

Functional finishing of polyamide fabrics using ZnO–PMMA nanocomposites

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Abstract Polymer nanocomposites offer possibility of developing a new class of nanofinishing materials for textiles with their own manifold of structure property relationship. Approaches to modify the polymer nanocomposites by various inorganic substances can lead to a huge number of additional functionalities which are increasingly demanded by the textile industries. In the present work, zinc oxide nanoparticles were prepared by wet chemical method and ZnO–PMMA nanocomposites were prepared by dispersing the ZnO nanoparticles in solution of poly(methylmethacrylate) (PMMA) and applied on polyamide fabrics by padding. The aims are to impart superhydrophobicity and UV protection function to the polyamide textile surface and the functional properties of coated fabrics were studied. The nanofinished polyamide fabrics showed superhydrophobicity of about 163° . The results also showed that the impregnation of fabrics with ZnO–PMMA nanofinishings also enhanced the protection of polyamide fabrics against UV radiation.

Introduction

The increasing demand for multifunctional fabrics requires strong multidisciplinary approaches as well as the merging of the traditional scientific disciplines [1–3]. The first commercial application of nanofinishes is found in textiles in the form of nanoparticles through finishing processes. But these finishes do not withstand subsequent washing due to poor fixing of these nanoparticles on the textile surface. Using hydrophobic/hydrophilic functional polymer matrices as dispersion medium for nanoparticles will result in nanofinishings with improved bonding properties in fabrics and also impart desired wettability with different functional properties like UV resistance, antimicrobial, and flame retardancy which are unique characteristics of different nanoparticles.

The application of finishings based on nanoparticles to textile materials aimed at producing finished fabrics with improved performance. For example nanoAg has antimicrobial properties [4, 5]. NanoTiO₂ has UV resistance and self cleaning properties [6–8] and ZnO nanoparticles have been used for antibacterial and UV-blocking properties [9–11]. Zinc oxide and titanium dioxide are nontoxic and chemically stable under exposure to high temperature and capable of photo catalytic oxidation [12]. Zinc oxide is actually one of the best biofriendly absorber of UV radiation that mainly comes on earth from sun through the atmospheric ozone layer [13].

According to the Cassie–Baxter equation [14] superhydrophobic surfaces can be produced by the use of system consists of low surface energy materials (polymers) as well as fillers and nanoparticles for the creation of rough surfaces.

The wetting behavior of a water droplet on a superhydrophobic surface can be described by the equation of Cassie and Baxter [14, 15]

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$$\cos\theta_{CB} = f_l \cos\theta_0 - f_v$$

where θ_{CB} is the observed water contact angle (CA) on a rough porous surface. θ_0 is the intrinsic water CA on the corresponding smooth surface f_l is the liquid/solid contact area divided by the projected area and f_v is the liquid/vapor contact area divided by the projected area. The above equation has been modified now to account for the local surface roughness on the wetted area [15–17]

$$\cos\theta_{CB} = r_f f \cos\theta_0 + f - 1$$

where f is the fraction of the projected area of the solid surface wetted by water (thus, $f_v = 1 - f$) and r_f is the surface roughness of the wetted area.

Two approaches were followed to produce superhydrophobic textile surfaces

- (i) Nanoparticles were deposited on textile surfaces to induce nanoscale roughness. The roughened fabrics were then chemically treated or covered with low surface energy coatings [18–20].
- (ii) Particles were mixed with polymer solutions and then coated on fabrics [21].

In the latter approach either one of the two components of the polymer–particles mixture was an intrinsic hydrophobic material (polymer or particle). The idea was tested previously by Hsieh et al. [22], who observed that superhydrophobicity is obtained by applying a mixture of a perfluoroalkyl methacrylic copolymer with titanium oxide nanoparticles.

In the present work we present a strategy for the production of superhydrophobic and UV protective polyamide fabrics surfaces by using ZnO–PMMA nanofinishings. Poly(methylmethacrylate) (PMMA) is known to be suitable medium to disperse inorganic particles to enhance the dispersion stability [23, 24]. It is also an attractive engineering polymer due to its unique properties such as high strength, special optical properties, environmental durability, biocompatibility, and low toxicity. This paper describes the steps involved in the synthesis of nanoparticles preparation of ZnO–PMMA nanocomposite and its application on polyamide fabrics to impart novel functions and test them. The nanoparticles and nanocomposites were then characterized by evaluating their chemical composition through FT-IR spectroscopy, crystallinity of nanoparticles by X-ray diffraction (XRD), and their shape size and distribution in polymer matrix by SEM. The ZnO–PMMA composites were applied to polyamide fabrics by padding in order to evaluate superhydrophobicity/contact angle and UV protection function in the nanofinished fabrics through standard test procedures. In our study we demonstrated that superhydrophobicity can be achieved by using nanofinishing of ZnO nanoparticles dispersed in PMMA.

