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Environmentally friendly plasma pretreatment for preparation of self-cleaning polyester fabric with enhanced deposition of TiO_2 nanoparticles

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Abstract

Tio_2 nanoparticles (NTO) were loaded on plasma pretreated polyester fabric during a pad-dry-cure process. The influence of plasma treatment on the TiO_2 nanoparticles adsorption and surface properties of the polyester fabric was investigated. Thermal treatment was used to determine the residual NTO on the surface of the fabrics and indicated more residual NTO after ten washing cycle for plasma and NTO treated samples. Acceptable self-cleaning and UV protection properties obtained on NTO treated samples especially in plasma pretreated ones due to the photocatalytic activity of NTO. Vertical wicking results showed that the hydrophilicity of NTO treated samples was improved. It was found that plasma treatment as a surface modification method increased the NTO adsorption on polyester fabric due to increase in surface functional groups on the polymeric chain. SEM images also showed an almost even distribution of the nanoparticles on the surface of the fabric.

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Introduction

In recent years, the use of nano titanium dioxide photo-catalyst to cover textiles and improve their surface properties has expanded due to their ability to absorb ultraviolet irradiation (Uddin *et al.* 2011; Wang *et al.* 2005). Polyester (PET) fabric has also a widespread range of use due to the easy care properties and good strength and many researchers all around the world investigated different methods to improve its properties (Wang *et al.* 2005). Nowadays, garments with simultaneous self-cleaning, antimicrobial and UV protection properties are desirable (Cai *et al.* 2006; Fujishima *et al.* 2008). NTO particles have been of great interest for environmental cleanup since they are stable, harmless, and inexpensive and potentially can be activated by solar energy (Carp *et al.* 2004; Cassaignon *et al.* 2007; Chatterjee and Dasgupta 2005; Linsebigler *et al.* 1995). In addition, the coating of NTO particles on fabrics will not affect their breathability or hand feel (Nazari *et al.* 2011). It is known that the durability of nano finishing on polyester is low because of the lack of functional groups (Hashemizad *et al.* 2012). So it is necessary to create functional groups on the surface of polyester fibers to attach the nanoparticles to them. Several methods have been used to modify the polyester surface such as alkaline hydrolysis, grafting and corona discharge treatment. The chain scissions caused by plasma treatment create radicals at the PET surface which will react with present radicals in the plasma gas to create hydroxyl, carbonyl and carboxyl groups. Moreover plasma treatments modify the polymer surface roughness (Lee *et al.* 2006; Lehocký and Mráček 2006; Leroux *et al.* 2009; Poletti *et al.* 2004; Samanta *et al.* 2010; Yuen *et al.* 2007). Low temperature plasma treatment is one of the most frequently investigated treatment methods for fabric modification and the discharge input power can strongly affect the modification rate to be grown (Lee *et al.* 2007; Ogawa *et al.* 2001; Shin *et al.* 2006). Since chemical methods like alkaline hydrolysis affect the fabric properties adversely, plasma treatment, as a surface specific and environmentally friendly treatment, is considered as an alternative approach to modify the surface properties of textile fibers without affecting their bulk properties.

In this research the effect of plasma treatment of polyester fabric on the adsorption of TiO_2 nanoparticles on the fabric is studied. It has already been reported that crosslinking agents can potentially increase the binding efficiency and the durability of nanoparticles on the fiber surface (Dastjerdi *et al.* 2010; Nazari *et al.* 2009). Here, citric acid (CA), as crosslinking agent, and sodium hypophosphite (SHP), as catalyst, were used to obtain the nano finishing with desirable durability. The photo catalytic activity of TiO_2 nano particles deposited on the PET fabrics was evaluated by degradation of methylene blue as a model stain. The hydrophilicity of NTO treated plasma modified and unmodified samples were defined using a vertical wicking test. Also the UV blocking properties of the nano TiO_2 treated fabrics was investigated and compared. Scanning electron microscopy (SEM) was used to observe the fabric surfaces and distribution of the nano particles on the fibers surface. All of these were applied to investigate the improvement of the polyester fabric treated with nano TiO_2 functionality after plasma pretreatment as a surface modification method.

Material and methods

Materials

Plain polyester fabric was used with a weight of 130 g/m^2 and 150 Den filaments in warp and weft (from Hijab textile Co., Shahrekord, Iran). Sodium hypophosphate (SHP) (Merck, Germany), Citric acid (Merck, Germany), Nano TiO_2 (21 nm, Degussa P25, Evonik, Germany) were used.

Methods

The fabric was scoured with solution containing 1 g/L nonionic detergent at 60°C for 20 min then rinsed with distilled water to remove any impurities and dried at ambient temperature. The fabric samples were conditioned overnight under standard conditions, at 20°C and 65% (R.H), before the treatment. The PET fabric samples were pretreated using radio frequency (13.56 MHz) low pressure plasma equipment (model: Junior plasma, Europlasma, Belgium) with oxygen gas. The sample chamber was evacuated to 100 mTor and maintained at this pressure during process. Then, oxygen was introduced with a flow rate of 30 sccm (Standard Cubic Centimeters per Minute). Plasma was generated at 150 W for five minutes. After that, air was introduced into the chamber and the plasma treated sample was removed.

