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Polymer Nanocomposites for Multifunctional Finishing of Textiles - a Review

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What is This?

# Polymer Nanocomposites for Multifunctional Finishing of Textiles – a Review

**Abstract** Improvement of existing properties and the creation of new material properties are the most important reasons for the functionalization of textiles. Polymer nanocomposites offer the possibility of developing a new class of nanofinishing materials for textiles with their own manifold of structure property relationship only indirectly related to their components and their micron and macro-scale composite counterparts. Though polymer nanocomposites with inorganic filler of different dimensionality and chemistry are possible, efforts have only begun to uncover the wealth of possibilities of these new materials. Approaches to modify the polymer nanocomposite system by various inorganic or organic substances can lead to a huge number of additional functionalities which are increasingly demanded by the textile industries. In this review, we have compiled the current research in polymer nanocomposite-based nanofinishes for multifunctional textiles which provides a snapshot of the current experimental and theoretical tools being used to advance our understanding of polymer nanocomposites and their applications in textiles.

**Key words** functional textiles, nanoparticles, polymer nanocomposites

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The increasing demand for multifunctional fabric materials requires a strong multidisciplinary approach as well as the merging of traditional scientific disciplines [1–3]. The first commercial application of nanofinishes is found in textiles in the form of nanoparticles through finishing processes. However, these finishes do not withstand subsequent washing due to poor fixing of these nanoparticles on the textile surface. Assuring improved bonding of the nanoparticles with textile surfaces not only increases the durability property, but also provides an ecofriendly consideration of preventing release of loosely-bound nanoparticles into the environment. Using hydrophobic/hydrophilic functional polymer matrices as the dispersion medium for the nano-

particles will result in polymer nanocomposites (PN) with improved bonding properties and impart desired wettability with different functional properties like ultraviolet (UV) resistance, antimicrobial and flame retardancy which are unique characteristics of different nanoparticles. In this review article, we focus mainly on the applications of PN to textiles for achieving desired wettability, UV protection, antimicrobial and conductivity properties.

Nature has already developed PN with an elegant approach that combines chemistry and physics to create

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super-repellent hydrophobic surfaces. Lotus leaves are unusually water-repellent and keep themselves spotless due to micro protrusions and hydrophobic wax covering the surface [4, 5]. A surface with receding and advanced water contact angle above 150° is considered to be ultrahydrophobic. In fact, surfaces with water contact angle more than 150° can be developed by introducing proper roughness on a material's boundary having low surface energy [6-8]. Classical work of Wenzel [9] and Cassie and Baxter [10] established that roughness as well as surface energy are the factors that determine wettability of a surface. It was proved that increasing the surface roughness enhances both hydrophilicity of hydrophilic surfaces and hydrophobicity of hydrophobic surfaces. Therefore, addition of nanoparticles to the hydrophobic/hydrophilic functional polymers will improve the properties of the polymer with additional incorporation of the functional properties of nanoparticles. Gao and McCarthy emphasized that contact angle hysteresis (the difference between the advancing and receding contact angles), and not high contact angle, controls water-repellency of a surface [11].

Moisture management/hydrophilic finishes on textiles are very important to impart absorbency, which is one of the main considerations in the applications of sportswear which are generally made with functional jersey with cellulosic fiber on the outside. The mode of action consists of the finest fibrilled microfibers transporting moisture rapidly from the skin through the capillary interstices to the absorbent outer layer.

The properties imparted to textiles having PN include UV protection, antibacterial, flame retardancy, antistatic and conductivity. The inorganic UV blockers are preferable to organic blockers as they are non-toxic and chemically stable under exposure to both high temperature and UV. Usually certain semiconductor oxides such as TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> are used as UV blockers [12, 13]. Rayleigh's scattering is dependent upon the wavelength where the scattering is inversely proportional to the wavelength to the fourth power. This theory predicts that in

order to scatter UV radiation between 200 to 400 nm, the optimum particle size will be between 20 to 40 nm. For imparting antibacterial properties, nanosilver, TiO<sub>2</sub> and ZnO are used [14–17]. Nanosilver is very reactive to protein when contacting with bacteria and fungus; it will adversely affect the cellular metabolism and inhibit the cell growth [18]. Fabrics treated with nano TiO<sub>2</sub> can provide effective protection against bacteria and discoloration of stain due to the photo catalysis effect of this agent [19, 20]. Nano ZnO provides effective photo catalytic properties once it is illuminated by light and it is employed to impart antibacterial properties to textiles [21–23].

Some inert textile surfaces need to be pretreated making certain functional groups available for bonding with PN finishing. Some of the treatments, such as hydroxylamine treatment and plasma discharges, are used for surface pretreatment of fabrics [24, 25]. Plasmatic treatments in several textile substrates like cotton, linen, wool and synthetic fibers were studied proving that this type of treatment increases whiteness degree, removal of waxes and sizing agents, absorption and fixation of dyes and finishing agents, improves durability of functional effects and is able to provide certain functional groups available to bind PN [26-30]. Alay et al. [31] studied the effect of plasma treatment of cotton fabrics on fluorocarbon-based water-repellent finishing. It was found that the hydrophobicity of the fabric is significantly improved after plasma pretreatment and the hydrophobic character is maintained even after five washings with contact angle higher than 120° (Figures 1 and 2).