Experimental details

Materials

Zinc nitrate (98% purity) was procured from Acros Organic, New Jersey, USA. PMMA with molecular weight of 120,000 g/mol was purchased from Alfa Aesar GmbH & Co, Germany. Toluene and ethanol were obtained from Analyticals, Farmitalia Carlo Erba, Milano. Sodium hydroxide and deionised water, of laboratory grade, were obtained from indigenous sources.

Synthesis of ZnO nanoparticles

Zinc oxide nanoparticles were prepared from Zn nitrate solutions after neutralizing with sodium hydroxide to pH values of 12. Conventional heating experiments were conducted on magnetic stirrer. When the reactions were completed, the solid and solution phases were separated by centrifugation and the solids were washed free of salts with deionized water (3×) and ethanol (2×). Then a white powder obtained was calcined at higher temperature and then grinded manually for uniformity of the powder.

Pretreatment of polyamide fabrics

A fine medium weight 100% polyamide fabric of plain weave was used. The fabric was treated in a dielectric barrier discharge (DBD) atmospheric plasma device, which is a laboratory prototype; model Lisboa, constructed by Softal. The surface chemistry and surface topography may be influenced by the plasma treatment and will result in improved adhesion/impregnation of dyes/finishing [25, 26]. The plasmatic barrier discharge treatment of polyamide fabrics significantly increases the adhesion of coatings on the surfaces. Plasma treatment was performed in air atmosphere on polyamide fabrics at 10 kV, frequency of 5 kHz, 1 kV of power, and process energy of 4 J/cm². Plain polyamide fabrics with average thickness of 0.4 mm were passed between the electrodes continuously and both sides of the fabric were exposed to the plasma treatment.

Coating polyamide fabric with ZnO–PMMA

Poly(methylmethacrylate) (PMMA) was dissolved in toluene to prepare stock solution of 5 wt%. Different percentages of ZnO nanoparticles (0.1, 0.5, and 1) were mixed with PMMA. The mixture was stirred vigorously in order to get a homogeneous dispersion. The plasma treated fabric was cut into size of 30 × 30 cm and immersed in the solutions containing nanoZnO at different concentrations for 15 min under ultrasonic vibrations. Then the fabric was passed through padding mangle which was running at a

speed of 9.6 m/min with the pressure of 4.9 bar to remove excess solution. After padding the fabric was air dried. Then the fabric was rinsed with deionised water and air dried again.

Characterization of ZnO nanoparticles and ZnO–PMMA nanocomposites

The chemical compositions of the synthesized nanoparticles ZnO and ZnO–PMMA were checked by FT-IR spectroscopy with Nicolet Avatar 360 spectrophotometer. The XRD pattern of nanoparticles was analyzed with X-ray diffractometer (Model: Bruker D8 Discover) using Cu K α radiation at wavelength $\lambda = 0.15406$ nm, scan range $2\theta = 20^\circ$ – 90° , scanning rate = 0.02 deg/s (applied voltage 40 kV, current 20 mA).

The SEM analysis of nanoparticles and its dispersion in PMMA matrix was done by Nano SEM (Model: FEI Nova 200, FEG/SEM) after gold coating in sputter coater. Silicon wafers were used as model flat substrate after washing with piranha solution and plasma treatment.

Dynamic light scattering (DLS) measurements were performed using a Malvern Instruments particle sizer (Zetasizer Nano ZS, Malvern Instruments, UK) equipped with a He–Ne laser ($\lambda = 632.8$ nm). The scattering data were recorded at 25 °C. The aqueous sample solutions were placed into a square glass cuvette. Prior to measurement, the samples were filtered with a 0.45 μm millipore syringe filter to remove dust particles.

The ability of the coated fabric to block UV light is given by the ultraviolet protection factor (UPF) values. The measurement of UPF values was performed in Cam-spec M350 UV/Visible Spectrophotometer with software

version: 990824.01, using an integrating sphere loaded with fabric sample from 290 nm at an interval of 10 nm. The percentage blocking of UV-A (315–400 nm) and UV-B (280–315 nm) was calculated from the transmittance data. The UPF was calculated using the following equation:

$$\text{UPF} = \frac{\sum_{\lambda=280}^{400} E_{\lambda} \cdot S_{\lambda} \cdot \Delta_{\lambda}}{\sum_{\lambda=280}^{400} E_{\lambda} \cdot S_{\lambda} \cdot T_{\lambda} \cdot \Delta_{\lambda}}$$

where E_{λ} is the relative erythral spectral effectiveness, S_{λ} is the solar spectral radiance. T_{λ} is the average spectral transmission of the specimen and Δ_{λ} is the measured wavelength interval (nm). The UPF equation weighs the UV-B radiation more heavily than UV-A.

