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Effect of Zinc Oxide Nanoparticles and Sodium Hydroxide on the Self-Cleaning and Antibacterial Properties of Polyethylene Terephthalate

Učinek nanodelcev cinkovega oksida in natrijevega hidroksida na samočistilne in protibakterijske lastnosti polietilen tereftalata

Original Scientific Article/*Izvirni znanstveni članek*
Received/*Prispelo* 08-2017 • Accepted/*Sprejeto* 08-2017

Abstract
In this study, the synthesis of zinc oxide nanoparticles was carried out, together with the hydrolysis of polyethylene terephthalate, using sodium hydroxide to increase surface activity and enhance nanoparticle adsorption. Polyester fabrics were treated with zinc acetate and sodium hydroxide in an ultrasonic bath, resulting in the formation of ZnO nanospheres. The presence of zinc oxide on the surface of the polyethylene terephthalate was confirmed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The self-cleaning property of treated fabrics was evaluated through discolouring using methylene blue stain under solar irradiation. The antibacterial activities of the samples against common pathogenic bacteria, including *Escherichia coli* and *Staphylococcus aureus*, were also assessed. The results indicated that the photocatalytic and antibacterial activities of the ultrasound-treated polyethylene terephthalate improved significantly.
Keywords: zinc oxide nanoparticles, polyethylene terephthalate, self-cleaning, antibacterial

Povzetek
V študiji je bila izvedena sinteza nanodelcev cinkovega oksida sočasno s hidrolizo polietilentereftalata z natrijevim hidroksidom za povečanje površinske aktivnosti in izboljšanje adsorpcije nanodelcev. Poliestrske tkanine so bile obdelane s cinkovim acetatom in natrijevim hidroksidom v ultrazvočni kopeli, kar je povzročilo nastanek nanokroglic ZnO. Prisotnost cinkovega oksida na površini polietilentereftalata je bila potrjena z vrstično elektronsko mikroskopijo (SEM) in energijsko disperzijsko spektroskopijo rentgenskih žarkov (EDS). Samočistilne lastnosti obdelanih tkanin so bile ocenjene z razbarvanjem madežev metilensko modrega barvila pod vplivom sončne svetlobe. Ocenjena je bila tudi protibakterijska aktivnost vzorcev proti pogostim patogenim bakterijam, vključno z bakterijama Escherichia coli in Staphylococcus aureus. Rezultati so pokazali, da so se fotokatalitične in protibakterijske lastnosti polietilentereftalata, obdelanega z ultrazvokom, bistveno izboljšale.
Ključne besede: nanodelci cinkovega oksida, polietilentereftalat, samočistilnost, protibakterijske lastnosti

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Tekstilec, 2017, ***60****(4), 269-274*
DOI: 10.14502/Tekstilec2017.60.269-274

1 Introduction

The use of self-cleaning coating technology is an innovative strategy for the functional finishing of textiles [1−3]. Different semiconductors have been used for the preparation of textiles with a self-cleaning property. For example, Karimi et al. produced self-cleaning cotton fabrics using nano-TiO_2 [4]. Along the same lines, Behzadnia and colleagues obtained photocatalytic fabrics based on zinc oxide coatings on wool fabrics [5]. Moreover, a chemical coating of cotton with zirconium dioxide nanoparticles with a self-cleaning property was reported by Moazami- and Montazer [6]. Textiles with multiple characteristics can also be fabricated by applying nano-semiconductors. The deposition of semiconductors such as TiO_2, ZnO, and ZrO_2 on textiles provides multifunctional properties such as self-cleaning, UV-protection, superhydrophilicity, antibacterial and flame retardant properties, etc. [7−8]. Textiles treated with nano-semiconductors can be used in practical applications such as medical devices, healthcare, wound dressing, military, protective suits, personal care products, clothing and others [9]. Polyester is one of the most widely used versatile polymers owing to its high strength, high modulus, abrasion resistance, heat setting stability, light fastness and chemical resistance [10]. However, due to its poor wettability and lack of functional groups, the durable functional finishing of polyester fabrics has become a concern for the textile industry. Several studies have reported that the surface of polyester could be modified using different pre-treatments and techniques such as plasma treatment, hydrolysis and aminolysis [11]. The treatment of polyester fabric through alkaline hydrolysis enhances hydrophilicity and surface reactivity.