# The PN Finishing Concept in Textile Applications

What are PN and what makes them interesting in textile applications? The answer to these questions resides in the fundamental length scales dominating the morphology and

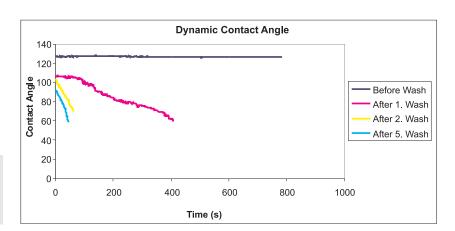


Figure 1 Dynamic contact angle in cotton fabric treated with fluoro-carbon finishing without Corona/DBD plasma treatment.

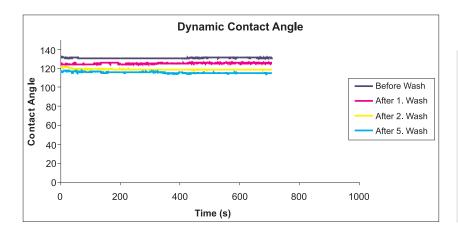
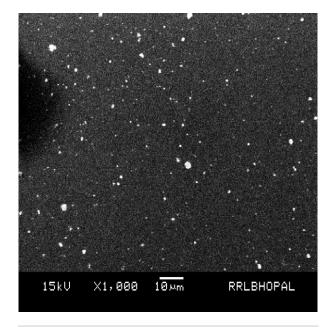


Figure 2 Dynamic contact angle in cotton fabric treated with fluorocarbon finishing with Corona/DBD plasma treatment. The conditions of the plasma treatment were: the samples were treated under conditions of 1.5 kW power and 2.5 m/min velocity by using a laboratorial prototype Lisboa Corona machine designed and constructed by Softal Electronics.

properties of these materials. PN are an emerging class of mineral-filled polymer that contain relatively small amounts (usually < 10%) of nanometer-sized inorganic particles. They represent a radical alternative to the conventional polymer composites [32–36]. Three major characteristics define and form the basis of PN performance: nanoscopically-confined matrix of polymer; nanoscale inorganic constituents; and nanoscale arrangements of these constituents. The drive for current research is to optimize and enable full exploitation of the potential of their unique characteristics in the textile industry.

PN are prepared by mixing a polymer (or monomer) with dissimilar material or additives that have one or more dimensions on the nanometer scale. Over the past few decades, a wide variety of materials and synthesis approaches has been developed that allows molecular-level control over the design and structure of nanocomposite materials. PN have been prepared by sol-gel methods [37], by *in situ* polymerization routes and by using simple compounding methods [38]. All of these approaches share a common theme, the intermingling on the nanometer scale of dissimilar materials with properties not available from either of the component pure materials.

The retention of homogeneous dispersion of nanosized particles in the preparation process of nanocomposites is very difficult, since there is a strong tendency for nanoparticles to agglomerate. In the form of PN, the polymers can effectively inhibit the aggregation of the nanoparticles and keep the nanoparticles well dispersed in polymer solution. The surface interaction does not seem to affect the structure of the nanoparticles. The polymers significantly increase the stability of the composite particle dispersion and its compatibility within polymeric matrix, making the application of nanoparticles in many fields easier. We have studied polyvinyl alcohol (PVA) as the polymer system and various nanoparticles such as Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZnO with particle size ranging between 20-150 nm as the inorganic particles. The polymer composites were prepared by dissolving 1 g of PVA in 35 ml deionized water



**Figure 3** SEM image of polymeric film with  $Al_2O_3$ .

and stirring with a magnetic stirrer for one hour, then mixing with 2 Wt% of each nanoparticle separately and stirring until the solution became clear. The solutions were spin-coated on treated silicon wafers and dried in a vacuum oven for one hour at 90 °C. Silicon wafer substrates before applying the coatings were initially cleaned with deionized water in an ultrasonic bath for 30 minutes. The wafer was then placed in piranha solution (3:1 concentrated sulfuric acid:30% hydrogen peroxide) for approximately one hour, and then rinsed several times with deionized water. Following rinsing, the substrates were dried under a stream of nitrogen. Scanning electron microscopy (SEM) analysis was performed on the resultant substrates. The SEM figures (Figures 3–7) show dispersion of

Figure 4 SEM image of polymeric film with CaO.

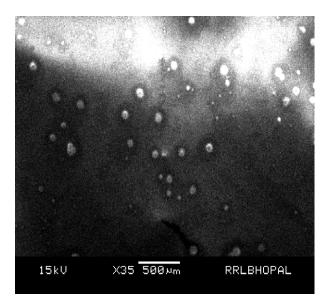


Figure 5 SEM image of polymeric film with Fe<sub>2</sub>O<sub>3</sub>.

oxide nanoparticles in PVA. It can be seen that the nanoparticles are well dispersed in polymer matrix, i.e. PVA. The SEM images show the morphology of the nanoparticles and the particles are loosely agglomerated. The PVA polymers can effectively inhibit the aggregation of the nanoparticles and keep the nanoparticles well dispersed in PVA matrix or aqueous PVA solution on the nano-meter level.

