

Functional polyester fabric through simultaneous aminolysis and nano ZnO synthesis

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Abstract

Here, in situ synthesis of nano zinc oxide, along with aminolysis of polyester fabric, has simultaneously been carried out by using triethanol amine (TEA) and zinc acetate. The ZnO nano particles (NPs) were formed and stabilized on the fabric surface by amine compound at 130 °C for 1 h. The synthesis of nano ZnO particles on the polyester fabric were confirmed by X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images. The mean size of ZnO NP was obtained with SEM about 51.38 nm, however, XRD data indicated the crystalline ZnO NPs with a mean crystal size of 14.68 nm on the fabric surface. Further, self-cleaning performance of the treated fabrics was studied by degradation of methylene blue (MB) in aqueous solution under daylight irradiation. The stability of ZnO NPs on the fabric surface was studied by evaluating the self-cleaning and hydrophilicity properties of the samples after standard washing. Also, the hydrophilicity of the treated polyester fabric was improved due to aminolysis of the fabric and the required time for water droplet to spread on the treated fabric after one week exposure to daylight reduced. Overall, TEA was a suitable reducing agent to prepare homogenous ZnO NPs on the polyester fabric.

Keywords: *Aminolysis, Nano zinc oxide, Self-cleaning, Photo activity, Triethanol amine*

1. Introduction

Poly (ethylene terephthalate) (PET) is a semi-crystalline and semi-aromatic thermoplastic polyester is produced heavily with applications in textile, packaging, filtration, automobile, and biomedical field. It is often necessary to introduce specific functional groups on PET surface to improve its performance and obtain new applications [1].

Several surface modification methods have been developed to improve polymer without altering their bulk properties, such as, plasma treatment, UV irradiation, ozone oxidation and grafting. Aminolysis has been recently developed to modify the surface of polymers to enhance their hydrophilicity and biocompatibility without affecting the bulk of polymer. The reaction between ester and

amine groups forms covalent bonds which are anchored to the polymer surface [2]. The amine attacks the PET, breaking the polymer chain producing amide and hydroxyl groups. Aminolysis renders PET textiles more wettable increasing garment comfort improving the handle and dye ability [3]. Also, recently simultaneous synthesis of nano silver and aminolysis of polyester has been done on polyester fabric by Poortavasoly *et al.* [4].

ZnO is an important material due to its low cost, large band gap (3.31 eV), large excitation binding energy (60 MeV), luminescent properties and biocompatible antimicrobial material. As compared to nano-silver, ZnO NPs have the advantages of cost effectiveness, whiteness and UV blocking property. Moreover, ZnO NPs are more stable when compared to organic UV-blocking agents [5]. Several new routes have been developed recently to synthesis ZnO NPs (ZnO NPs), such as the sonochemical, oxidation, sol-gel, polymerization, precipitation, solvothermal and hydrothermal methods [6–8]. Nano sized zinc oxide powder were synthesized by chemical method at room temperature in alcohol base solution using triethanol amine as capping agent [9]. Aligned ZnO nanorods were also fabricated on PET fabric using a two-step hydrothermal growth method at low temperature and normal atmospheric pressure [10].

The structural and optical properties of ZnO thin films depend on preparation methods, substrate temperature, substrate material and subsequent annealing treatment. The selection of substrate is very important for the growth of thin film because matching in lattice parameters and crystal structure between the film and substrate strongly affects the crystal growth behavior of the film [11].

In this study, synthesis of nano zinc oxide along with aminolysis of polyester fabric has simultaneously been carried out in one-step and short time. The proposed novel method had no additional step for pre-treatment of the polyester fabric to enhance the adsorption properties; since the triethanol amine in the preparation procedure was responsible for simultaneous synthesis of NPs and surface modification of polyester fabric, introducing functional groups on the fiber surface. Triethanol amine (TEA) acted as reducing and

stabilizing agent to control the morphology of the nano zinc oxide on the fabric. The effect of amine concentration of aminolysis was studied and the size, morphology, and crystallinity of ZnO-NPs on the treated fabric were investigated. In addition, the photo activity, self-cleaning performance of nano-ZnO treated fabrics were investigated.