In this study, the synthesis of zinc oxide nanoparticles and the alkaline hydrolysis of polyethylene terephthalate (PET) were performed in one step using an ultrasound method. The functional PET samples were prepared by applying zinc acetate as a zinc oxide precursor, and using sodium hydroxide as both a strong base to provide the alkaline condition for zinc oxide formation and as an agent capable of the hydrolysis of a fabric's surface . The role of concentrations of zinc acetate and sodium hydroxide over the photocatalytic self-cleaning performance and antibacterial activities of treated PET was investigated.

2 Materials and methods

2.1 Materials

Plain weave polyester fabric with a fabric weight of 188 g/m^2 was used. Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as a precursor to synthesis nano-ZnO and sodium hydroxide (NaOH) provided by Merck Co. (Germany) were utilised, while Direct Green 6 (CI 30295) was purchased from Alvan Sabet Co. (Iran).

2.2 Instruments

A 350 W, 50/60 Hz Euronda Eurosonic® 4D ultrasonic bath (Italy) was used for synthesis processing. SEM images and EDS patterns were identified using a Phenom ProX scanning electron microscope (SEM) (Netherlands). Fourier transform infrared spectroscopy (FT-IR) was performed using a Bruker FT-IR spectrometer (Germany) to analyse the changes that appeared in functional groups on the surface of polyethylene terephthalate through alkaline treatment.

2.3 Methods

To synthesise nano zinc oxide (nano-ZnO) particles on polyester fabric, diverse amounts of zinc acetate were used as a precursor in 100 mL of water in an ultrasonic bath. The polyester fabrics were immersed in zinc acetate solutions (1, 2, 3, 4, and 5 wt.%), and different amounts of sodium hydroxide (1, 2, 3 and 4 wt.%) were added to the bath under ultrasonic irradiation. The solution was irradiated at 65 °C for 45 minutes. The treated samples were dried at 60 °C for 30 minutes and then cured at 130 °C for 4 minutes. Finally, the sono-treated samples were washed with distilled water and dried at 70 °C for 24 hours.

2.4 Test methods

In order to investigate the self-cleaning properties of treated PET samples, colourant stains were created on the samples. The treated PET samples were stained using methylene blue with a concentration of 100 mg/L. After being stained, the samples were exposed to solar (Yazd, Iran) irradiation for seven consecutive days. The sample colours were measured before and after illumination. Their self-cleaning properties were then compared based on their colour difference (ΔE^*). Colour coordinates were determined by colour measurement software using the CIE L^* a^* b^* colour space at D65/10°. In the CIELAB system, colour is expressed in terms of CIE L^*, a^* and b^* values, where L^* defines lightness, a^* denotes the red-green value and b^* indicates the yellow-blue value. The total colour difference (ΔE^*) was calculated according to Equation 1:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1).$$

The antibacterial properties of the treated samples were measured using the AATCC 100-2004 test method against *Escherichia coli* (*E. coli*, ATCC 25922, gram-negative bacterium) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923, gram-positive bacterium) as common pathogenic bacteria. Antibacterial activity was calculated and expressed in terms of the percentage reduction of microorganisms:

$$(R)\% = \frac{(A-B)}{A} \times 100 \quad (2),$$

where A and B are the number of microorganism colonies on untreated and treated samples, respectively.