The samples (plasma treated and untreated) were then treated with NTO dispersions (0.1%, 0.2%, 0.5% w/v) for 30 min in an ultrasonic bath (Retch, Germany) in the presence of 10 g/lit citric acid and 5 g/lit SHP. Then the samples were padded with 100% wet pickup. The fabrics were then dried at 100°C for 8 min followed by curing at 150°C for 3 min in an oven (Memmert, Germany).

Self-cleaning properties were investigated by evaluating the degradation of 10 µl Methylene Blue (0.01% (w/v)) as a model stain under day light irradiation for washed samples after 5, 10 and 15 h exposure. The color changes were studied based on reflectance data using a Color Eye 7000A Spectrophotometer (X-Rite, USA, 2000) and the color difference (ΔE) was calculated by formula (1):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$

Where L, a, and b are the values of lightness, redness– greenness and yellowness– blueness respectively.

Vertical wicking was examined by using fabrics in dimensions of 10mm×30mm kept in vertical direction as 10mm of their height was dipped in the distilled water and the time of water movement in a defined height (2 cm) was recorded.

To evaluate the UV protection properties of the samples, A Varian Cary 500 UV-Vis-NIR spectrophotometer instrument (Australia) was used to measure the diffuse UV reflectance of the plasma and NTO treated samples as well as nano treated raw samples in the wavelength ranging from 200 nm to 400 nm.

A XL30 (Philips, Netherland) scanning electron microscopy (SEM) was used to observe the fabric surfaces after NTO and plasma treatment.

Results and discussion

Surface modification of PET fabric with plasma treatment, is a versatile method for imparting certain desirable properties due to introducing hydrophilic groups such as (OH) and (COOH) on the surface of the fabric.

Self-cleaning properties

The degradation of Methylene Blue was evaluated on the plasma modified sample, unmodified sample with NTO and plasma treated and nano coated PET with 0.2% TiO_2. The ΔE values related to the unmodified and plasma modified PET after daylight irradiation are shown in Table 1. It can be clearly seen that the amount of ΔE has significantly increased in nano treated sample showing the photo catalytic activity of TiO_2. This means the more discoloration occurred on the TiO_2 treated PET comparing to the blank sample. The values of ΔE in plasma and nano treated sample is higher than the unmodified fabrics indicating that the rate of discoloration increased for the plasma treated samples as a result of more NTO adsorption after plasma treatment and photo catalytic activity of TiO_2 nanoparticles.

Table 1. ΔE values of unmodified and plasma modified PET after daylight irradiation.

Sample	plasma treated	NTO treated	plasma and NTO treated
ΔE	7.84	18.43	21.34

The discoloration rate of different samples treated with 0.2% NTO are compared in Fig. 1. As it can be seen the discoloration increases with increasing the exposure time to the sun. It also shows better color degragation for plasma pretreated and nano finished samples even after 10 hours.

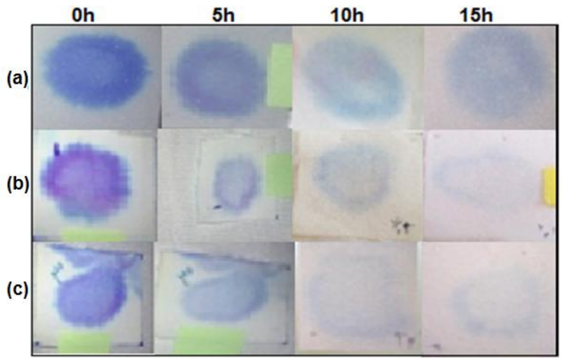

Fig. 1. Discoloration of Methylene Blue (0.01%) on the various PET samples with different exposure times under daylight, (a) plasma treated (b) NTO treated (c), plasma and NTO treated.

Vertical wicking

Vertical wicking results of the plasma treated and untreated fabrics loaded with TiO_2 Nano particles showed a decrease in the time required for the water to move upwards for the plasma modified samples as shown in Table 2. However in the case of the vertical wicking of the nano TiO_2 treated fabrics, the hydrophilic nano TiO_2 particles help to adsorb water and transfer it to the other hydrophilic groups or particles and also decreasing the inter fibers and inter yarns capillary spaces by nano TiO_2 leading to the rapid vertical wicking of water molecules. Thus the presence of nano TiO_2 leads to improve vertical wicking and wettability.

Table 2. Vertical wicking time for the plasma treated and untreated coated with NTO.