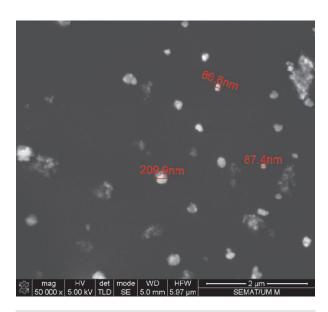


Figure 6 SEM image of polymeric film with SiO<sub>2</sub>.

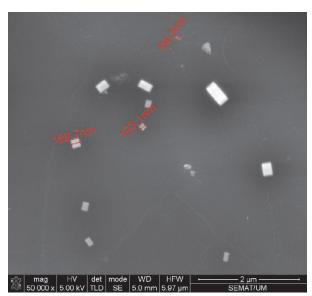


Figure 7 SEM image of polymeric film with ZnO.

An example of the way to combine tradition and innovation is represented by fibers having skin care activity, which are able to release on the wearer cosmetic and perfume agents. The active agent embedded into the fabric can be transferred by humidity exchange between skin and fiber surface [39, 40]. For this application, the nanofiller acts as a carrier which absorbs and promotes the dispersion of the cosmetic substance through the polymer matrix.

**Table 1** The effect of plasma discharge and repeated washing on the silver concentration in samples finished with Silpure FBR-5.

Sample property	Concentrati	Concentration of silver (%)	
_	Before wash	After 30 washes	
With Corona/DBD plasma treatment	0.55	0.10	
Without Corona/DBD plasma treatment	0.27	Below detection limit	

Wash fastness is a particular requirement for textiles and it is strongly correlated with the binding of nanoparticles to the fibers. Alay et al. [31] studied Corona/double barrier discharge (DBD) plasma-treated and untreated 100% cotton fabrics finished by nanosilver compound Silpure FBR-5 (Thomson Research Associates) with a 30 g/l concentration to investigate the washability of antibacterial finishing following the treatment. Padded fabrics were cured at 170 °C during 1.5 minutes. The samples were analyzed using the ICP elemental analysis method to determine the effect of plasma on the washability of antibacterial finishing. The results showed that Corona/DBD plasma treatment increases the washability of antibacterial nanosilver finishing on the fabric. The silver concentrations of treated and untreated samples finished by Silpure FBR-5 are given in Table 1. Silver concentration in samples plasma discharged and finished with 30 g/l of Silpure FBR-5 is higher than that of samples without plasmatic treatment.

Wash fastness can still be improved with the formation of covalent bonding between nanoparticles and textile surface through polymer matrix [41, 42]. In practical applications of PN in textiles a polymer matrix can stabilize nanoparticles, preventing their aggregation and serving as a protection shell against the environment. Inorganic nanoparticles can be embedded not only in bulk materials and their film, but also in the walls of polymer capsules [43–46].

Now, the preparation of PN by melt blending a polymer and nanoparticles is a straightforward procedure, but due to the agglomeration of nanoparticles it is less efficient when the reinforcing nanoparticles are of nanoscale dimensions. To overcome this limitation, a fine strategy was proposed by Hausslein and Fallick [47]. A second approach was also proposed which relies upon the chemical modification of the nanoparticle surface by functional silanes and titanate esters. These coupling agents promote adhesion of the nanoparticles to the polymer matrix [48–53]. There are also some other methods such as *in situ* sol-gel processing of nanoparticles from suitable precursors for PN [54].

Two principal ways can be considered for the use of PN in textile applications. Melt spinning of PN yarns which can be subsequently woven or knitted has been demonstrated for textile applications [55]. Coating of textile surface by PN formulation is another interesting way which has not been investigated to date. In addition, the latter approach

confers to textile surfaces combined functional properties. Also, the use of PN allows a reduction in the weight content of additives.

Several methods can apply the PN to fabrics, including spray transfer printing and padding. Of these methods, padding is the most commonly used. The PN are attached to the fabrics with the use of a padder adjusting to suitable pressure and speed, followed by drying and curing.

There are many reasons for the interest in using PN coatings to functionalize textiles:

- PN with oxide nanoparticles form well-adhering transparent oxide layers on textiles.
- These oxide layers are very stable against high heat, chemical and microbial attack.
- They influence the mechanical properties of textiles, whilst offering possible methods of varying the surface properties.
- The oxide coatings can act as a carrier for embedded functional additives such as organic or biological compounds, inorganic particles and polymers since it is easy to control layer porosity and the degree of immobilization of the embedded compounds.
- The coatings can be prepared at room temperature and normal pressure in conventional coating devices used for textile finishing such as pad application or exhaust processes. Also, ordinary processes like dipcoating or spraying can be used.

