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Different plasma-based strategies to improve the interaction of anionic dyes with polyester fabrics surface

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ABSTRACT

Low-pressure plasma treatments with subsequent immobilization of functional macromolecules from aqueous solution have gained an increasing popularity for its applications in new industrial processes. In this work, two different strategies to endow polyester fabrics (PET) with accessible primary amino groups are compared.

(a) NH_2 groups were produced directly using low-pressure ammonia plasma. (b) Negatively charged groups were introduced by low-pressure oxygen plasma to hydrophilize the fabric surfaces and used as anchor groups for the immobilization of water-borne polyelectrolyte copolymers poly(vinyl amine-*co*-vinyl amide) (PVAm).

To study the effects of these surface modifications, a combination of various surface-sensitive characterization techniques such as X-ray photoelectron spectroscopy (XPS), streaming potential measurements and time-dependent contact angle measurements were used. Furthermore, the influence of the pre-treatments on the interaction of PET fabrics with water-soluble dyes was evaluated. For that purpose, color strength and fastness tests were carried out to prove the effectiveness of pre-treatments.

1. Introduction

In recent years, surface modification of textile materials by low-pressure plasma treatment has opened up new possibilities in textile industries. The interest in low-pressure plasma treatments of textiles is growing rapidly due to their effect is restricted to the uppermost thin layers of a material surface without affecting their bulk properties. The amount of toxic by-products is low compared to finishing processes based on wet chemistry [1,2]. Plasma has long been recognized as a source of ions, photons, chemically reactive atoms and molecular radicals [3,4]. It has been increasingly used in insert chemically reactive functionality onto non-reactive substrates to improve surface properties [5].

Poly(ethylene terephthalate) (PET), the main member of polyester polymers, is the most widely used fabric in the textile industries. PET fabrics exhibit desirable properties, including high tensile strength, dimensional stability, resistance to many chemicals and environmental conditions [6]. These remarkable attributes make it an excellent candidate for a variety of potential applications including, but not limited to, technical textiles, domestic textiles, the automotive industry and medical textiles [7]. Statistics show that sharing of PET in the total textile production (about 42%) still dynamically grows and has begun to grab market share from cotton [8]. This is due to the above-mentioned advantages combined with the material's cheapness and availability of the raw materials with the possibility to recycle PET fibers. For example, PET bottles and other PET products have recently attracted attention as new recyclable resources for the production of fibers. Moreover, PET is stronger than the most natural fibers. Therefore, it is used with those fibers to produce more resilient and wrinkle free blend fabrics (i.e., PET/wool and PET/cotton) [9]. Unfortunately, like other synthetic polymers, PET does not possess good adhesion and wetting properties, due to its inherently low surface free energy. PET does not exhibit reactive functionalities, such as $-NH_2$, $-COOH$, and/or $-OH$ groups wanted for different interactions, which makes the molecule of PET has limited reactivity and innately hydrophobic. The low surface free energy and the resulting poor adhesion to other materials have created numerous technical challenges, such as less wearing comfort, limitation in coloration properties, build-up of electrostatic charges, insufficient soil release, and difficulties in finishing and poor washability [10]. These limitations in functional properties of PET fabrics have constrained their further application in garments and other industries. For instance, coloration of PET/wool blend fabric requires two classes of dyes during two-stage process to produce solid shades [11,12]. This greatly hinders simultaneous process of coloration. On the other hand, there are some dyes specifically designed for high-technology

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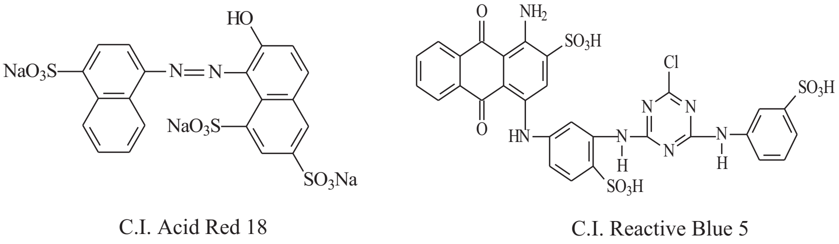

Fig. 1. Structures of used dyes.

(Hi-tech) applications such as optoelectronic and biomedical those are inappropriate for application to PET. As the PET fiber market grew, developments and innovations in surface functionalization of PET fabrics to improve the reciprocal reaction characteristics between PET surface and dyes molecules (classic and Hi-tech dyes) would be valuable which facilitate a broad spectrum of uses. As a result, significant efforts have been expended to overcome the PET limitations and to facilitate a broad spectrum of uses [13].