3 Results and discussion

3.1 Characterisation

The surfaces of the treated and untreated PET samples were observed using scanning electron microscopy. The SEM images of untreated PET (A) and treated PET with zinc oxide (zinc acetate 3 wt.%) in an ultrasonic bath (B and C) are presented in Figure 1. While the surface of the untreated PET is smooth, synthesised ZnO nanoparticles are distributed on the surface of the treated PET. The zinc oxide nanoparticles on the surface of PET treated in an ultrasonic bath (Figure 1B) are easily recognisable. The sono-synthesised zinc oxide nanoparticles are uniformly spread over the surface of the sample as the result of ultrasonic irradiation. Images at higher magnification indicate the presence of spherical-shaped particles, with an average size of 52.6 nm (Figure 1C). The successful formation of zinc oxide nanoparticles on the treated fabrics was verified by

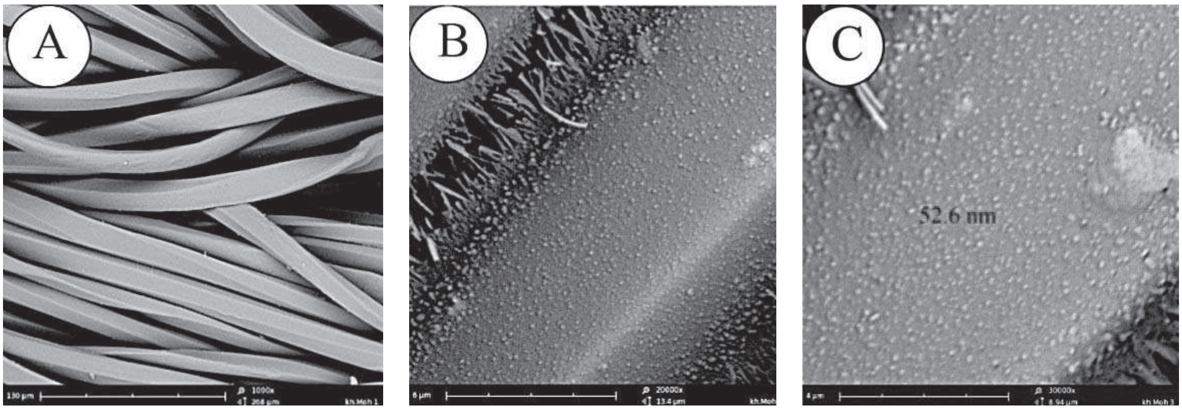

Figure 1: SEM images of various PET samples: (A) untreated and (B and C) treated with zinc oxide (3 wt.%) in an ultrasonic bath

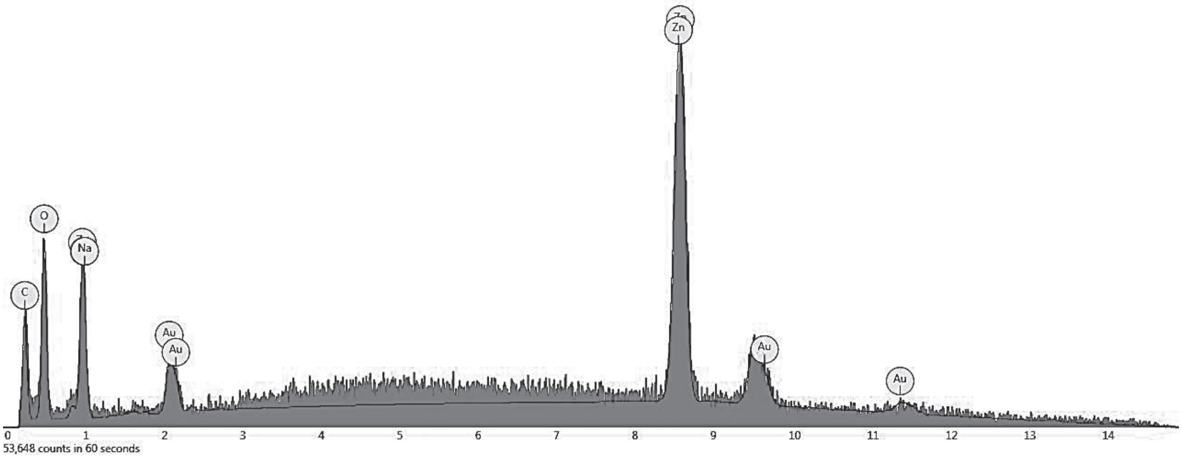

Figure 2: EDS spectra of PET sample treated with zinc oxide (3 wt.%) in an ultrasonic bath

chemical compositions analysed using EDS. As shown in Figure 2, zinc and oxygen are two elements on the treated samples, in addition to the carbon that relates to the polyethylene terephthalate. Because the fabrics were coated with a gold layer before SEM observation, Au peaks are also seen in the spectra.