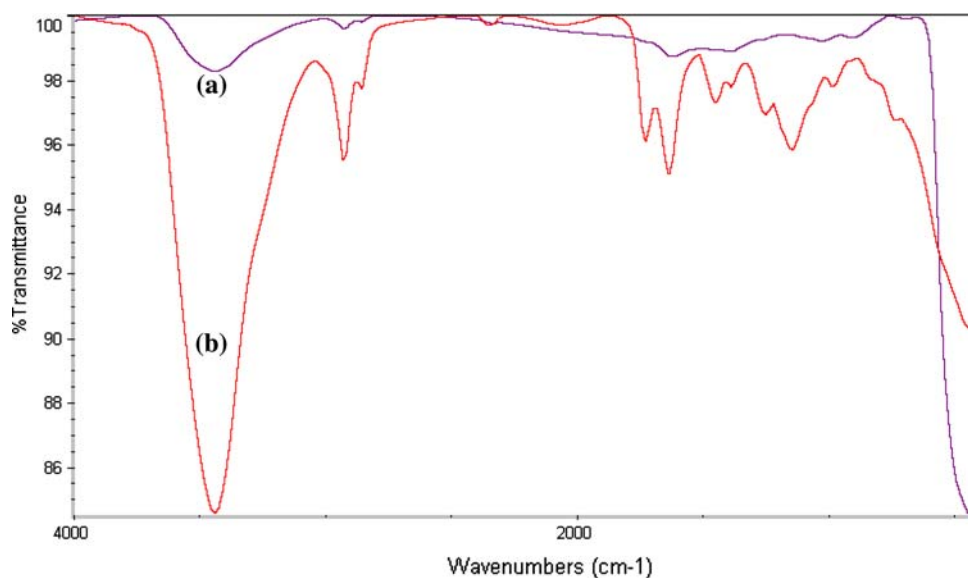
Contact angle measurements were carried out in OCA 20, DataPhysics Instruments GmbH, Filderstadt apparatus using distilled water. Water droplets (5 μL) were delivered to different points of each specimen and from a height sufficiently close to the substrate so that the needle remained in contact with the liquid droplet. Then the delivery needle was withdrawn with minimal perturbation to the drop and the image of the drop was captured immediately for static (θ_s) contact angle measurement.

Results and discussion

FT-IR and XRD

Figure 1a shows the FT-IR spectrum of the synthesized nanoZnO. The spectrum shows clearly ZnO absorption band near 438 cm^{-1} . The peak at 3446 cm^{-1} corresponds to hydroxyl groups (–OH) probably due to atmospheric moisture. The FT-IR spectrum of ZnO–PMMA composite

Fig. 1 FT-IR spectra of (a) ZnO nanopowders (b) ZnO–PMMA nanocomposite



(Fig. 1b) indicates the details of functional groups present in the composite. A broad peak is revealed around 3400 cm^{-1} probably due to the absorbance band from O–H stretching modes of hydroxyl groups on the ZnO surfaces and of adsorbed water molecules within the sample [27]. Peaks ranging from 2929 to 2842 cm^{-1} corresponds to the CH_2 and CH_3 group stretching vibrations of PMMA. A peak at 1727 cm^{-1} appeared due to the presence of ester carbonyl group stretching vibration of PMMA. This peak shift to short wave number compared to that of the standard PMMA FT-IR spectrum. The main reason is that PMMA can coordinate with Zn^{2+} ions in the surface of the ZnO particles and form delocalized π bonds [28]. As a result, the electron density and force parameters of C=O bond in PMMA are decreased. The band at 1634 cm^{-1} shows the existence C=C group stretching vibration of methacrylic acid. A small band at 1346 cm^{-1} may be due to a $-\text{CH}_3$ group [29, 30]. Peaks ranging from 1260 to 1146 cm^{-1} can be explained owing to the C–O (ester band) stretching vibration. Bands at 978 and 737 cm^{-1} are due to the bending of C–H.

