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Careful Use of Silica Nanoparticles in the Textile Treatment for Potential Large-Scale Production

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In this work, silicon dioxide nanoparticles (SiO_2) have been used as a treatment for common polyester-based fabric in light of imparting the hydrophobicity to the respective surface. In view of preserving the durability and the eco-friendliness of the developed products, by promoting the entrapment of the particles within the textile weaving, as a binder, polyurethane water-based dispersion (PUD) has been adopted. This resin has been chosen solvent-free, and endowed with the flexibility for retaining the elasticity of the overall textile structure. The nanoparticles (content up to 5% in wt.) were combined with PUD, also including crosslinking agent, by utilizing a magnetic stirring at high rotational speed. The samples were prepared through the impregnation method and dried at room temperature in order to reproduce as much as possible the continuous production process on a large scale with low energy and environmental impact. The prepared specimens were tested in terms of tensile, tear, abrasion and water repellency. Experimental results demonstrated the benefits arisen from the polyurethane application to the textile weaving in tensile, abrasion and water resistance. On the contrary, the tear strength of the fabric structure was lowered by the presence of the polymer treatment. As expected, the introduction of silica particles within the aqueous solution has been particularly relevant for further increment of the water resistance of the PUD-impregnated materials without causing an excessive increase in the weight and changes in the final appearance. This outcome has been intended as a sign of the potential applicability of the developed products in the fields of luggage or bags production and for the indoor or outdoor uses.

1. Introduction

Nowadays, the textile industry has become part of an evolutionary process in which different technologies have been applied to gain advantages on the properties and special functionalities of fabrics: possible applications of the 3D printing as an add-on process to 3D structures on textiles (Korger et al.), smart textiles in sensor, actuator integration, and communications (Schneegass and Amft), digital printing for more attractive pattern design (Ugur Koseoglu), nanomaterials for creating garments able to respond to external stimuli (Yetisen et al.). At regard, the nanoparticles just involved in the coating technologies for antimicrobial activities (Blanco et al.) and superhydrophilic properties (De Falco et al.) have been also considered in the textile treatment to supply common products with new functionalities, (Rivero et al.). Depending on the application technology, the toxicity risk of nanoparticles release during washing or in the atmosphere should be considered (Yetisen et al.), representing not only a question on the durability of the achieved benefits but also regarding the environmental sustainability.
For solving this drawback, a useful approach has concerned the attachment of the nanoparticles to the fabric by the means of binder resin that formed a film on the fibers and entrapped the particles. Unfortunately, due to the hardness and stiffness achieved by the application of the binder, the tensile and bursting strength of the final products were partially lost (Riaz et al.). Among the different types of the used fillers in the textile treatment, numerous studies reported on the benefits coming from the silica particles on the hydrophobicity of

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the treated surfaces. Jeong et al. (Jeong and Kang) realized a transparent silica coating on cotton by spraying an alcohol suspension containing the nanoparticles. Depending on the alcohol type, extremely water repellency features have been verified in the coated textiles through the contact angle and the surface wettability measurements. Attia et al. (Attia et al.) formulated a novel coating, based on silica (by waste agriculture rice husk) and silver nanoparticles dispersed in an acrylic-based binder. Due to the applied coating, the protection against the UV rays, microbial attack, and water contact of the treated fabrics was remarkable increased compared to the untreated ones. Another multifunctional coating, realized through an aqueous dispersion, containing alkoxy silanes, organic fluoropolymer, silane quaternary ammonium salt, and silica nanoparticles, has been exploited for silk protection against the microbial growth and the wetting by water or oil drops (Aslanidou and Karapanagiotis). The presence of nano-silica was found to be essential for building micro/nano structures, considered responsible of superior wetting properties and antimicrobial activity.
In this framework, the study aimed to verify the effectiveness of silica nanoparticles in imparting hydrophobic characteristics for technical synthetic common polyester-based textiles. In order to improve the durability of the SiO_2 on the weaving, and avoid the release in the atmosphere, the nanoparticles have been dispersed in a polyurethane binder (in the form of aqueous dispersion). As application method, the impregnation was preferred to the most applied coating technique. In fact, the former allowed to protect the surface of the neat fabric without altering significantly the final aesthetics. A complete characterization of the impregnated samples has been performed by tensile, tear, abrasion, and water resistance testing.