### Application of PN for Desired Surface Wettability Properties

The primary parameter that characterizes wettability of a surface is the static contact angle ( $\theta$ ), which is defined as the measurable angle that a liquid makes with a surface. The contact angle depends on several factors, such as roughness and the manner of surface preparation and its cleanliness. If the liquid wets the surface and the value of static contact angle is  $0 \le \theta \le 90^\circ$ , it is referred to as hydrophilic surface; whereas if the liquid does not wet the surface and the value of the contact angle is  $90^\circ \le \theta \le 180^\circ$ , it is referred to as hydrophobic surface. In the case of textile materials, the level of hydrophobicity is often deter-

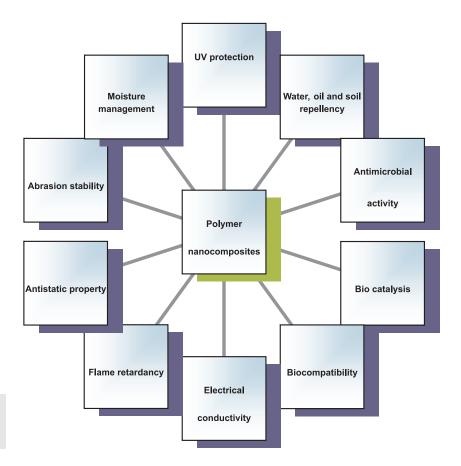


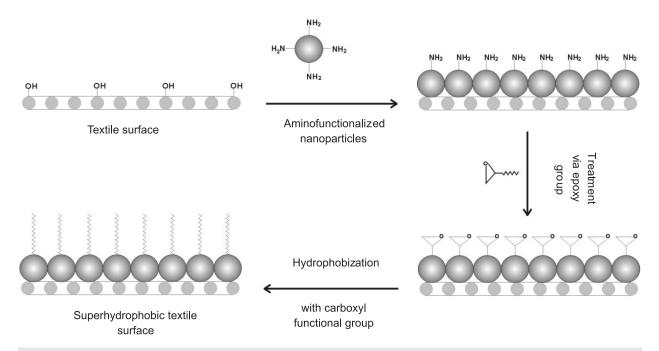
Figure 8 Some possibilities of textile functionalization using polymer nanocomposites.

mined by measuring the static water contact angle only, since it is difficult to measure the contact angle hysteresis on a textile fabric because of the high levels of roughness inherent in textile structures. PN confer desired wettability properties to textiles like hydrophilicity and hydrophobicity depending on the area of requirement of textile applications. In addition, PN can be used for achieving countless functional properties (Figure 8).

### Superhydrophobic, Self-cleaning Textile Finishes using PN

Superhydrophobic surfaces have considerable technological potential for textile applications due to their extreme waterrepellent properties. Finished surfaces with a high contact angle can also exhibit a self-cleaning effect. Extremely waterrepellent superhydrophobic surfaces can be produced using roughness of nanoparticles combined with hydrophobicity of polymer matrix. Effective attempts have been made to incorporate hydrophobic compositions such as organic silicon and organic fluorine into the synthesized materials [56–58]. By adopting such methods, the contact angle of the resultant surface can easily reach as high as 120°. However, for conventional technologies, great difficulties still exist in reaching higher values of water contact angle. With the fast development of nanotechnology, it has been possible to fabricate the superhydrophobic surfaces from the micro-cosmic scale by diverse techniques including the solgel method [59], self-assembly [60, 61], plasma treatments [62, 63], laser etching [64], etc. Nevertheless, these methods normally require special equipments and stringent conditions. A simple method of obtaining a superhydrophobic surface for wool textile finishing has been reported by Zhang et al. [65]. Their method involves devising a comblike polymer comprising acrylate and organic siloxane. This combination can exhibit some unique characteristics like an increase of the cohesiveness and film form-favoring properties. Also, the long Si-O-Si chain with low surface energy can be utilized to enhance the water-repellency.

The textile surface modification methods mainly include sol-gel methods to fabricate a fluorinated inorganicorganic coating on polyamide 6.6 textiles [66], grafting poly(acrylic acid) on a polyamide polymer surface and then grafting fluoroamine or alkylamine on the poly(acrylic acid) chains [67]. Cotton-based superhydrophobic surfaces can be fabricated mainly by modification of hierarchical nanos-



**Figure 9** Schematic illustration of preparation of superhydrophobic surfaces on textiles using polymer nanocomposite finishing.

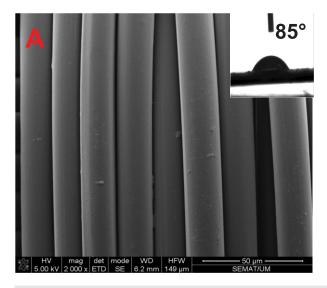
cale structure that can confer superhydrophobicity on the cotton substrates. These modification methods include solgel deposition of silica nanoparticles modified with fluorinated silane-coupling agents [68], deposition of poly(butilarylate)-modified carbon nanotubes [69], and deposition of gold nanoclusters followed by chemisorptions of n-dodecanethiol, self-assembled monolayers on cotton textiles [70]. With these modifications, the wetting property of cotton textiles can change from hydrophilic to superhydrophobic, meanwhile, the other properties of textiles such as warmth and softness can be kept to some extent.