2. Experimental

2.1. Material

PET fabric with 88 g/m², zinc acetate (218.5 g/mol, 98% pure, Sigma), triethanol amine (85% pure) from Petrosimi Arak Co., methylene blue (C.I. Basic Blue 9) (Merck), nonionic surfactant (Diadavin EWN01) was used. IR Elite Lab Dyeing Machine was used for polyester fabric treatment.

2.2. Pre-treatment of PET fabrics

The PET fabrics were scoured in a bath containing 1 g/L nonionic detergent with L:G=40:1 (liquor to good ratio) at 60°C for 20 min and rinsed with distilled water and finally dried at room temperature.

2.3. In situ synthesis of ZnO nano particles

The zinc oxide NPs were prepared by wet chemical method using triethanol amine as reducing and stabilizing agent. Triethanol amine (0.06–0.12 % v/v) and zinc acetate (0.05–0.20% v/v) was used for synthesis. Zinc acetate dehydrate was dissolved in water under vigorous stirring. An amine was slowly added to aqueous solution of zinc acetate and stirred at room temperature to obtain colorless solution. The PET fabrics were immersed into the aqueous solution and then transferred to a stainless steel related to HT-IR device. The temperature was increased at 3°C/min to 130°C and treated for 1 h, and then cooled to room temperature. The samples were then rinsed by deionized water and dried at room temperature. The samples were finally heated at 80 °C for 24 h to obtain ZnO NPs.

2.4. Characterization

The structural characterization of the NPs were analyzed by X-ray diffraction (XRD, model EQUinox3000, INEL, France) with nickel-filtered CuK α radiation to study the presence and crystalline structure of the

absorbed NPs on the fabric surface and to estimate the size of crystalline structure. The crystalline size was calculated through Scherrer's equation (Eq. 1):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad \text{Eq. (1)}$$

In this equation, D is the crystalline size (nm), $\lambda=1.540560 \text{ \AA}$, θ is the Bragg's angle of diffraction, β is the full-width at half-maximum intensity of the peak observed and $k=0.9$ [12].

The size, morphology, and distribution of ZnO on the fiber surfaces were characterized by scanning electron microscopy (SEM).

The photo catalytic activities of ZnO powders were evaluated by measuring the degradation of Methylene Blue (MB) in water under daylight irradiation through measuring the ΔRGB of samples according to Eq. (2):

$$\Delta RGB = (B_2 - B_1)^2 + (G_2 - G_1)^2 + (R_2 - R_1)^2 \quad \text{Eq. (2)}$$

where $R_2G_2B_2$ and $R_1G_1B_1$ are color coordinates of samples after and before irradiation, respectively, and the higher ΔRGB values correspond to the higher self-cleaning property [13].

The percentage of weight change ($\% \Delta W$) of each sample was determined according to Eq. (3):

$$\% \Delta W = \frac{W_1 - W_2}{W_1} \quad \text{Eq. (3)}$$

where, W_1 and W_2 are the weights of the samples before and after treatment, respectively [14].

To investigate the effect of aminolysis and synthesized ZnO NPs on finishing fabrics, ability of treated fabric to absorb water was studied by measuring the time required for the water droplet to adsorb and spread on the fabric surface before and after daylight irradiation, according to AATCC Test Method 79-2000 [15].

3. Result and discussion

3.1. Nano ZnO synthesis mechanism

Mechanism of aminolysis reaction of polyester is shown in Figure 1. It is known that the aminolytic cleavage of the PET chains occurs as a result of a nucleophilic attack of the hydroxylamine groups on the ester bond, generating chain fragments, including oligomers and even low-molecular compounds ended with hydroxyl groups. These functional groups attract ZnO NPs [16].

