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Nanocoat Finishing of Polyester/Cotton Fabrics by the Sol-Gel Method to Improve their Wear Resistance

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Abstract
A serious drawback of the commonly used textiles of polyester/cotton fibres blends (PET/CO), especially those containing worse cotton brands, is their great susceptibility to form pilling, which adversely affects their performance durability and aesthetic values. Among the many methods of preventing this phenomenon, the thin-coating finishing performed by sol-gel methods provides interesting possibilities in this field. By a proper selection of precursors and synthesis method as well as the deposition of sols, it is possible to form xerogel coats on the fibre surface characterised by considerable hardness and abrasion resistance, thus reducing the formation of pilling, without any deterioration in the aesthetic values of textiles. Moreover, these coatings are strongly combined with the fibre surface and are resistant to the conditions of use and care, including multiple washing processes. The thin-coat finishing of this type also increases the abrasion resistance of textiles with a dominating content of polyester fibres, and thus it positively influences the performance value of textile fabrics. This paper presents the test results of using the hybrid modified SiO_2/Al_2O_3 sol developed, synthesised with the use of two precursors: (3-glycidoxypropyl) trimethoxysilane (GPTMS) and aluminium isopropoxide (ALIPO), and the conditions of its application to the thin-coat finishing of PET/CO (67:33) woven fabrics were selected to increase their abrasion resistance and prevent the formation of pilling. Consequently, the fabric susceptibility to form pilling was practically completely eliminated (assessment at level 5 according to the Martindale test), and the fabric abrasion resistance was increased by 38%, with the effects obtained being resistant to prolonged laundering.

Key words: *textile fabric, PET/cotton blends, sol-gel coating, thin-coat finishing, hybride modified sol, xerogel, performance durability of textiles, abrasion resistance, pilling.*

Introduction

Woven or knitted textile fabrics made of blended yarns, mostly polyester/cotton (PET/CO), constitute a large group of commonly produced textiles designed for various uses, such as clothing, footwear and technical applications. Such a widespread popularity of these textiles results from their good aesthetic and performance properties such as wrinkle resistance, shape/dimensional stability, good hygienic properties, ease of care as well as a relatively great service durability, including resistance to abrasion. The term "resistance to pilling" describes the formation of fuzz that is converted into small fibrous balls, called piles, due to the abrasion occurring during exploitation. These balls are formed by filaments drawn out from the fabric during abrasion, a portion of which consists of loose fibres uncombined with the fabric, with the rest of them being broken and linked to the fabric. Consequently, the piles formed in this way are strongly combined with the surface of the fabric, which disqualifies it with respect to both functional and aesthetic values. Omitting here the causes resulting from the structure of yarns and fabrics, the phenomenon of pilling occurs, first of all, in the case of fabrics of staple synthetic fibres with a high tensile strength and resistance to abrasion, as well as their blends with natural fibres characterised by considerably lower strength parameters. The most common examples are woven and knitted fabrics made from blends of polyester and cotton fibres. In such fabrics, due to abrasion taking place under the conditions of use, the weaker cotton fibres are broken and separated from the fabric, while the considerably stronger polyester fibres are only broken but remain jammed with their other ends in the fabric. Thus both types of fibres form piles that remain strongly combined with the fabric surface. This mechanism explains the rare occurrence of pilling or even its absence in the case of fabrics made from cotton fibres, especially from the worse grades of cotton, characterised by a lower tensile strength.

The intensity of pilling depends on the characteristics of fibres constituting the composition of the blend, the components' contents, the yarn and fabric structures, as well as on the conditions of fabric use, especially abrasion intensity/abrasive forces, and the humidity and temperature of the environment [1, 2].

These conditions are particularly rigorous in the case of the textile internal elements of footwear such as inserts and linings. Therefore PET/CO blend fabrics with a dominating content of PET fibres require proper finishing treatment to make them resistant to abrasion and pilling. Within the scope of chemical treatment, great opportunities are created by so-called coating finishes that consist in depositing on protective polymeric coats on the fibre/fabric surface. These are usually of micro-meter thickness, but they are not a satisfactory solution to the problem because of their generally low hardness, abrasion resistance and air and water vapor/perspiration permeability, as well as their tendency to stick to feet at high humidity and temperature inside footwear, which adversely affect the hygienic properties and comfort of using shoes [4 - 6]. New possibilities in this area are created by the use of coat finishing for textile fabrics, in which, instead of organic polymers, cross-linked hybrid inorganic-organic materials are formed directly on the surface of the fabrics undergoing finishing by the sol-gel method [6 - 9].