Ming and his co-workers [71] reported a method for preparing superhydrophobic films, which mimic the surface topology of self-cleaning plant leaves, from silicabased raspberry-like particles covalently bonded to an epoxy-based polymer matrix. The robustness and simplicity of this method make it suitable for widespread applications including textiles. A PN-based approach was taken by Hoefnagels et al. [72] for the fabrication of superhydrophobic cotton textiles. A one-step or two-step reaction generated in situ silica particles with amine groups on their surface, which were covalently bonded to the cotton fibers. The amine groups were then utilized to hydrophobize the surface via the reaction with mono-epoxy-functionalized polydimethylsiloxane. In addition to the approach mentioned above, superhydrophobic cotton fabrics were prepared by surface hydrophobization by Chao et al. [73]. The above

studies [71–73] show the possibility of preparing superhydrophobic surfaces on textile through functionalization of nanoparticles, as shown in Figure 9.

Using poly glycidyl methacrylate (PGMA) as an anchoring interlayer, Viktor et al. [74] synthesized a suitable polymer nanolayer on the surface of a Poly(ethylene phthalate) (PET) fabric, which was hydrophobic after exposure to toluene and hydrophilic after exposure to methyl ethyl ketone. The wettability changes are reversible. They also used the PGMA layer to attach an initiator for atom transfer radical polymerization to the textile surface and conducted grafting of polymers initiated from the surface to synthesize the layer possessing high grafting activity.

Various fluorine-based PN have been used because of their high water and oil resistance, organic solvent resistance and lubricity [75]. These PN have been commonly used for hydrophobic applications because of their lower surface energy property. It has been reported that the surface free energy decreased in the order -CH<sub>2</sub>>-CH<sub>3</sub>>-CF<sub>2</sub>>-CF<sub>2</sub>H>-CF<sub>3</sub> which predicts that the close hexagonal packing of -CF<sub>3</sub> group gives the lowest surface free energy of the material [76]. Hence, ultrahydrophobic surfaces have been generally prepared by modifying the surface with various fluorinated polymer base PN such as Poly(tetrafluoroethylene) (PTFE) coating [77, 78], fluoroalkylsilanes [79, 80] and perfluorinated polymer nanolayers [81]. Karthick et al. studied methods to create surfaces that lead



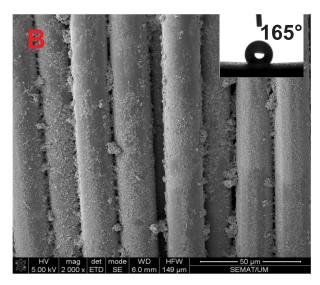


Figure 10 SEM images of untreated (A) and ZnO/PMMA-treated (B) polyamide fabric surfaces. Shown in the insets are the images of static water droplets (5  $\mu$ l).

to ultrahydrophobicity using hydrophobic polymer/nanoparticles system. Regarding this system, the silver nanoparticles approach was found to have a slight or no aggregation problem. The result with both the silver and silica nanoparticles independently showed that fabric construction is an important parameter to consider when attempting to create lotustype fabrics [82]. Recent research on the development of ZnO-polymethylmethacrylate (PMMA) nanocomposites and their application to polyamide fabric showed that the contact angles increase significantly by the application of these nanocomposites [83]. Superhydrophobic surfaces have been successfully prepared on polyamide fabric by the above strategy (Figure 10).

### Moisture Management/Hydrophilic Textile Finishes using PN

The application of PN is expected to serve synthetic textiles particularly well, as no such hydrophilic finishing exists in the fields of sportswear and underwear which require perspiration absorbency.

As one of the most widely used textile materials, wool is mainly applied in cold weather clothing because of its excellent insulation quality, resilience and felting properties. To widen the application of wool fiber, it has been considered for close-fitting clothes. Wool fiber can absorb large amounts of water vapor; its moisture regain is about 13.6% under standard conditions. The water cannot be absorbed by wool raw fibers because of the water repellence of the surface layer of the wool scales (cuticles) [84]. Besides, the scratching effects from the coarse fibers that

stick out of the yarn make it difficult to use for close-fitting clothes. Wool fabric, with its fiber cuticle scale layer removed, has good water absorption properties [85]. However, obtaining water absorption properties by the removal of the scales of wool fiber is not worthwhile, because of the high expense of further finishing and the loss of original properties of wool. Techniques to produce pure wool fabric with good water absorption are still unavailable.

The use of PN as fiber-forming polymers makes it possible to produce fibers with increased functionality and new features, incomparable with those of conventional synthetic fibers. Heat-resistant polyimidoamide (PIA) fibers with increased porosity and moisture absorption and with tenacity being suitable for textile processing [86, 87] have been obtained by modification of the fiber-forming polymer and proper selection of fiber-spinning conditions. These features are of great importance for protective clothing as they provide an enhanced comfort for its use. However, the increased fiber porosity may result in some decrease in the protective property of clothing against flame.

The montmorillonite packages coated with a thin layer of carbonized polymer on their structure, and dispersed in the fiber-forming polymer matter constitute a barrier which cuts off oxygen access and consequently prevents flame propagation. At the same time, the laminar structure of montmorillonite and the strongly developed interface surface provide an increased porosity and moisture absorption to the fabrics.

Studies of nanosilica-containing PIA fibers made from other fiber-forming polymers have shown [88] that the incorporation of nanoparticles leads to increased fiber porosity and moisture absorption. This feature is important for heat-resistant protection clothes, as it provides improved comfort of use, extending the functional use of the resultant fiber. Mikotajzyk and Magdalena found that by selecting the proper conditions for spinning fibers from PIA nanocomposites, multifunctional properties such as highly porous, with good thermal stability and water absorption can be obtained [89].