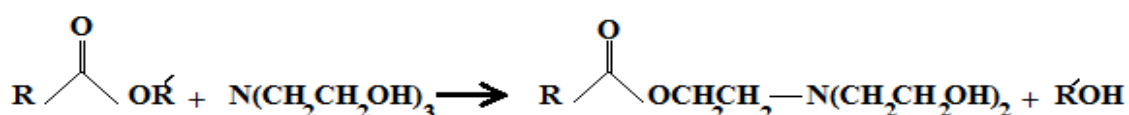
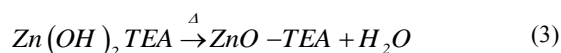
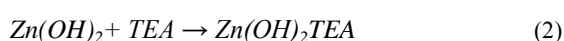
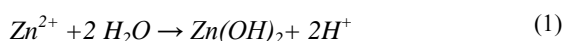


Fig. 1. Mechanism of aminolysis reaction of polyester chain [17]

Zinc acetate dissolves in water produced $[Zn(OH)_2]$ (**Reaction 1**). TEA can be coordinated with $Zn(OH)_2$ and formed stable $Zn(OH)_2$ TEA complex (**Reaction 2**). By heating the sample at $80 \text{ }^\circ\text{C}$, the complex break down to release H_2O and the hydroxyl groups of TEA interact with ZnO NPs (**Reaction 3**) resulting in a linkage of the neighboring ZnO NPs [18].



3.2. XRD pattern

The XRD pattern of the treated and untreated polyester fabrics with ZnO NPs is shown in Figure 2. The synthesis of ZnO NPs on the aminolyzed polyester fabric was confirmed by the characterization of peak at $2\theta = 31.88, 34.55$ and 36.48° attributed to (100), (002) and (101) facets, respectively, in addition to the main peak of original polyester fabric at $2\theta = 17^\circ - 25^\circ$ [14]. On the untreated polyester fabric, no peak detected after $2\theta = 30^\circ$. Planes indicate the formation of ZnO confirmed the crystalline phase of ZnO NPs. However, based on Scherer equation and FWHM data, the

crystalline size of NPs on the polyester fabric surface was about 14.68 nm.

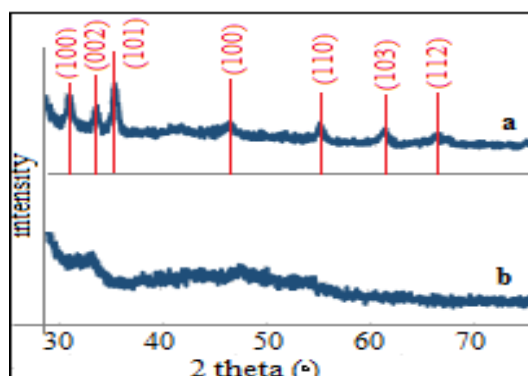


Fig. 2. XRD pattern of the a) treated and b) untreated polyester fabric with ZnO nano particles

3.3. Wettability

To investigate the effect of aminolysis on finished fabrics, ability of fabric to absorb water was studied. The time of absorption of a drop of water on the fabric is measured before and after 7 days under daylight irradiation based on BS4554 Standard. This procedure was repeated 10 times and the mean time recorded.

The surface properties of polyester is modified through aminolysis, without affecting the bulk of polymers and the amines have been proved to enhance the hydrophilicity of PET surface [1, 19].

Increasing amine concentration leads to more hydroxyl groups on the surface of PET and water absorption on the treated fabric [15].

The time of water absorption on the treated fabric increased after 24 h heating (calcination), however reduced after exposure of the samples to daylight for 7 days (Table 1).

Before heating the sample, [Zn(OH)₂TEA] combinations helps to absorb water through hydroxyl groups on the surface of treated PET fabric. The complex was broken and converted to nano ZnO by heating at 80 °C. This led to lower hydroxyl groups on the surface of PET and also absorption of zinc oxide NPs between the fibers lowering water absorption through capillary action [20,21].