This technique is based on the preparation of colloidal suspensions - sols - from appropriately selected precursors, mostly metal oxides or organometallic compounds such as metal or semimetal silicon-containing alkoxides. These compounds, which are subjected to hydrolysis in an acidic medium, are converted into corresponding hydroxides that are unstable and susceptible to further condensation processes resulting in the formation of particles with nanometer dimensions. The conditions used in the synthesis of nanosols, such as the solvent type, pH value, temperature and concentration are of primary importance for the structure of particles and their dimensions. As a result of these reactions, the precursor is converted into sol. Sols prepared in this way are deposited on fibres/fabrics and dried at an elevated temperature to condense them into cross-linked lyogels containing a considerable content of liquid phase. During further drying, the liquid phase is removed and a porous layer is formed on the fibre surface. Further treatment at elevated temperatures and the progressing polycondensation convert this layer into a physically and possibly chemically combined, cross-linked gel coat, whose mechanical properties depend on the intensity of thermal treatment , i.e. treatment temperature and duration. It has been found that under thermal conditions permissible for textiles, i.e. causing no fabric damage due to thermal polymer destruction, the coat is cross-linked to an extent corresponding to that of xerogels. Such products have a lower hardness and mechanical resistance than those of typical ceramic materials requiring thermal treatment at a temperature of about 600 °C, but they do show a higher elasticity, which is of primary importance for textile applications. By proper selection of precursors, sol synthesis conditions and doping suitable functional nanoparticles, e.g. Al_2O_3, as well as conditions for the deposition and thermal cross-linking of such modified sols on textiles, one can obtain hard protective coatings imparting increased abrasion resistance to them [6 - 16].

The xerogel coats obtained in this way show several properties that make them suitable for wear resistant finishing and protection against pilling. Moreover, their very low thickness, amounting to 200-500 nm, makes it possible to maintain the 'textile' character of the fabrics, which are also finished without deterioration in their hygienic properties. Such coatings are characterised by a high hardness and abrasion resistance. On the other hand, it is required to provide them with a high elasticity and resistance to chipping as well as a satisfactory and durable combination with the textile substrate during use. Another problem may arise from the increased rigidity of the fabrics caused by improper characteristics of the sols used, by the conditions of their deposition, and by undesired combinations between the coated fibres, so-called bridges. These considerably reduce fibre motion and even slight displacement, which results in the stiffening of the fabric structure [17 - 19].

As for the force of the coat combination with the fibre surface, numerous literature reports suggest that this can be increased by using properly selected organo-silica precursors in the synthesis of sols. This makes it possible to synthesise sols containing particles with functional groups capable of reacting and forming chemical bonds with functional groups present on the fibre surface, mostly –OH groups (in the case of cotton fibres). Good results can be obtained by modifying silica sols with epoxysilanes such as (3-glycidoxypropyl)trimethoksysilane (GPTMS). The addition of this compound increases the adhesion of the nanosol coat to the fibre surface, thus increasing its mechanical resistance. Under the conditions of sol synthesis and in further thermal processes, the epoxy ring of GPTMS is opened to react with hydroxyl groups on the fibre surface. According to literature reports, the addition of GPTMS also increases the hardness of the hybrid inorganic-organic coating and improves the bonding power between the sol-gel coating and cotton fibre surface. The beneficial influence of GPTMS addition on coat elasticity has also been observed. Consequently, one can expect that the use of this compound in sol synthesis can improve the resistance to chipping of the coating obtained and eventually the wear resistance of textiles finished by the sol-gel method [20 - 22].

As for the reduction in the thickness of the xerogel coat deposited on fabrics, it should be mentioned that its low thickness really exerts a positive influence on the coat elasticity, resistance to chipping and the extent of adhesion to the fibre surface. However, one should bear in mind that the lower the coat thickness is, the weaker its resistance to abrasion [17, 19]. This dependence requires particular attention in the finishing of textiles by the sol-gel method as it creates contradictions between the basic aim of nanocoat deposition i.e. to obtain increased abrasion and wear resistance and the necessity of eliminating the disqualifying phenomenon of coat chipping and maintaining the textile character of fabrics. The coat chipping phenomenon during fabric exploitation is of particular importance in the case of fabrics designed for internal footwear elements as hard microparticles with sharp edges formed during use could act as an abrasive powder and intensify the wear of both the footwear linings and socks, additionally causing skin irritation or even escoriation.

The above considerations suggest that the apparently simple technology of sol-gel coating, meant to protect fabrics against abrasion and pilling, appears, in practice, to be very problematic, and despite many positive reports from various centers, it still requires further study [24, 25, 29]. This also concerns the particular case of fabrics designed for footwear inserts and linings

The aim of this study was to optimise the performance properties of woven fabrics made of polyester/cotton blends with respect to increasing their resistance to abrasion and pilling by finishing with the use of the sol-gel method.

