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Polyester hydrophobicity enhancement via UV-Ozone irradiation, chemical pre-treatment and fluorocarbon finishing combination

Jalal Rahmatinejad [a,*], Akbar Khoddami [a], Zahra Mazrouei-Sebdani [a], Ozan Avinc [b]

[a] Department of Textile Engineering, Isfahan University of Technology, Isfahan, 84156-8311, Iran
[b] Department of Textile Engineering, Pamukkale University, 20070, Denizli, Turkey

ABSTRACT

Enhancement in polyester substrates hydrophobicity was carried out by surface modification via chemical pre-treatment, UV-Ozone irradiation and fluorocarbon finishing combinations, which are referred to as CUF-process in this paper. Polyester fabrics were impregnated with different chemicals (Na_2CO_3, H_2O_2, H_2O_2/Na_2SiO_3, NaOH and CH_3NH_2) before UV-Ozone gases exposure to investigate the effects of these precursor surface pre-impregnation on the effectiveness of UV-Ozone modification and final superhydrophobicity formation. The changes in substrate properties were by measuring 3 M water repellency (Water/Alcohol Drop Test), water sliding angle (WSA), water contact angle (WCA), wash and abrasion fastness, air permeability, tensile strength and visual appearance of treated fiber surfaces via SEM. The results indicated the usefulness of UV-Ozone treatment for creating proper surface roughness to improve the hydrophobicity of polyester fabrics after fluorocarbon finishing, especially when the fabric was pre-treated with NaOH and H_2O_2 solutions. The lowest WSA value of 7.9° and the highest WCA of 142.2° were achieved on polyester fabrics using pre-treatment with 60 g/l NaOH and 42 ml/l H_2O_2 CUF-treatments. Also, the obtained highest water repellency levels and the best air permeability properties led to significant increase in the substrate hydrophobicity did not show any adverse effect on tensile properties and strength deterioration.

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1. Introduction

Many functions of the polymer materials are not related to the bulk of the materials, but rather to their topmost layer. Amongst a wide variety of surface treatment techniques, gaseous active species excited by gas molecules have been widely used to modify the surface wettability, adhesion, adsorption, chemical reactivity and sensitivity to light [1]. The simultaneous utilization of both short-wave-ultraviolet (UV) and ozone-gaseous is a new, dry, inexpensive and environmentally-friendly surface treatment technique which can be used for both cleaning and modifying purposes on the solids surfaces [2]. Good oxidative efficiency can be achieved by coupling both UV-radiation and ozone, leading to improved adhesion and high quality products [3–5]. In this case, UV light decomposes O_3 to form active species and then, the treatment proceeds [6]. One of the effects of surface modification by UV-Ozone

irradiation is surface etching with controllable roughening formation which could affect the surface wetting properties. Creating proper surface roughness is of the necessities for manipulating a superhydrophobic substrate.

Superhydrophobic surfaces possessing interesting characteristics such as easy dust-removal and self-cleaning properties have recently aroused growing interest. Many congenital examples of the superhydrophobic surfaces such as lotus-leaves can be found in the nature [7,8]. Superhydrophobic surfaces are generally characterized by water contact angle of more than 150° and/or water sliding angle of typically less than 15°, while it is widely accepted that the threshold is below 10° or 5° [9–12]. Two main requirements for manufacturing superhydrophobic surface should be considered: low surface energy and proper surface roughness [13]. The superhydrophobic surfaces have been created by tailoring the surface topography using various techniques such as anodic-oxidation, electro-deposition, laser-treatment [14], chemical-etching [15], nanoparticles [16–18], plasma-etching [19–21], chemical vapor deposition [22,23], atomic layer deposition [24], electro-spinning [25,26], sol–gel [27] and spray [28] processing in combination with the low surface energy materials like silanes and fluorochemicals. However, these meth-

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ods are not so feasible for textiles. Accordingly, it is crucial to find out new methods with possible application for this certain purpose. In most of these methods, inorganic nanoparticles have been deposited onto the substrates to enhance their surface roughness. However, these nanoparticles can be released from the surfaces of the fibers and entered to the human's skin, leading to serious health problems. On the other hand, green chemistry technology is of interest for many researchers, scientists and industries due to their harmless surface modification formation with the low energy consumption. Thus, applications of gaseous phases such as plasma, UV and ozone, as new technologies, can fulfill this goal. Use of the UV/Ozone treatment for the polymer surface modifications has been reported in few studies [6] although this treatment is applicable on the three-dimensional substrates capable of generating surface patterns by area-selective irradiation, etc. [29]. Therefore, the ultimate purpose of this study is to create the superhydrophobic polyester fabric via the surface roughening effect of the dried UV/Ozone gas to achieve proper surface roughness and a layer of fluorocarbon to attain low surface energy. Prior to UV/Ozone gases exposure, the polyester fabrics were pre-treated with different chemicals in an attempt to investigate their effects on the etching effect of the UV/Ozone irradiation on the polyester substrate. Accordingly, repellent and physical properties were investigated to examine the surface characteristics of the finished polyester fabrics.