2. Materials and Methods

2.1 Materials

Commercial synthetic woven fabric based on polyester (100%, PES) was used as basic material for the experimentation. Fumed hydrophilic Silica nanoparticles (AEREOSIL 200), average primary particle size of 12 nm and a specific surface area of 200 ±25 m^2/g, were kindly supplied by Evonik Resource Efficiency GmbH. Soft aliphatic polyether-based polyurethane, in form of an anionic waterborne dispersion (CLEANCAP 808A), 35% in solid content, was gentle provided by ICAP SIRA-Chemicals and Polymers Spa (Milan, Italy). A universal crosslinker (ICAPLINK X3), based on an aliphatic polyisocyanate for polymers containing carboxylic, hydroxyl or amino groups, was gentle offered by ICAP SIRA-Chemicals and Polymers Spa (Milan, Italy).

2.2 Sample preparation

The impregnating dispersions were based on PUD and silica nanoparticles (1, 3 and 5% in wt.). In some cases the crosslinking agent, in content of 2 and 4% in wt. was added to the formulations. All the components were mixed under magnetic stirring at 800 rpm for 15 minutes at ambient conditions. The percentage of each additive was referred to the nominal PU weight in dispersion. The so-prepared solutions, summarized in Table 1, were poured into an impregnation container, where the fabric was introduced and remained for 15 minutes. Then, the wetted textile was squeezed between two rollers (pressure of 2 bar, speed of 3 m/min) and dried at ambient conditions (Figure 1). For comparison, treated samples with an aqueous solution of silica nanoparticles (5% in wt. in water) have been also prepared.

2.3 Characterization techniques

A dynamometer (mod. Tensometer 2020) produced by Alpha Technologies INSTRON (Hudson, Ohio, USA), was used for measuring the tensile and the tearing properties of the PUD impregnated samples. The tensile tests were performed according to the European Standard EN ISO 13934-2 (Grab Method), whereas the tear tests followed the described procedure in the standard ASTM D2261. During the experiment, the load displacement curves were recorded by Tensile 2020 software. The tensile strength was evaluated by considering the maximum load before the sample breakage, while the tear strength was calculated as an average value of the five highest peak forces, obtained for each individual specimen, on load-displacement curve. For reproducibility, at least five samples of each developed material have been tested.
The mass per unit of area of the final samples has been calculated according to the standard UNI EN 12127 by dividing the weight of a piece of fabric and the surface area.
A Martindale tester (C&B Tessile SrL , Milan, Italy), has been utilized for evaluating the abrasion resistance of the developed specimens in accordance with the standard UNI EN ISO 12947. During the test, the piece of fabric was rubbed with translational movements, against a reference abrading textile. The abrasion resistance was expressed by the number of cycles required for achieving the breakage of the sample surface.
The surface wettability was evaluated through the Spray tester (C&B Tessile SrL, Milan, Italy), in compliance with the standard UNI EN 24920. Distilled water was dropped on the fabric surface, mounted on a circular inclined support, by reproducing the rain. At the end, the wetted fabric was compared with the reference

pictures, associated with the ISO index by the aforesaid standard, i.e. a numerical value ranging from 0 (totally wettable surface) to 5 (completely water repellent surface).
An optical microscope (Olympus SZ-PT, Tokyo, Japan) equipped with a digital camera (Olympus U-PMTVS) was used for verifying the alteration in fabric aesthetics due to the Silica/PUD treatment.
A scanning electron microscope (SEM, Mod. TM 3000, by Hitachi Company, Tokyo, Japan) was adopted for investigating the covering of the textile yarns by the applied dispersion.

Table 1: Developed Formulations

Sample	PUD	SiO_2	Water	Crosslinker
PES-PU	100%	/	/	/
PES-5 SiO_2	/	1.75%	98.25%	
PES-PU/2Cr	99.3%	/	/	0.7%
PES-PU/4Cr	98.6%	/	/	1.4%
PES-PU/1SiO_2	99.65%	0.35%	/	/
PES-PU/3SiO_2	98.95%	1.05%	/	/
PES-PU/5SiO_2	98.25%	1.75%	/	/
PES-PU/2Cr/3SiO_2	98.25%	1.05%	/	0.7%