Experimental

Materials

Woven fabric

A commercial woven fabric designed for footwear inserts and linings, consisting of a polyester/cotton blend (67% PET and 33% CO), with twill weaves, a surface weight of 165 g/m^2 and thickness of 0.36 mm was used in this study. Warp and weft yarns were of 23 tex and the number of threads was warp 42/cm and weft 21/cm. The fabric was finished according to industrial standards (precleaning/desizing, bleaching, washing, drying and heat-setting) but without the application of any auxiliary agents. Test samples were first washed under standard conditions according to PN-EN ISO 6330:2002. "Textiles. Domestic Washing and Drying Procedure for Textile Testing. Procedure 5A"[28] at a temperature of 40 °C for 30 min. and then dried at 50 °C. This woven fabric, owing to a high content of strong and resistant to abrasion PET fibres, is characterised by a high abrasion resistance, determined by the Martindale Abrasion Test method [26] to be 40 000 cycles, which fulfills the requirements of both the footwear industry and manufacturers of protective clothing. However, a crucial and unsolved problem is the susceptibility of this type of fabric to form pilling, which – especially with respect to footwear materials - is of primary importance and can cause significant discomfort of use, while in the case of application in protective clothing, it deteriorates aesthetic values.

Precursors

- *(3-glycidoxypropyl)trimethoxysilane 98% [GPTMS]* (ABCR GmbH&Co. KG)
- *aluminium (III) isopropoxide $Al(OCH(CH_3)_2)_3$ [ALIPO]* (ABCR GmbH&Co.KG)

Preparation of sols

a) Preparation of modified SiO_2 sol with the use of GPTMS as a precursor

Silica sol modified with glycidoxy groups was prepared by the hydrolysis of GPTMS in a water-alcohol medium at a temperature of about 80°C while stirring with a high-speed stirrer for about 2 h until a transparent colloidal solution was obtained.

b) Preparation of Al_2O_3 sol based on aluminium isopropoxide $Al(OCH(CH_3)_2)_3$

Al_2O_3 sol was prepared according to the procedure given in literature [2] by mixing ALIPO precursor with a mixture of ethanol and water (in a molar proportion of 1:1) using a high-speed stirrer for about 2 h at a temperature of about 80 °C (boiling point of EtOH), after which time the pH value of the mixture was set at 3 by means of hydrochloric acid, followed by the addition (as a stabilising agent) of a small amount of poly(vinyl alcohol) – (POCH S.A.). The mixing was continued until a homogeneous transparent colloidal solution was obtained.

c*) Preparation of hybrid modified SiO_2/Al_2O_3 sol*

This sol was prepared by the combination of sols (a) and (b), which was intensively stirred at 20-25 °C. The resultant stable and transparent sol was used for padding fabrics after its dilution with water in the proportion 1:20.

Preparation of sol-gel coats

Deposition of sols on fabric samples, drying and heating

The film-forming sols containing functional nanoparticles were applied on the fabric surface by padding with the use of a laboratory two-roller padding machine with a horizontal position of the squeeze rollers, produced by BENZ GmbH (Switzerland), using the following padding conditions:

- Pressure: 15 kG/cm
- Padding rate: 1 m/min
- Pick-up of liquor: 70 - 85%

The padded fabric samples were dried at a temperature of 60 °C and then heated at 160 °C for 1 min.

Examination of the fibre surface with deposited sol-gel coatings

Microscopic observation of the fibre surface

Scanning Electron Microscopy (SEM) examination

The structure and morphology of the fibre surface with a deposited xerogel coat were examined by means of a JSM-5500 LV SEM (Jeol, Japan).

Atomic Force Microscopy (AFM) examination

The structure and morphology of the fibre surface with deposited xerogel coats and their changes due to wearing were examined by means of a Nanoscope IIIa AFM microscope from Digital Instruments (Santa Barbara, USA), using contact and oscillating modes.

Xerogel coats were also prepared on a smooth glass plate for investigation of their structure by means of AFM.

Testing the resistance to abrasion of fabrics finished with nanocoatings

The tests were carried out according to PN-EN-ISO 12947-1:2000+AC:2006 ”Textiles. Determination of the abrasion resistance of flat fabrics by the Martindale method. Determination of sample failure” [26] with the use of Nu-Martindale 864 apparatus (James H. Heal & Co. Ltd., England). The pressure of abrasive heads was 12 kPa. A standard wool woven fabric was used as the abrasive element. According to the standard, the test is terminated when two threads in the fabric tested are broken due to abrasion. At the same time, the number of revolutions of the abrasive head is recorded, after which the fabric was scraped out.