2. Experimental

2.1. Materials

Plain weave polyester fabric ($155 \, g/m^2$) derived from 100% polyethylene terephthalate (PET) fiber was used as a substrate. The selected fluorocarbon derivative, Rucostar EEE, was obtained from Rudolf, Germany. It was a fluorocarbon resin with polymeric, hyperbranched dendrimers in a hydrocarbon matrix with cationic nature and acrylate base. It is noteworthy that this finishing agent is a modified type free of perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) and alkylphenolethoxylate (APEO). The used non-ionic detergent was Sera Wet C-NR, from DyStar. Other chemicals were of analytical grade from Merck, Germany.

2.2. Scouring

Fabrics were scoured in a bath containing 1 ml/l non-ionic detergent and 0.2 g/l Na_2CO_3 (pH = 8-9), with 30:1 liquor ratio at 60° C for 30 min to remove any possible impurities which may adversely affect the treatment. Fabrics were then washed off at 30 °C for 45 min and cooled gradually, and finally rinsed with cold tap water and air dried without any tension. The liquor ratio was 40:1. The flow chart for superhydrophobic polyester fabric formation is shown in Fig. 1.

2.3. UV-Ozone treatment

The scoured fabrics were impregnated by padding in a pre-treatment bath containing different chemicals: Na_2CO_3 (10 g/l), CH_3NH_2 (methyl amine, 10 g/l), H_2O_2 (7 ml/l)/Na_2SiO_3 (sodium silicate, 7 g/l), H_2O_2 (7, 21, 42 ml/l) and NaOH (10, 30, 60 g/l). These applied chemical concentrations were selected after preliminary-trials. Afterward, samples were passed through a padder at 100% wet pick-up to remove the excessive solution. Then, both side of the fabrics were immediately exposed to dried UV/Ozone gas to achieve possible surface roughness. The modification operation with dried UV-Ozone gas was carried out in a UV-Chamber (Cog-2a/France) containing five parallel-UV-lamps (Philips-TUV-11-W mercury-vapor with 253.7 nm UV-radiations) placed horizontally at the top of the sample with 1 cm exposure distance. Each fabric side was
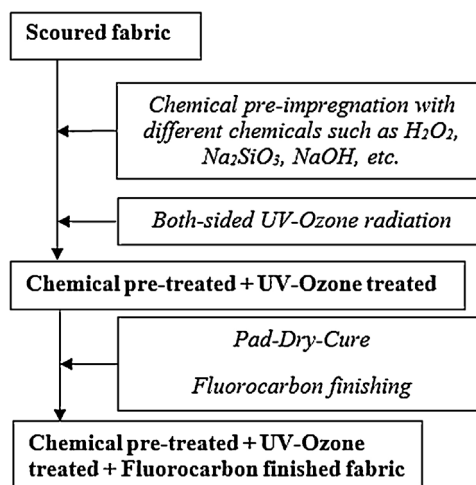

Fig. 1. The flow chart for superhydrophobic polyester fabric formation.

irradiated by UV/Ozone for 20 min, since prolonged UV-Ozone irradiation could cause higher strength losses [30]. Immediately after the irradiation process, samples were washed with 1 g/l detergent at 60 °C for 15 min. They were then treated by warm and cold rinses for 15 min and finally, flat air-dried without any tension.

2.4. Fluorochemical treatment

The scoured, chemically pre-treated and surface-modified fabrics were impregnated in a treatment bath containing 45 g/l fluorochemical, CH_3COOH (pH 5) and 5 ml/l propane-2-ol as a volatile wetting-agent. Afterwards, impregnated samples were passed through padder at 75–80% wet pick-up, dried at 100 °C for 2 min, and cured at 160 °C for 2 min using Warner Mathis AG-dryer (Niederhasli/Zurich).

2.5. Fabric evaluation test methods

The samples repellent and hydrophobicity properties were evaluated by measuring water sliding angle (WSA) [31], 3M-water-repellency [32] and water contact angle (WCA). WSA has been described as the angle at which water drops on a fabric start rolling down when the substrate is gradually inclined from its initial horizontal level and this angle illustrates the adherence of polar liquid to a textile surface [33]. WCA was measured with a Kruss contact angle analyzer (model G10) at ambient temperature with 4 μl distilled water. Water droplets were dropped carefully using an adjustable needle on the conditioned strip sample. The average CA (contact angle) value was determined by measuring at 10 different positions of 3 strips of the sample.

In the 3M-water-repellency test, water repellency of samples was tested using the water/alcohol drop test. The samples were placed on a smooth, horizontal surface. Beginning with the lowest numbered standard test liquid (Table 1), 3 small droplets (approximately 5 mm in diameter) were placed on the sample using a pipette. The droplets were observed for 10 s. If, after 10 s, 2 of the 3 droplets were still visible as spherical to hemispherical, the fabric would pass the test. The number of each test liquid remaining visible after 10 s had to be given to the sample as the 3 M water repellency rating. In general, water repellency rating of 2 or greater is desirable [32].

In addition, the re-orientation of fluorocarbon polymer chains after repeated washings and abrasion was evaluated in accordance with AATCC Test Method 61–1994: No. 2A by Polymat (AHIBA1000 Datacolor; ZÜRICH) in order to assess how samples