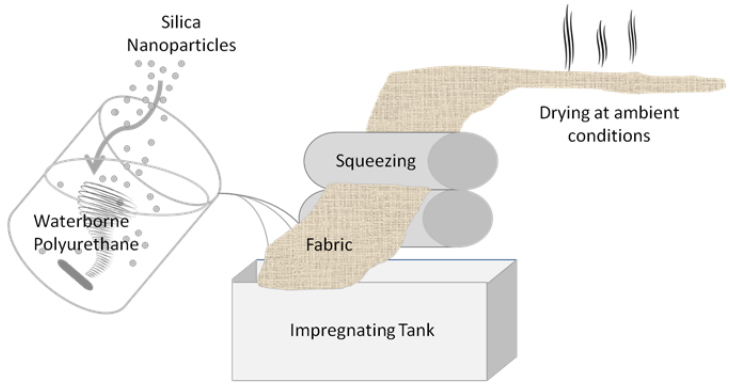

Figure 1: Processing Flow Chart

3. Results and discussion

In the figure 1, the surface imagines of the neat fabric (Figure 1 (a)), the PU impregnated one (Figure 1 (b)), the treated with the PU solution containing the silica nanoparticles (Figure 1(c)) have been reported. From these pictures, it could be well established that the presence of polyurethane treatment not strongly affected the fabric aesthetics, leaving the visible surface almost unaltered. The introduction of silica, on the contrary, produced a whitening of the surface slightly evident only from the microscopic point of view.
The weight gain, the mechanical properties (in terms of tensile, tear, and abrasion), together with the water resistance results have been summarized in Tab. 1 for all the developed specimens.
Due to the polyurethane impregnation the fabric mass per unit of area was increased of approximately 27%, and a further augment of 10% was verified by introducing the silica in the aqueous solution (5% in wt.). As concerning the tensile features, both in the weft and warp direction, the PU impregnation determined an increase of the strength equal to 40% for the neat textile. In fact, starting from a value of about 1200 N for the basic material (PES), the breaking load arrived up 1400 N for the PU-treated samples (PES-PU). The introduction of the crosslinker, alone or in combination with silica, seemed not to strongly affect the tensile strength of the impregnated specimens that remained approximately around 1300 N. As concerning formulations containing the SiO_2 nanoparticles, the breaking load seemed to slightly increase (13%) compared to the treated specimens with PU alone. In this case, a value of 1600 N has been achieved in correspondence of 3% in wt. of added particles content. Yet, higher SiO_2 concentrations (5% in wt.) seemed to determine no improvement, indeed a worsening of the investigated characteristics (breaking load of ~1500 N). This effect could be attributed to the well-known agglomeration phenomena, involving the nanoparticles dispersion in a polymer, explored several times in the relevant literature (Qianga et al.), and confirmed by SEM imagine (Figure 2). In fact, the micrograph for the PES-PU/5SiO_2 reported the silica, bonded to the textile weaving of

PES fabrics, given the polyurethane layer, more in the form of aggregates (order of magnitude of few microns) than of nanoparticles.

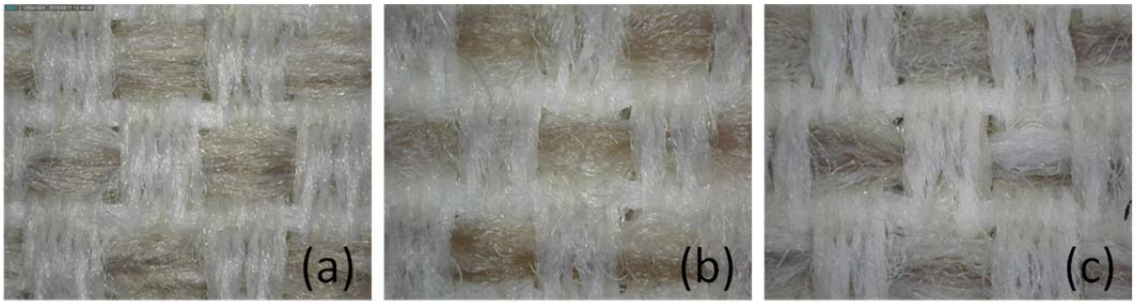

Figure 1: Surface pictures of: (a) Pure PES-Fabric; (b) PES-PU; (c) PES-PU/5SiO_2

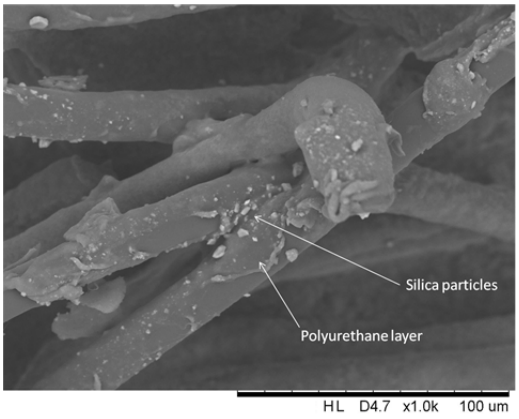

Figure 2: SEM Imagine of Silica nanoparticles embedded in the polyurethane layer by covering the fibers in the PES-PU/5SiO_2

