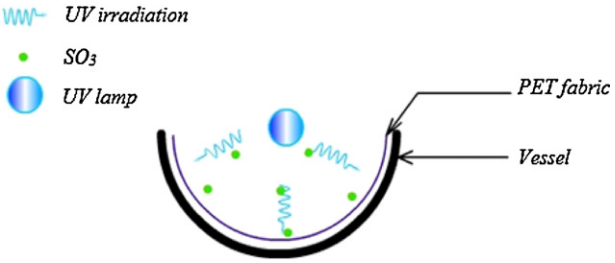

Fig. 2. The cross-section of UVC treatment device.

controlled temperature. In this work, the grafting reaction is applied in a solvent-free reaction system involving solid polyester (fibres and fabrics) and gaseous sulphur trioxide. Since the reaction media does not involve dissolution or even swelling conditions, our hypothesis is that the modification will be limited to the surface and consequently the mechanical properties of the polyester under investigation will be preserved.

The presence of the sulfonated groups in the treated fabrics is analysed by SEM, IR, DSC, ATD, and elemental analysis. Moreover, the effect of grafting sulfonic groups on the wettability of the surface of PET fabrics will be investigated. For this purpose, the moisture uptake, and the water retention of the sulfonated PET fabrics were established.

2. Materials and methods

2.1. Materials

Scoured PET plain weave fabric was purchased from SOBOLUX Company, Ksar Hellal – Tunisia. This material has the following characteristics: basis weight of 55 g m^{-2}, 42 ends per cm, 40 picks per cm. Before testing, the fabric was washed by a solution containing 2 g L^{-1} non-ionic detergents at 60 °C for 1 h, in order to remove the impurities from the fabrics. The sulphur trioxide used for sulfonation was extracted from oleum (sulphuric acid containing 20% of fuming SO_3 from Sigma–Aldrich). The SO_3 gaseous molecules were injected into the UVC treatment reactor by bubbling the oleum solution with a stream of air. The Philips UVC lamp (G13 TL 25W) was used to functionalize the PET fabric with high voltage power supply (220 V, 50 Hz).

2.2. Sulfonation technique

The new technique proposed in this work is presented in Figs. 1 and 2. The air flow containing fuming SO_3 molecules is injected into the vessel between which is composed of an UVC lamp and the fabric to be treated. The UVC lamp emits intense and nearly monochromatic light (254 nm). In fact, the UVC lamp emits 512 kJ mol^{-1} per photon, which allows the PET fibres functionalization without damaging their bulk properties [16]. In fact, such a technique has been previously applied to modify the polymer surfaces without affecting their bulk properties [12,14,17].

Sulfonic (SO_3H) groups can be introduced into aromatic compounds through an electrophilic substitution reaction (Fig. 3). Such a reaction is referred as sulfonation [18]. Sulphur trioxide reacts nearly instantaneously. Its kinetic rate is much faster than that observed in the reaction between sulphuric acid and benzene. The formation of sulfones is often side products. After modification, the obtained samples were washed several times using soxhlet extraction until reaching a neutral pH. All the prepared modified fabrics were prepared at least three times.

2.3. Characterization methods

Numerous methods were used in order to ascertain the sulfonation reaction. Several techniques were used to determine the properties of the treated fabrics.

2.3.1. Microscopy analysis

The SEM (scanning electron microscopy) technique with EDX analysis (FEI QUANTA 200) was used to analyse the surface of fabrics. The Energy Dispersive (ED) X-ray spectrometer was used to reveal the surface atomic composition.

2.3.2. Elementary analysis

The elemental composition of the unmodified and modified fabrics was performed by using the atomic elemental analysis at the "Service Central d'Analyse – Vernaison (CNRS)".

2.3.3. Spectroscopy and thermal analysis

The ATR-FTIR spectra were performed using a bio-Rad spectrophotometer with a resolution of 4 cm^{-1} and scanning a wavelength range from 500 to 4000 cm^{-1}. For each sample, the Diamond crystal of an attenuate total reflectance (ATR) apparatus was used. The torque applied was kept constant to ensure the same pressure on each sample. All spectra were recorded with a resolution of 4 cm^{-1} and using 16 scans. A minimum of 2 spectra were obtained on different area of the paper for each sample.

Differential Scanning Calorimetry (DSC) experiments were performed using a DSC Q100 device from TA instrument. For each prepared materials, about 10 mg of the sample were placed in a DSC cell and then heated from −90 to 350 °C, under a stream of nitrogen, a heating rate of 10 °C min^{-1}. These measurements were carried out at least in duplicate.

ATD/TGA Thermogravimetric Analysis measurements determine the amount and the rate of weight change of a material as a function of temperature, under a controlled atmosphere. The measurements were used primarily to determine the decomposition of materials and to predict their thermal stability at temperatures

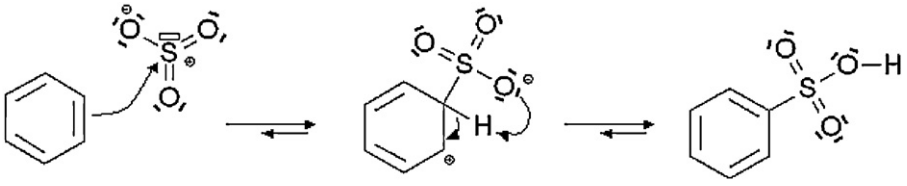

Fig. 3. Sulfonation of aromatic ring.