In addition, electrons and holes play a prominent role in changing the water absorption properties of the treated fabrics after sunlight irradiation due to photo activity of the ZnO NPs. When treated fabric are

exposed to the daylight for 7 days, a photon with an energy of $h\nu$ exceeds the energy of the band gap an electron (e^-) is promoted from the valence band to the conduction band leaving a hole (h^+) behind (Reactions 4, 5& 6). Excited electrons tend to react with Zn^{2+} and reduced to Zn^+ . Excited holes also tend to react with anions O_2^- and oxidized. Then oxygen atoms removed and water molecules filled their vacancies resulted OH groups on the surface with increased hydrophilicity [13, 20 and 21].



3.4. Weight change

The amine attacks the PET, breaking the polymer chain. It is known that the attack occurs throughout the fiber decrease the molecular weight. The aminolyzed sample was treated with the same concentrations of amine without other materials for 1 h at 130 °C with IR machine showed a lower weight (negative ΔW %) (Table 1). This is because of breakage of the ester chains of polyester, formation of oligomers and other low molar mass fragments removed from the fibers during aminolysis and rinsing [1]. Increasing concentrations of triethanol amine led to higher nucleophiles attack on the ester bond of polyester and also higher weight loss within the worked concentration. By increasing the concentrations of zinc acetate and TEA, more ZnO NPs were formed led to increased fabric weight.

3.5. Self-cleaning properties

The ability of the treated polyester fabrics with ZnO NPs to decompose methylene blue by daylight irradiation indicates self-cleaning properties. Hence, each specimen was immersed in methylene blue solution for 1 min and dried in dark. All specimens were then placed under daylight for 7 days and ΔRGB (color change) of samples measured according to Equation (2). The higher ΔRGB value corresponds to the higher self-cleaning properties [19].

With increasing concentrations of ethanol amine and zinc acetate, more ZnO NPs

produced and the self-cleaning properties of treated fabric improved, indicating higher Δ RGB. Hydrophilicity along with the photocatalytic properties of ZnO NPs enhanced the self-cleaning properties of the treated fabric [20].

Finally, the optimization was carried out to obtain the best combination of the factors to achieve the maximum hydrophilicity and self-cleaning with minimum weight. As higher

wettability and self-cleaning properties and lower percentage of weight change can be attributed to the enhanced aminolysis and surface activity for the treated fabric. As a result, the properties of the optimized sample treated with 0.11 (% v/v) TEA and 7.20 (% w/w) zinc acetate indicated in Table 1. Also a polyester fabric was treated with distilled water alone at 130 °C for 1 h in the same device and considered as control sample.

Table 1. Different properties of control, aminolysis and optimum treated polyester fabrics

sample	Zinc acetate (W/W%)	TEA (V/V%)	Water absorption time before irradiation (s), CV%*	Water absorption time after irradiation (s), CV%	Δ W%, CV%	Δ RGB, CV%
Control	0.00	0.00	2.70 0.13	2.68 0.30	0.00	32.42 1.35
Aminolysis	0.00	0.11	0.74 0.14	0.72 0.14	-0.20 0.45	43.25 2.33
Optimum	7.20	0.11	21.54 1.62	5.98 1.39	+1.10 0.31	89.05 2.60

* CV is the coefficient of variance calculated for 3 repeated measurements.

Aminolysis reaction leads to creation of more hydroxyl groups on the surface of PET fabric, consequently the water absorption of aminolyzed sample increased when compared with control one. The irradiation of sunlight on the aminolyzed sample has not affected the water absorption time and Δ RGB of the aminolyzed sample showed no significant change. The water absorption and Δ RGB of the optimized sample containing ZnO NPs improved after daylight irradiation indicating the photo activity and self-cleaning properties of ZnO NPs on the polyester fabric. Water absorption time of the optimized sample before irradiation was more than control, and reduced sharply after irradiation under sunlight due to the electron-hole formation at the surface of the nanoparticle as described in wettability section (Table 1).