An XRD pattern was used to confirm the presence of zinc oxide on the fabric surface and to study crystalline status (Figure 3). The peaks at 2θ values of 17°, 23.1° and 26.4° represent the diffraction peaks of the original polyester substrate. The seven reflection peaks that appeared at 2θ values of 31.9° (100), 34.6° (002), 36.5° (101), 47.7° (102), 56.8° (110), 63.1° (103) and 67.1° (202) could be indexed as the hexagonal Wurtzite structure of ZnO, and were consistent with the values in the standard card (JCPDS 36–1451). Treated fabric confirmed the formation of a Wurtzite zinc oxide phase in the XRD pattern.

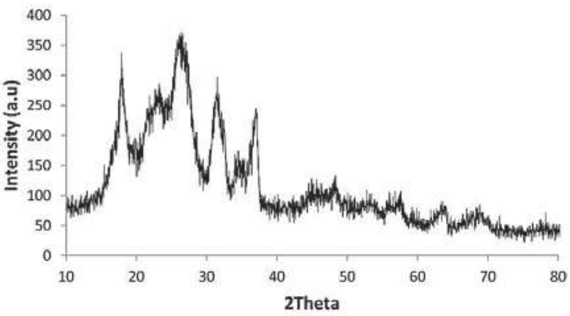

Figure 3: XRD pattern of polyester fabric treated in an ultrasonic bath

The treatment of PET with sodium hydroxide is a versatile method for producing hydrophilic groups such as hydroxyl and carboxyl on the surface of the fabric. The effect of alkaline hydrolysis on the chemical properties of PET was studied using FT-IR spectroscopy. The FT-IR spectrum of the sample treated with NaOH indicated the characteristic peaks attributed to C=O (carboxylic acid), C–O (ester acid), C–H (stretching vibration) and C–H (bending vibration) at 1715, 1000–1500, 2928, and 722 cm^{-1}, respectively. Also, the peak at approximately 3450 cm^{-1} confirmed the forming of terminal groups of –OH on the surface of polyester fabric following the alkaline process, as the result of the interaction of hydroxide ions with electron-deficient carbonyl groups, (Figure 4).

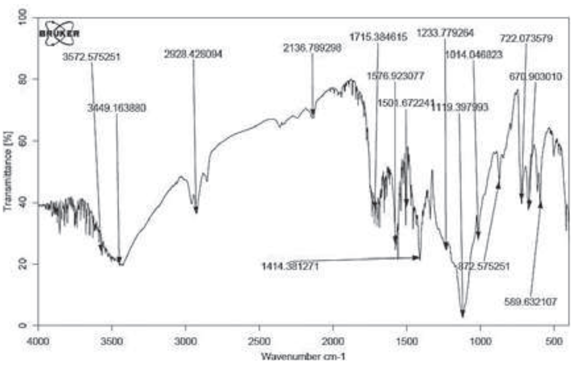

Figure 4: FT-IR spectrum of polyester fabric alkaline-treated with sodium hydroxide (4 wt.%) in an ultrasonic bath

3.2 Self-cleaning performance

The PET samples were stained with a Direct Green 6 dye solution and exposed to solar irradiation. The fabric colour coordinates were calculated before and after solar irradiation, and the self-cleaning performance obtained based on the colour difference (ΔE^*). The untreated PET samples were not photoactive (ΔE^* in the range of 1–3). As seen in Figure 5, all of the zinc oxide-treated samples showed higher ΔE^* values as the result of the photocatalytic activity of ZnO nanoparticles used to degrade the dye stain.