Accordingly, the surface design and development of highly functional PET fabrics have become increasingly important in various industrial fields such as adhesives, food packaging, printing and biomedical technologies. To improve PET's performance and obtain new applications, it is often necessary to introduce specific functional groups onto its surface. In particular, nitrogen-containing PET fabrics can be considered as a potential substrate for the versatile applications [14,15]. Grafted amino groups, with their associated polarity and reactivity, can be useful in the coupling and immobilization of a variety of functional molecules, which typically contain functional groups able to interact with amino groups.

With this idea in mind, many research groups have been studied several non-thermal plasma technologies to form amino group-decorated PET material surfaces while preserving its bulk properties [16]. In many publications, PET materials were treated in one-step process by plasma. Various plasma gases such as ammonia, nitrogen, allylamine, etc. were employed to endow PET materials with amine functionalities [16]. The main problems of these routes are the relative low degree of functionalization, the durability of the plasma modification (effect can be lost by surface recovery and weak-boundary layers), and the non-selectivity of plasma reactions (including the limited possibilities to control the kind of functional groups formed by the plasma process). Considering all these disadvantages the two-step synthetic route plasma/polyelectrolyte adsorption seems to be useful to endow PET surfaces with a high number of accessible and reactive primary amino groups. Works in this field, in particular for fibers and fabrics were scarcely done.

Therefore, in this study, different plasma-based synthetic concepts were compared to find out appropriate engineering methods, which can be further accepted by textile industries for surface functionalization of PET fabrics to overcome its limited reactivity and to keep the bulk characteristics unaffected. In this work, coloration with anionic dyes was used to evaluate the effectiveness of different plasma-based surface modifications of PET fabrics.

2. Experimental

2.1. Materials

Commercial PET 100% plain weave fabric of (165 g/m^2) used as the substrate for modification throughout this study was supplied by private sector Co., Egypt. To remove any residual impurities from fabric such as weaving and finishing oils, fabrics were treated before use with an aqueous solution containing 0.5 g/L non-ionic detergent Tissocyl CSB (Zschimmer & Schwarz, Burgstädt, Germany) and 1 g/L sodium carbonate. The liquor-to fabric ratio of aqueous solution was kept at 50:1 for 60 min at 70 °C. The fabrics were then thoroughly rinsed and allowed to air dried at room temperature until constant weight before use in the experimentation. The samples used for the modification procedures were 4 cm × 4 cm in size and 0.3 mm in thickness. The PET film was kindely supplied from Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung (IFAM), Bermen, Germany. PET film with a thickness of 16 μm was cut to a dimension of 4 cm × 4 cm to be used as a model specimens to investigate surface modification by ATR-FTIR experiments. Prior to the surface modification experiment, the PET films were rinsed for 10 min in an ultrasound bath successively in acetone and water to remove surface contaminants, then dried in air at the room temperature. Two commercial anionic dyes (Fig. 1) were used in this study kindly supplied from Bruno Ludewig GmbH (Emsbüren, Germany). Poly(vinylformamide-*co*-vinylamine) (PVAm-*co*-PFA) (Lupamine®9095) PVAm (Fig. 2) was obtained from BTC Specialty Chemical Distribution GmbH as a 22 wt.% aqueous solution (Mw = 340,000 g/mol) with charge density 5.47 meq/g used as received without further purification. Ammonia (99.99%) and oxygen (99.95%) were used as process gases for plasma treatments of PET fabric samples and purchased from Messer Griesheim, Germany. 4-Trifluoromethylbenzaldhyde (TFBA) was purchased from Merck. Guar gum, sodium alginate and urea were purchased from Sigma–Aldrich Chemie GmbH (Taufkirchen, Germany), mild oxidizing agent (Ludigol) kindly supplied by BTC Speciality Chemical (Köln, Germany).

2.2. Plasma treatments

2.2.1. Ammonia plasma treatment

Ammonia plasma treatment was carried out in a computer-controlled MicroSys apparatus by Roth & Rau, Wüstenbrand, Germany. The cylindrical vacuum chamber, made of stainless steel, had a diameter of 350 mm and a height of 350 mm. The base pressure obtained with a turbomolecular pump was <10^{-7} mbar. On the top of the chamber, a 2.46 GHz electron cyclotron resonance plasma source RR160 by Roth&Rau with a diameter of 160 mm and a maximum power of 800 W was mounted. The plasma source can be operated in a pulsed mode. The process gas was introduced into the active volume of the plasma source via a gas flow control system. When the plasma source was on, the pressure was measured by a capacitive vacuum gauge. Samples were introduced by a load lock system and placed on a grounded aluminum holder near the center of the chamber. The distance between the sample and the excitation volume of the plasma source was about 200 mm. For

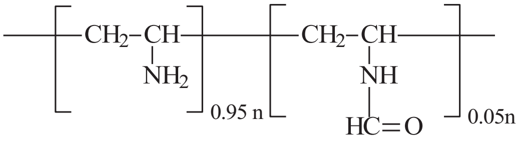

Fig. 2. Schematic structure of PVAm.