Qufu et al. studied the use of  $\mathrm{TiO}_2$  in polypropylene fibers [90]. The fibers were prepared by melt-compounding and sputter coating, respectively. They found that the hydrophilic nature of the fiber surface is only slightly increased by melt-compounding. Hydrophilicity is increased much more after sputter coating, as would be expected from better surface coverage by  $\mathrm{TiO}_2$  nanoparticles.

The development of alginate fibers has been stimulated to a growing extent by their utilization for the production of novel dressing material. In addition to basic features such as high moisture absorption and capability to be partly gelatinized [91], the alginate dressings are also capable of supporting the wound healing process because of the specific properties of mannuric acid. The alginate fiber is used for the production of most commercial dressing materials consisting of calcium alginate or calcium-sodium alginate. High moisture absorption values, being crucial to the use of alginate as dressing materials, are connected mostly with the hydrophilic character of the polymer. On the other hand, the effect of the porous structure created during fiber-forming processes on moisture absorption properties is considerably smaller than that in the case of hydrophobic fibers [92]. Mikotajczyk et al. [93] studied the effects of the structure of polymers and nanosilica additives on the water absorption properties of various alginate fibers. It has been found that regardless of the differences in the chemical structure and the presence of nanosilica, the examined types of alginate fibers show similar values of moisture absorption at relative humidity up to 85%. It has been found that the amount of moisture absorbed by the fiber-forming polymer of alginate fiber exerts a strong influence on its electrical properties.

## Application of PN for Desired Functional Properties in Textiles

By changing the surface structure of textiles by PN, several diverse textile functionalities can be obtained for profitable exploitation of functional textiles in special applications.

Out of the many possible applications of PN for functional properties other than surface properties, some of the most successful ones are antimicrobial, UV protection, flame retardancy and conductivity properties of textiles.

### Pn in Antimicrobial Finishings of Textiles

Heavy metals are usually toxic and very reactive with proteins [94, 95]. They are believed to bind protein molecules, the cellular metabolism is inhibited and the microorganism dies. For instance, silver is referred as an antiseptic and disinfectant [96]. Bacterial cells are constantly exposed to stressful situations and an ability to resist these stresses is essential for their survival. The powerful antimicrobial activity of silver is known to be effective against nearly 650 types of bacteria. In literature, silver is reported to be skin friendly and does not cause skin irritation [97].

PN with silver nanoparticles are supposed to improve the properties of textiles. Silver PN deposited on textile surfaces can be used to make smart functional textiles, which have great potential for application as antibacterial materials.

Poly(acrylic acids)-silver nanoparticles have attracted much interest in recent years due to the wide range of their applications that span from inkjet printing [98] and the creation of stimuli-responsive films [99] to the enhancement of fluid thermal conductivity [100] and as surface-enhanced spectroscopy substrates [101]. Poly(acrylates) can actually act as growth modifiers in inverse micellar solutions for silver nanoparticles [102].

Ester et al. [103] synthesized silver-poly(acrylate) clusters and used them to functionalize cotton, wool, and polyester samples in order to obtain antimicrobial textiles for biomedical applications. The treated textiles exhibit antimicrobial activity for *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Pseudomonas aeruginosa* and *Candida albicans*, depending on the strain, as indicated by the inhibition ring and the absence of growth underneath and on top of the fabric.

Marek et al. [104] studied the application of hybrid (SiO<sub>2</sub>/Ag) silica particles with nanosilver introduced into the polymer matrix and deposited on the textile surface. Microbiological tests were carried out on these textiles and confirmed their good antimicrobial activity. The role of silica spheres in SiO<sub>2</sub>/Ag is as Ag metal carriers and effective matrix causing good dispersion of silver nanoparticles in polymer matrix.

Chitosan, a natural polysaccharide is a derivative of chitin that comes from the shells and exoskeletons of some crustacea. The polymer is antibacterial, non-toxic, biodegradable and biocompatible [105–111]. Research work has been done on the preparation of chitosan/silver nanocomposites in solid forms, such as fibers, powders and films [111–115]. Yeon et al. [116] developed an emulsion of chitosan-silver oxide nanoparticles which can be easily applied onto textile fabrics using conventional pad-dry-cure process. The finish was found to be durable and wash fast as it remained effective after 20 washings. It may offer another antibacterial finishing option for the textile industry.

Nanosized TiO<sub>2</sub> is of great interest in the development of PN due to its high chemical stability, non-toxicity and

good heat resistance [116–118]. Nano TiO<sub>2</sub> has three crystal structures: anatase, rutile and brukide. Anatase has higher activity and is particularly suitable for use as an antibacterial material [119, 120]. The interaction between nano TiO<sub>2</sub> and the fabric substrate is relatively weak, and therefore the durability would normally be affected. TiO<sub>2</sub> PN form would solve the problem of poor binding of nano TiO<sub>2</sub> with the fabric substrate.