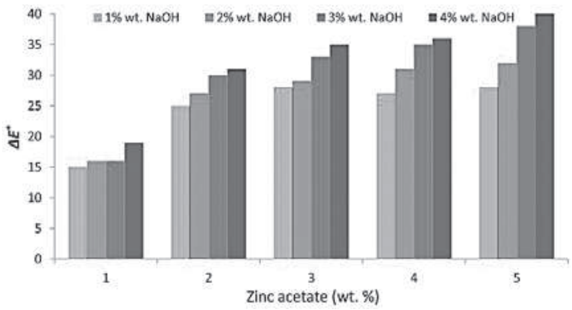

Figure 5: Comparative diagram of self-cleaning performance results of PET samples treated in an ultrasonic bath

The results indicate that the level of self-cleaning for the treated samples is higher when treated at an alkaline condition. Increasing the concentration of sodium hydroxide increases the photodegradation of Direct Green 6. This could be a result of the increase of polar groups such as carboxyl and hydroxyl groups on the surface of the fibres, which may favour the adsorption of ZnO nanoparticles on the samples. The increase in the zinc acetate concentration also had a tangible effect on the self-cleaning performance of treated PET, while the ΔE^* of treated samples increased incrementally due to the higher zinc oxide content on the PET surface. Moreover, ultrasound-treated PET confirmed increased self-cleaning activity. Ultrasonic irradiation prevents particles from aggregating on the surface of polyester fibres. As seen in SEM images, the distribution of zinc oxide on ultrasound-treated samples is more uniform compared to conventionally treated samples due to the use of ultrasound. This may lead to higher photocatalytic activity in terms of self-cleaning.

3.3 Antibacterial assay

Zinc oxide nanoparticles possess unique photocatalytic, electrical, optical, dermatological and antibacterial characteristics that can make it possible to produce a textile with self-cleaning and antibacterial properties. The antibacterial activities of the samples were evaluated quantitatively using a suspension method against both *E. coli* and *S. aureus* bacteria. The percentages of bacteria reduction by ultrasound/ZnO treated and untreated polyester samples are illustrated in Figure 6. Untreated PET provides a suitable medium for the growth of microorganisms. The antibacterial efficiency of the ultrasound-treated samples against bacteria was 100%. It has been proven that the transmission of finer-sized materials results in higher antibacterial activity compared to materials of typical size.

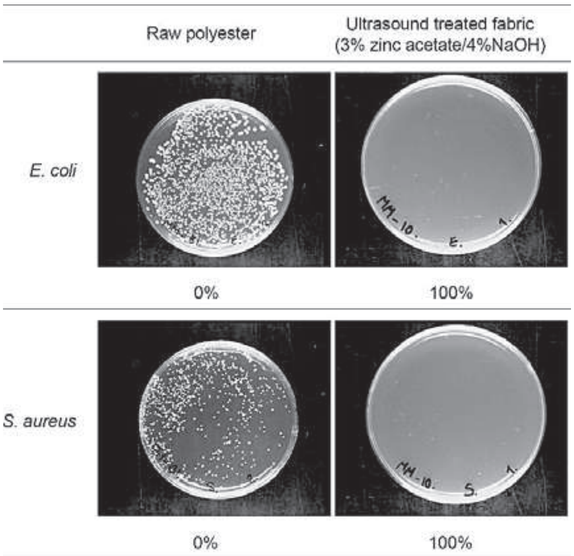

Figure 6: Antibacterial efficiency of PET samples

4 Conclusion

As demonstrated, the simultaneous synthesis of zinc oxide nanoparticles and the alkaline hydrolysis of the surface of PET samples was developed. PET samples with a self-cleaning property and antibacterial efficiency were obtained through ultrasound treatment. SEM and EDS patterns were used to confirm the presence of zinc oxide nanoparticles on the surface of the treated PET samples. It was determined that zinc oxide nanospheres were synthesised on PET samples treated using ultrasound. Applying ultrasonic irradiation in the treatment process led to synthesised zinc oxide of a finer size and homogenous distribution on the fibre's surface.

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