Figure 2 shows the XRD spectrum of the ZnO of the synthesized solid nanopowders. The spectrum shows well defined peaks typical of ZnO in the crystal structure of Zincite. The diffractogram of ZnO sample shows characteristic peaks of crystalline ZnO at 2θ values: 31.8 , 34.5 , 36.2 , 47.6 , 56.6 , 62.9 , 66.4 , 67.9 , 69.1 , 72.9 , and 79.9 [31]. This indicates the crystallinity of the synthesized solid. Rather broad diffraction maxima indicate very small size of the crystallites similar to the size of subunits observed by the SEM. Traditionally, the broadening of the peaks in the XRD patterns of solid is attributed to particle size effects [32].

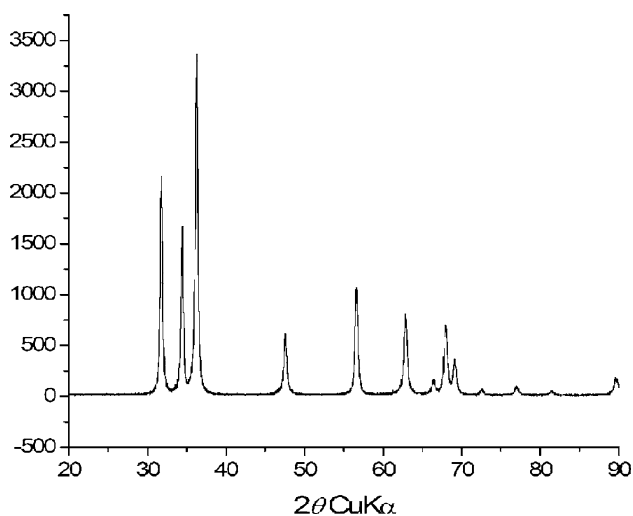


Fig. 2 XRD pattern of ZnO

Morphology of ZnO nanoparticles and ZnO–PMMA nanocomposite films

The particles are granular and the size of the ZnO particles is in the range from 58 nm to 250 nm (Fig. 3). The distribution of particles reflects similar microgranular structures. The size distribution of ZnO nanoparticles in polymer matrix were also confirmed by SEM. Figure 4a–d represents the SEM image of ZnO–PMMA nanocomposite without ZnO, 0.1%, 0.3%, and 1.0% ZnO, respectively. It can be seen that ZnO nanoparticles are well dispersed in polymer matrix. This fact has shown a good adhesion between the surface of ZnO nanoparticles and PMMA matrix.

The SEM figure of nanocomposite shows morphology of ZnO particles protruding above the smooth polymer surface. It is proven that each small aggregate consist of nanostructures that implies an augmented roughness on the nanoscale.

In Fig. 4b–d distinct particle aggregates embedded in a continuous polymer matrix can be observed in the surface of the film produced by using concentrations of 0.1%, 0.5%, and 1.0% ZnO. Smooth areas of polymer film PMMA are found in between the particles.

The figures suggest the randomly distributed protruding particles/aggregates consisting of further nanostructures implying that a two-length-scale hierarchical structure is formed on the surface. It is known that such structures exist in the lotus leaf which exhibit water repellent properties [33].

Figure 5a is the SEM micrograph of the untreated polyamide fabric while Fig. 5b–d represents the polyamide fabric treated with 0.1%, 0.5%, 1.0% ZnO, respectively.