The antibacterial properties of nano TiO<sub>2</sub> dispersions and treated cotton fabric were studied by Deng et al. [121]. Aqueous nanodispersions of the nano TiO2 exhibited positive results as an antibacterial finishing agent for cotton fabrics. The treatment solution of nano TiO<sub>2</sub> possesses antibacterial rates of over 92% and 88.9% against Escherichia coli and Bacilus subtilis, respectively. The treated fabrics were found to be slightly down graded, but still maintained over 89% and 83% of reduction towards the same bacteria. After 50 washings, the antibacterial performance of the treated fabric still remains at a relatively high level, indicating the durable characteristics of nano TiO<sub>2</sub> treatment.

Rinat et al. [122] demonstrated the ability of organoclays to render PN biocidal. Their approach provides an alternative to surface modification on coating technologies in the production of self-sterilized surfaces. However, their study shows that biocidal modifiers migrate from the clay and nanocomposites. Therefore, polymer/clay technology can be applied only in fields where surface migration is acceptable, for example in textile applications provided the washing operations are carefully done.

#### PN for UV Protection of Textiles

To impart UV protection, several PN can be applied on textile material. The most common nanoparticles used are ZnO, TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. They provide a protection benefit by reflecting, scattering or absorbing harmful UV. Due to the minute size of the particles, the light scattering predominates at approximately 1/10 of the wavelength of the scattered light. Hence, for UV radiation to be scattered between 200–400 nm, the optimum particle size required is about 20-40 nm. The UV-blocking treatment for cotton fabrics consists of forming a thin layer of TiO<sub>2</sub> on the surface of the treated cotton fabric, which has been found to give a very high UV protection to fabrics.

ZnO has a relatively high absorption band starting at 385 nm and extending with the far UV [123]. In addition to its excellent UV-absorption characteristics, ZnO has several other advantages, namely, it does not migrate, it is not degraded by absorbed light and in many cases may improve mechanical, optical and electrical properties of the bulk polymer. Washing fastness of the fabric can be improved with the formation of covalent bonding between the PN and the fabric surface. The excellent UV-blocking properties of PN-treated fabric are maintained after 55 home launderings [124–126].

Cotton fabric treated with bulk ZnO or nano ZnO shows different physical and mechanical properties. This reflects the improved properties of nanosized particles with respect to conventional materials. This basic difference has great consequences on the garment breathability and eventually on the comfort of the treated fabrics. For textile applications, the nanoparticles need to be dispersed homogeneously in the different polymer matrices and a number of new synthetic strategies have been developed in order to prevent particle agglomeration and increase the stability of ZnO nanoparticles/polymer composites [127-131]. UV protection provided by fabrics depends on several parameters such as fiber type, color, presence of UV absorbers and additives, porosity, thickness, mass per unit surface, other finishing processes, laundering and the wearing conditions [132–134].

Yadav et al. [135] synthesized and characterized the ZnO nanoparticles. In this work, the ZnO nanoparticles were applied on cotton fabrics using acrylic polymer binder and the functional properties of coated fabrics were studied. On average, 75% UV blocking was recorded for the cotton fabrics treated with 2% ZnO nanoparticles.

Nano ZnO/PMMA nanocomposites were synthesized by Erjun et al. [136]. These composites can limit aggregation of nano ZnO and enhance the compatibility between inorganic nano ZnO and organic polymer. The composites present perfect UV-shielding properties, indicating that they have potentially remarkable features of interest in textile applications.

Poly(styrene butylacrylate) latex-ZnO nanocomposites were prepared by Mingna et al. [137]. ZnO particles of 6 nm can more effectively shield UV rays than 100 nm ZnO particles, while micro ZnO particles basically have no effect on the UV absorbance of the composite polymers. A blue shift phenomenon was observed at 365 nm for nano ZnO in these nanocomposite polymers. Consequently, these nanocompounds can be widely applied in coatings, plastics, fibers and textiles [138–140].

Haifeng et al. [141] reported a conventional approach to fabricate ZnO/polystyrene nanohybrid coatings on cotton fabrics. The cotton fabrics treated in their study provided ultrahigh UV protection and superior washing fastness.

Application of nano titanium has been paid more attention because it is a material of many excellent properties such as absorption of UV light up to the proximity of visible light wavelength, transparency at visible wavelength and a very high refractive index. Therefore, titanium nanocomposites may be of interest for the textile finishing for UV protection [142–144]. Kequing and Muhuo [145] prepared PET/nano TiO2 fiber using suitable spinning parameters. The UV-blocking property of the PET/nano TiO<sub>2</sub> fiber improves remarkably even at very low nano TiO2 content. They found that PET/nano TiO2 fiber has a UV protection factor value above 50.

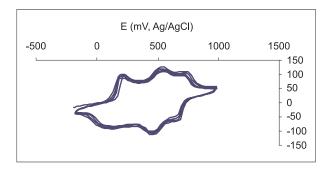
#### PN in Conductive Fibers and Fabrics

Conductivity in textiles can be imparted by the application of PN. By adding conductive nanoparticles to the polymer system, it is possible to develop coating materials for conductive polyester, polyamide and acrylics. Conductive inks are alternatives for conductive coatings to specific areas of fabric or garments.