3.6. Washing fastness

Washing fastness of the optimum treated sample was investigated in a way that each cycle of the washing process is equivalent to five cycles of primary washing at 60°C for 20 min in the presence of a non-ionic detergent. The stability of NPs on the surface of the fabric after washing was studied through self-cleaning and percentage of weight loss after

washing process. The results are illustrated in Table 2.

Table 2. Washing fastness of optimum sample

Samples	Water absorption		
	Time after irradiation(s) CV%	Δ W% CV%	Δ RGB CV%
Optimum	0.3	-0.5	86.91
after washing	0.1	0.38	2.21

The optimum sample showed no significant change in weight change, water absorption time and self-cleaning properties after washing and 7 days under daylight irradiation confirming the reasonable stability of the ZnO NPs on polyester fabrics against washing and light.

3.7. SEM photograph

SEM photograph in Figure 3 shows the size and distribution of ZnO NPs on the fabric samples. The images also indicated the NPs with spherical-shaped structure and uniform distribution on the surface of PET fibers with a mean particle size about 51.38 nm. No distinctive voids can be seen on the surface of the treated fabric due to low diffusion rate of triethanol amine and acting on the surface

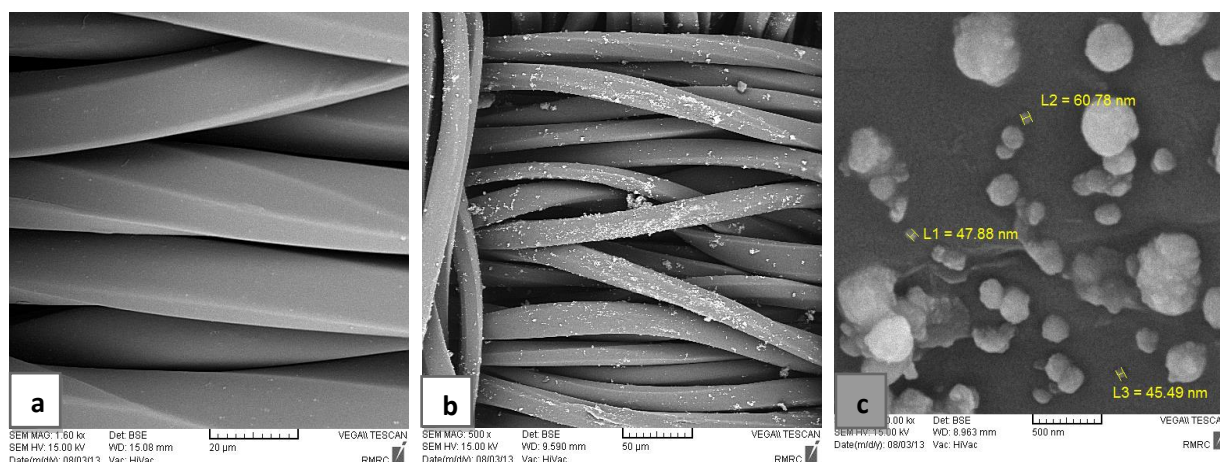


Fig. 3. SEM of the a) untreated and b,c) treated polyester fabric with ZnO nano particleu'

layer of polyester [21] (Fig. 3 b,c). Therefore, aminolysis of polyester fabric along with the synthesis of ZnO NPs indicated no damage to the fibers.

3.8. Conclusion

This study provides a novel and simple method for aqueous preparation of ZnO NPs on polyester fabric and their applications. Presence of ZnO NPs were confirmed with SEM images and X-ray diffraction patterns. The mean size of ZnO NP was obtained with SEM about 51.38 nm. Higher wettability and improved photo activities with no visible color change was successfully obtained by simultaneous aminolysis of polyester and synthesis of ZnO NPs on the fabric surface. The time of the water droplet to absorb on the treated fabric after 24 h exposure under daylight increased. The treated fabrics showed a very good photo catalytic activity with excellent washing fastness.

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