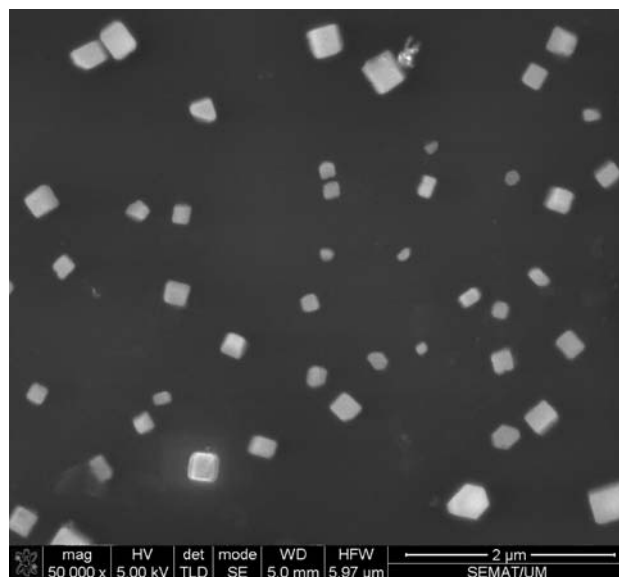


Fig. 3 SEM image of Nano ZnO

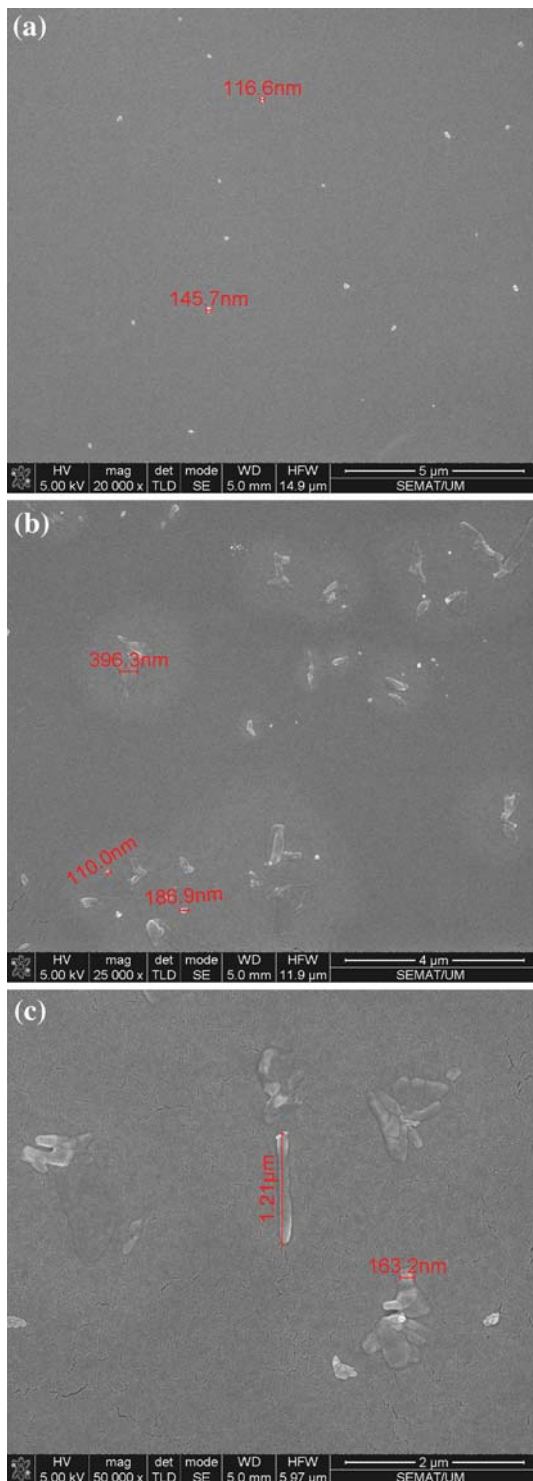


Fig. 4 SEM image of ZnO–PMMA nanocomposite with **a** 0.1% ZnO, **b** 0.5% ZnO, **c** 1.0% ZnO

Shown in the insets are the images of static water droplets (5 μ L) in the immediate contact with the treated fabric.

While it has been observed an even spread through the entire morphology of the polyamide fabric treated with

0.1% and 0.5% ZnO, there is slight agglomeration observed in 1% ZnO treated fabric but the size of the agglomerates are still in nanoscale.

Figure 6a–c shows a typical size distribution profile of nanocomposites with 0.1, 0.5, and 1% ZnO in PMMA. It was found that the nano particles have narrow distribution for size. The *z*-average particle sizes were 377.1 nm (PDI = 0.184), 379.5 nm (PDI = 0.157), and 418.9 nm (PDI = 0.209) for 0.1%, 0.5%, and 1% ZnO in PMMA, respectively. Slight increase in poly dispersity index (PDI) for the sample with 1% ZnO was probably due to slight agglomeration of ZnO nanoparticles. It was also found that the mean particle size of the dispersion was increased with increasing ZnO content. The results were consistent with SEM observations.

Evaluation of ZnO–PMMA nanofinished polyamide fabrics for UV protection

Table 1 shows the values of percent blockings of UV-A (315–400 nm) and UV-B (280–315 nm) regions are 27.4% and 13.8% for the untreated fabric, 7.2% and 5.0% for ZnO (1.0%) coated fabric, 10.4% and 6.1% for nanoZnO (0.5%) coated fabric, and 13.8% and 7.9% for nanoZnO (0.1%) coated fabric, respectively. From this data it can be seen that the nanoZnO coated polyamide fabric showed efficient blocking of UV radiation in both the regions. It can be construed that the presence of higher amount of nanoZnO has lead to the higher absorption of UV rays in both ranges as the fabric coated with 1% nanoZnO showed better absorption than the 0.1% nanozinc coated fabric.