ZnO nanoparticles have been used in PN for various applications like UV protection, mechanical, antibacterial finishes in textiles as discussed earlier in this review. Another area of application of ZnO is antistatic finishing agent in textiles. Alessio et al. [146] used ZnO nanoparticles to prepare the nanometer antistatic finishing agent, which was applied to treat cotton and polyester fabrics and then the antistatic performance of the treated textile was evaluated through the charge density.

Nano ZnO with amphoteric surfactant was used to prepare nanometer antistatic finishing agent and the effect of nano ZnO concentration, ratio of reactants and reaction temperature were analyzed by Fan and Junling [147]. The cotton fabric and the polyester fabric were both finished by pad-dry-cure process with the above antistatic finishing agent. They found that the charge density of the treated fabric decreased significantly in comparison with the original piece, showing that the fabric finished with the antistatic finishing agent was compounded with nano ZnO producing antistatic performance. It was found that a low concentration of finishing agent is able to achieve a better antistatic effect. Increasing the amount of ZnO nanoparticles added decreases the fabric antistatic property, because of the declined dispersion and increased agglomeration of nano ZnO finishing agent. The increased amount of nanoparticles results in the limitation of characteristics of nano ZnO. Through comparison between cotton and polyester treated fabrics, it was observed that the decline rate of charge density of the latter is more obvious than the former, revealing that the antistatic effect of polyester fabric finished with nanometer antistatic finishing agent is bet-

By adding nanoparticles such as graphite, carbon, silver, nickel and gold to conventional printing inks, conductive patterns can be directly printed on traditional fabrics [148]. Recently, expanded graphite/polymer electrically-conductive nanocomposites have attracted great interest [149]. Expanded graphite particles have been combined with polymers such as polystyrene, polyethylene, PMMA and polypropylene to prepare electrically-conductive nanocomposites [150, 151]. Nanocomposites of conducting polymers such as polyaniline (PANI) and inorganic materials have received much attention during the last few years [152–157]. They have shown various interesting properties that can be expected to be different from those of the polymers or the inorganic particles themselves [152]. One particular research objective has been the dispersion of metal nanoparticles within the polymer matrix [152, 158-163]. Since



**Figure 11** Cyclic voltammogram of electrochemical synthesis of PANI. The electrochemical synthesis conditions were: 0.05 M aniline in 1 M HCl + 0.2 M H $_2$ SO $_4$  (1:2) – work electrode: glassy carbon – secondary electrode: Pt – reference electrode: Ag/AgCl scan rate 20 mVs $^{-1}$  – potential sweep between –200 and 1000 mV.

the incorporation of metal nanoparticles is known to enhance the conductivity of the polymer [155], a great number of different applications (catalyst, sensors) can be expected for these materials [164–166]. We have synthesized PANI by a new green route by cyclic voltametry and characterized it (Figure 11). Further work is underway to incorporate nanoparticles in the newly synthesized PANI to study the effect of addition of the nanoparticles on various electrical properties.

Like in polyamide/montmorillonite composites [167], particle orientation along the filament axis can be accomplished by a high drawdown, with post drawing of the filaments, or both, because the post drawing process relies on plastic deformation in the filament. Studies on the dependence of electrical conductivity on the draw ratios of nanocomposite fiber and fabrics [168, 169] have shown that plastic deformation collapses and breaks the particle network and, therefore, decreases the electrical conductivity of the material in post drawing process. However, the melt drawdown process relies not on plastic deformation, rather it uses viscous flow deformation to elongate and attenuate the polymer [170]. Ceyhan and Warber [171] set out to produce oriented nanocomposite filaments with melt drawdown. They produced expanded graphite-filled poly(phenylene ether) atactic polystyrene nanocomposite fibers and found that the continuous graphite particle network improves the electrical conductivity. It was concluded that the particleparticle contact seems to determine the conductivity of the polymer loaded with conductive nanographite. In spite of the improved electrical conductivity of the treated filament, these PN were found to adversely affect the mechanical strength; it was observed that the tensile strength was decreased up to 20% and the elongation at break up to 24% in the PN-treated filaments.

### Summary

The introduction of inorganic nanoparticles as additives into polymer systems has resulted in PN exhibiting multifunctional high performance polymer characteristics beyond what traditional filled polymeric materials possess. The application of PN in the field of textiles is gaining importance. It has been found that PN-treated fabrics show improved performance in terms of many functional properties. Out of many possible applications in textiles, some of the most successful ones are moisture management, hydrophobicity/water repellency, UV protection, antimicrobial and antistatic finishes, as discussed in this review. Nanopolymer composites are gaining more importance because of the current explosion of interest in nanoscience and nanotechnology. The main thrusts in PN applications in textiles will be to:

- Enhance the functional properties and performance of existing materials;
- Produce textiles with combined functional properties:
- Increase the safe use of nanoparticles in technical textiles;

#### And

• Open up opportunities for textile sensors.

There is no doubt that in the next few years, PN will penetrate into every area of the textile industry. In spite of the tremendous scope of applications of PN in textiles, it has been felt that most of the technologies developed are limited to laboratory research and not suitable for industrial scale production. One step fabrication or other simple techniques are greatly needed to apply PN in textiles in large scale and good homogeneity.

The application of PN in textiles is a multidisciplinary field interfacing with surface chemistry, physics, nanoscience, textile engineering and so on, where researchers can make full use of their imaginations.

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