Vertical Wicking time (sec)		
TiO_2 (%)	**Untreated**	**Plasma treated**
0.1	26.5	19.45
0.2	18.2	12.7
0.5	14.3	9.6

UV protection

UV reflectance spectrum for the unmodified and the plasma pretreated fabrics with 0.2% (w/v) TiO_2 after 10 washing cycles reveals that increasing nano TiO_2 for all of the plasma pretreated and untreated fabrics causes a decrease in the reflectance percentage of irradiated UV ray, which means nano TiO_2 particles have blocked the UV rays and it proves the UV protection property of the nano TiO_2 treated fabrics [14]. It can also be seen that the reflectance is lower for plasma pretreated samples which leads to more UV absorption by the fabric surface due to the more adsorbed NTO as a result of plasma treatment.

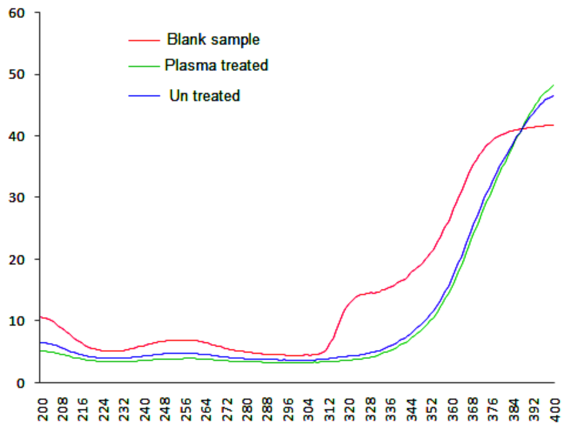

Fig. 2. UV Reflectance percentages of the modified and unmodified fabrics.

It can be resulted from Fig. 2 that the lowest amount of UV reflectance (R %) belongs to the plasma modified PET fabric treated with (0.2% w/v) NTO after the 10 cycles of washing. This could be explained by the evenly distributed TiO_2 nano particles on the fabric surface comparing to the unmodified sample. As it can be seen the UV reflectance in the unmodified fabric is more than that of the plasma treated sample after 10 cycles of washing.

This means that more UV rays are blocked by the plasma and nano treated samples rather than the unmodified one. Then using 0.2% nano TiO_2 on the plasma modified fabric is enough to obtain an acceptable UV protection level even after 10th washing cycle. This proves the effect of surface modification through plasma treatment on the durability of the nano TiO_2 deposited particles and UV protection properties.

SEM images

The effect of plasma treatment on the surface of fabric was completely clear in SEM images. Fig. 3 reveals an even distribution of nano TiO_2 on the surface of the plasma treated PET fabric. In Fig 3 (a) and (b), SEM micrographs show the surface of the unmodified and plasma modified PET fabric and Fig 3 (c) and (d) show nano TiO_2 coated surface of the unmodified and plasma treated fabric respectively. An even distribution of nano TiO_2 particles on the surface of the modified fabric was seen comparing to the unmodified fabrics. This could be a result of more nano Tio2 binding to the CA as a cross linking agent and created functional groups on PET surface after plasma treatment.

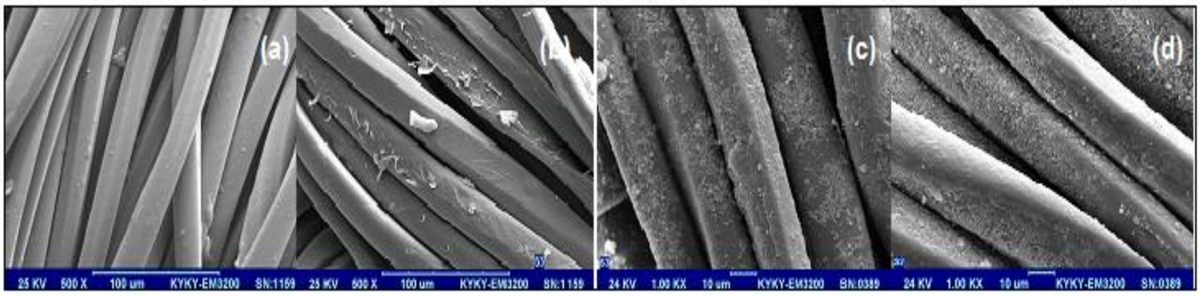

Fig. 3. SEM images of surface of the (a) unmodified, (b) plasma modified, (c) and (d) nano TiO_2 coated surface of the unmodified and plasma treated fabrics respectively.

All of these show the influence of plasma treatment on various properties of the PET fabrics. Plasma pretreatment improved the hydrophilicity of the PET fabrics with increasing the fiber surface roughness. It helps improving the wettability and wicking rate of PET fabric due to the more nano TiO_2 adsorption on the surface of the fabric causing acceptable self-cleaning and UV protection properties.

Conclusion

Plasma treatment of polyester fabric is a proper process for increasing its applications by introducing hydrophilic groups on the surface of the fabric to impart new specifications to the fabric such as better binding to nano TiO_2 particles. Also using poly-carboxylic acid such as citric acid can produce a good stability for TiO_2 nano particles on the polyester fabric surface even after 10 washing cycles proved by acceptable self-cleaning properties.

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