The UPF factor for the untreated polyamide fabric is calculated to be 6.6 while it is 19.4, 15.7, and 11.9 for 1%, 0.5%, and 0.1% concentration of nanoZnO nanocomposite coated fabrics, respectively. About three-fold increase in UPF factor has been obtained with this nanofinishing in comparison with control fabric. In the case of ZnO–PMMA treated fabric, the concentration of ZnO plays a crucial role in the enhanced efficiency of UV protection. The higher the concentration of nanoZnO present in the fabric leads to enhanced absorption of UV rays giving better protection (Fig. 7). Even at low concentration (0.1% ZnO) the efficiency of UV protection can be attributed to the uniform spreading of nanoZnO (as seen in the SEM micrograph) and enhanced absorption of ZnO nanoparticles in the UV-A and UV-B regions.

Measurement of superhydrophobicity

The characterization of superhydrophobic surface is one of the key issues in the research of superhydrophobic surfaces. Till now many methods have been developed to characterize the superhydrophobicity of a surface such as

Fig. 5 **a** SEM micrograph of the untreated polyamide fabric. SEM micrograph of polyamide fabric treated with **b** 0.1% ZnO, **c** 0.5% ZnO, **d** 1% ZnO

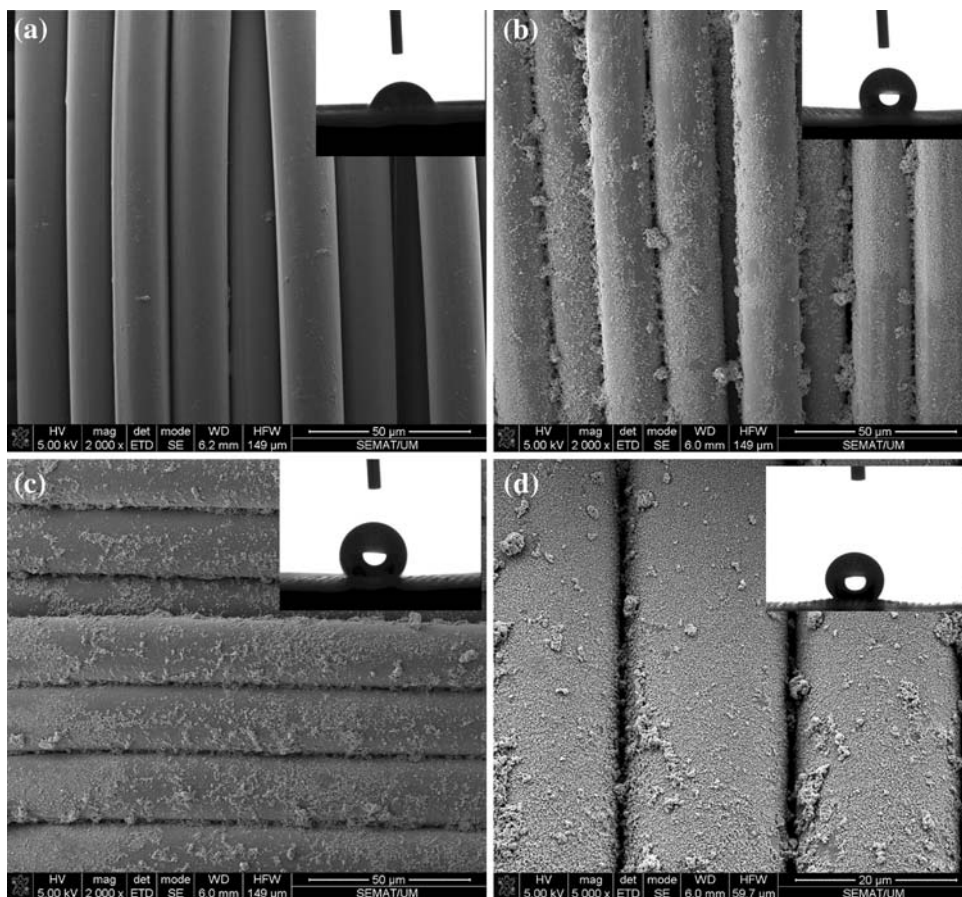


Fig. 6 Particle size distribution of ZnO nanoparticles in PMMA with 0.1% (a), 0.5% (b), and 1% (c) ZnO nanoparticles