Even if the strength of the yarns of the treated fabrics has been increased by the polyurethane application, as appeared evident by analyzing the tensile data, opposite results could be observed by taking into account the tear resistance. In all the developed formulations, when the impregnated textiles were subjected to a tear stress, a strong decrement in the maximum allowable load during the testing has been recorded compared to the untreated PES. In order to determine a higher resistance against the tear, the filaments should be free of movement and able to slip among themselves. Higher was the coating adhesion, lower was the availability of yarns motion, limited became the tear resistance (Eltahan). So, in the following cases, it could be reasonable hypothesized that the polyurethane, providing the bonding, had hindered the mobility and the possible slippage of the filaments, by leading to a deterioration of the measured parameter. The tear characteristics of the treated samples, involving PU/SiO_2 dispersion, continued to worsen, albeit with a very mild effect, as the content of added particles increased. Probably, this aspect could be intended as a higher rigidity achieved in the polyurethane due to the nanoparticles introduction, and in general in textile structure.
If on one hand, a loss of tear strength was an evident consequence of PU treatment, on the other hand a strong increase of the abrasion resistance should be highlighted in the impregnated textiles, amounted at 90,000 cycles, i.e. approximately 3 times compared to that evaluated for the starting PES (equal to 30,000 cycles). The abrasion test consisted in an erosion process of the material by acting on the mass removal, with a deterioration of the surface (Figure 3 (a)) until the puncture and final breakage (Figure 3(b)). In the case of PU treated textiles, besides the improvement of the mechanical strength, the polymeric protection has probably favoured the creation of smoother, less corrugated surfaces with a reduction in friction between the tested fabric and the reference abrading medium. The effect of PU polymer on the abrasion resistance of the PES fabric was so evident that, neither in the case of silica addition nor of crosslinker, any alteration of the abrasion properties has been provoked.
The effect of silica nanoparticles became particularly significant in the analysis of the wettability features. In fact, the presence of the PU polymer applied to the textile weaving had determined a protection of the yarn and fabric surface by promoting an augment of the ISO index from 0 to 1. On the other hand, as just verified

by the SEM microscopy (Figure 2) the addition of silica nanoparticles to the PU impregnating suspension created a micrometer (about 1µm) aggregates in form of protrusion (Manoudis et al.), by covering part of the yarn surface. This aspect could lead to a higher degree of superficial roughness of the yarns (Lei et al.), that hindered the contact between the water droplet and the treated textiles and increased the ISO index to a value of 2.

Table 2: Mechanical and water resistance of the developed materials.

Sample	Tensile Strength [N]	Tear Strength [N]	Abrasion Resistance [cycles]	Water resistance [ISO]	Areal mass [g/m^2]
neat PES	1115±31 warp 1193±33 weft	227±16 warp 101±6 weft	35,000	ISO 0	290
PES-5SiO_2	1023±37 weft	103±7 weft	35,000	ISO 0	290
PES-PU	1394±48 warp 1421±65 weft	137±8 warp 77±6 weft	90,000	ISO 1	370
PES-PU/2Cr	1351±37 weft	78±18 weft	85,000	ISO 1	375
PES-PU/4Cr	1315±71 weft	75±11 weft	90,000	ISO 1	375
PES-PU/1SiO_2	1430±42 weft	78±14 weft	90,000	ISO 1	390
PES-PU/3SiO_2	1603±35 weft	75±9 weft	85,000	ISO 2	400
PES-PU/5SiO_2	1492±70 weft	73±8 weft	90,000	ISO 2	410
PES-PU/2Cr/3SiO_2	1303±54 weft	77 ±9 weft	85,000	ISO 1	430

Figure 3: Surface modification (a) and final breakage (b) of the sample during the abrasion testing.

4. Conclusion

PES-based textiles have been impregnated by foulard method with an aqueous dispersion of silicon dioxide and polyurethane, in order to promote a durable bond of the nanoparticles within the textile weaving through the polymer application. The characterizations techniques, developed on the treated samples, aimed to verify the overall performance both in the mechanical and water resistance. In the PES-PU fabrics, given the presence of the polymer, an augment of the tensile strength have been shown of about 50% compared to the neat textile, whereas the abrasion was increased of 3 times and the water resistance was risen one level in

the ISO scale. The unique disadvantage in the PU treatment has regarded the tear strength that was reduced of approximately 30% compared to the pristine PES. The introduction of the SiO_2 particles, without PU polymer into the textile structure, did not bring any changes to the fabric features, and during the tests a visible diffusion of the white powder into the atmosphere was noted. On the contrary, if the SiO_2 was incorporated in the PU dispersion, depending on the content, the tensile strength seemed to be slightly increased, the abrasion remained unchanged, and the water resistance rose by another level on the ISO scale. In conclusion, the effect of the nanoparticles on the surface hydrophobicity seemed to be obtained only by promoting the adhesion on the filaments by the means of an appropriate binder.

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