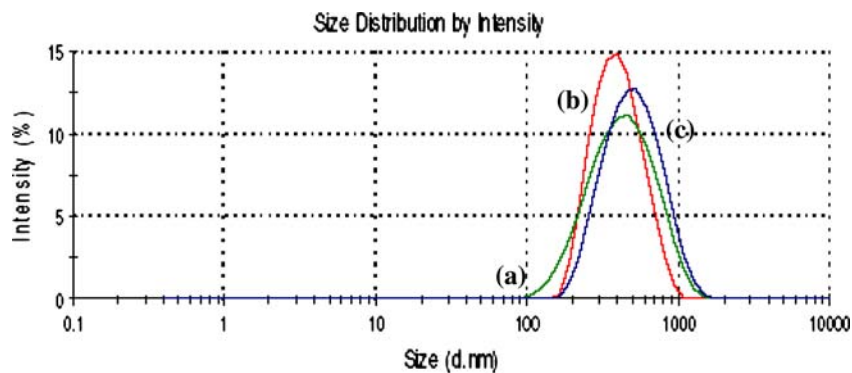


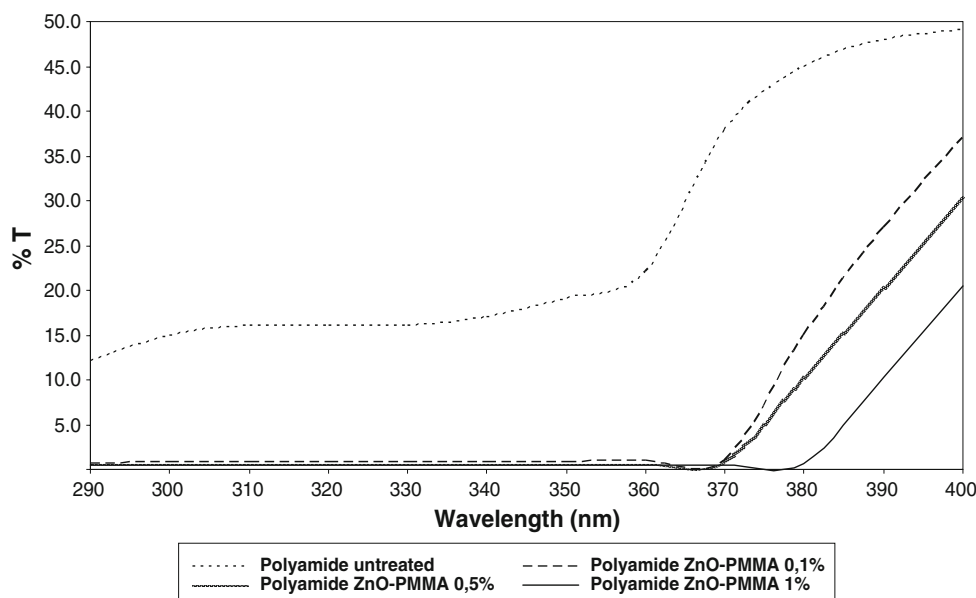
Table 1 UV transmissions (%) of PMMA–ZnO treated polyamide fabric

UV transmission (%)				
Nanometer range	Untreated fabric	PMMA with 1.0% ZnO	PMMA with 0.5% ZnO	PMMA with 0.1% ZnO
UV-A (315–340 nm)	27.4	7.2	10.4	13.8
UV-B (280–315 nm)	13.8	5.0	6.1	7.9

contact angle, tilt angle, and multiresonance thickness shear mode sensor (MTSM). Among them, the contact angle measurement is the main method of characterization of superhydrophobic surfaces. When the contact angle (θ) is $0^\circ \leq \theta < 90^\circ$ the surface is hydrophilic and when the

contact angle is $90^\circ < \theta \leq 180^\circ$ the surface is hydrophobic. There are numerous studies which define superhydrophobic surfaces as those having water contact angle close to or higher than 150° [34]. It should be noted that, due to the fibers sticking out from the fabric sample, the

Fig. 7 UV–visible transmission spectra of polyamide fabrics, representing control fabric and 0.1%, 0.5%, 1.0% ZnO coated polyamide fabrics



measurement of contact angles is often not straightforward, in terms of the difficulty of determining the baseline of the water droplet, which may in turn lead to possible underestimation of the contact angle data. Additionally, because the protruding fibers have some elasticity and can thus exhibit forces on the water droplet [35], it is also difficult to yield accurate values for advancing and receding water contact angles, so only static CAs by tangent searching mode of fitting for 5 μ L water droplets are reported here.

The main objective of pretreatment of polyamide fabric with plasma discharge is to increase its wettability to absorb more PMMA–ZnO when applied on it. Surface chemical and morphological changes occurred during plasma treatment were proved by earlier studies [23, 24]. The CA of untreated fabric is 85° (Fig. 8a) while after plasma treatment it is 52° (Fig. 8b). As expected with plasma treatment the hydrophilicity is increased and ultimately the desired wettability is achieved which will allow better absorption of the PMMA–ZnO finishing on the fabric. The water static CAs are 158°, 163°, and 164° for 5 μ L droplet on the fabric treated by 0.1%, 0.5%, and 1.0% ZnO nanofinishing, respectively. The samples are completely water nonwetable being considered as superhydrophobicity. In the case of pure PMMA, the contact angle was 87° (Fig. 8c). When ZnO–PMMA finishing was applied, the contact angles were found to be in the range from 158° to 164°. The contact angle data corresponding to particles concentration of 0.1%, 0.5%, and 1.0% ZnO concentrations show that the contact angle increases as the particle concentration increases from 0.1 to 1.0%.

It was found that the superhydrophobicity is achieved even at low concentration of 0.1% of nanoZnO. With the further increase in concentration gives no significant

increase in superhydrophobicity of the surface. It may be due to the fact that particle size or nature has more effect on the minimum particle concentration that is necessary to achieve superhydrophobicity. From the contact angle data, it is understood that once superhydrophobicity is achieved the increase in concentration of nanoparticles does not have any important effect on the wettability of the surfaces particle finished with ZnO–PMMA.

With the introduction of ZnO nanoparticles in PMMA matrix, the roughness of the finishing on the fabric increases. As the roughness increases, the contact angle increases according to the equation of Cassie and Baxter [14] as explained in the earlier section. Once roughness increases and reaches a certain level, air may become trapped between the nanoparticles underneath a water droplet, which would further enhance superhydrophobicity.

Conclusions

Based on the analysis of the results of the experimental study the following conclusions can be arrived:

- This work gives novel and simple method of development of ZnO–PMMA nanocomposites and its application on polyamide fabrics to impart superhydrophobicity and UV protection functions. The dispersion of ZnO nanoparticles is uniform in the polymer matrix PMMA at nanometer level as evidenced by the SEM analysis. The ZnO nanoparticles were analyzed through X-ray diffraction and SEM and FT-IR for their characterization. The nanoparticles size ranges from 58 to 250 nm as seen in SEM micrograph of the nanoparticles.

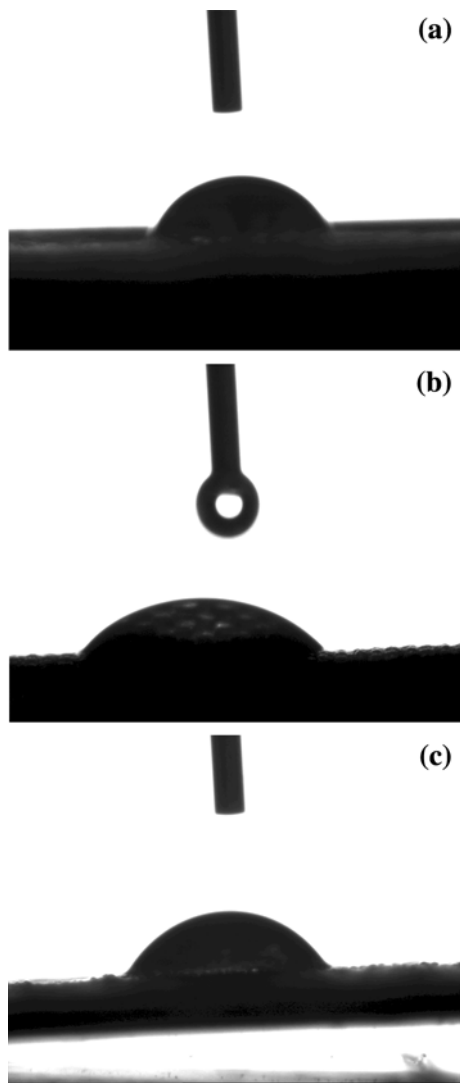


Fig. 8 Measurement of contact angle on **a** control fabric before plasma treatment **b** control fabric after plasma treatment **c** fabric with PMMA without ZnO

- The ZnO–PMMA nanofinishing on fabric proved to have better UV protection property than the untreated fabric. The broad band absorption of detrimental UV radiation and high transmittance of natural visible light make the ZnO–PMMA nanofinishing a very efficient UV protection for the UV shielding polyamide fabrics.
- Combination of low surface energy PMMA and nanosize ZnO in ZnO–PMMA nanofinishing on polyamide fabrics provides superhydrophobicity. In conclusion, the results provided a very easy and economical method for fabricating superhydrophobic polyamide fabrics. The superhydrophobicity of the fabric is achieved even at low concentration of 0.1% of ZnO in the polymer nanocomposite.

There is no doubt that in next few years polymer nanocomposites will penetrate into every area of textile industry. The present work can be exploited for the commercialization in the case of consumer textile with multifunctional properties such as UV resistance and desired wettability.

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