Testing the resistance to the formation of fuzz and pilling of fabrics finished with nanocoatings

The tests were performed according to PN-EN-ISO 12945-2 „Textiles. Determination of a flat fabric surface susceptibility to the formation of fuzz and pilling. Part 2: Modified Martindale method” [27] with the use of Nu-Martindale 864 apparatus (James H. Heal & Co. Ltd., England). The pressure of the abrasive heads was 415 G.

A standard wool woven fabric was used as the abrasive element. According to the standard, the test is terminated after 7000 revolutions, and then an assessment is made visually by comparison with a photographic standard.

Testing the resistance to laundering of fabrics finished with nanocoatings

Tests were performed according to PN-EN ISO 6330:2002. “Textiles. Domestic Washing and Drying Procedure for Textile Testing. Procedure 5A (40 °C)” [28] –, using a drum washing machine FOM 71MP LAB VASCATOR (Electrolux, Sweden).

Results and discussion

Considering the exploitation conditions of woven fabrics in footwear and protective clothing applications as well as our own studies, it was established that the most beneficial properties of xerogel coatings should be obtained in the case of their preparation from hybrid modified SiO_2/Al_2O_3 sol. The assumptions of hybrid sol synthesis with the use of two precursors, GPTMS and ALIPO, and the technology of making such a sol were developed taking into account the requirement that a hybrid sol of this type should show very good film-forming properties, which is of primary importance due to the fact that the fabric to be finished contains different fibres in its composition, among which hydrophobic polyester fibres with a smooth surface constitute the predominating component (67%) [29]. Moreover, xerogel coats should show great elasticity and resistance to chipping, as well as high hardness and abrasion resistance because of the severe exploitation conditions. They should also show as high an adhesion to the surfaces of both fibre types as possible, significantly assisted

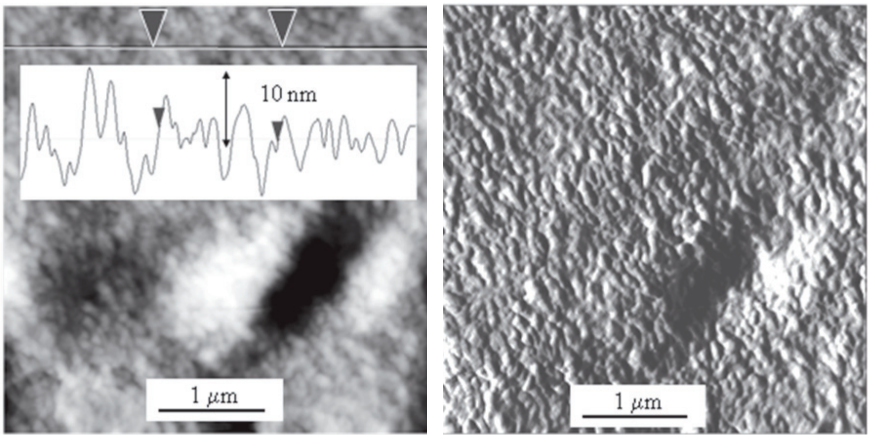

Figure 1. *AFM images (left height image, right phase image) of a thin layer of modifiedSiO_2/Al_2O_3 xerogel drop cast on a glass plate.*

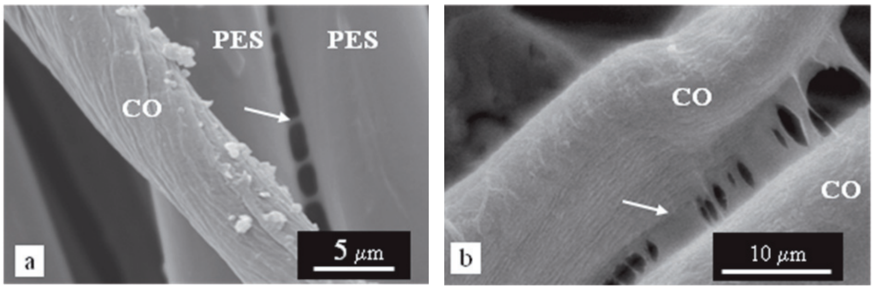

Figure 2. *SEM images of fibers in polyester fabrics (PET) and cotton fabrics (CO) coated with modified SiO_2/Al_2O_3. The arrows indicate bridges between fibers formed by the elastic coat covering PET (a) and CO (b) fibers.*

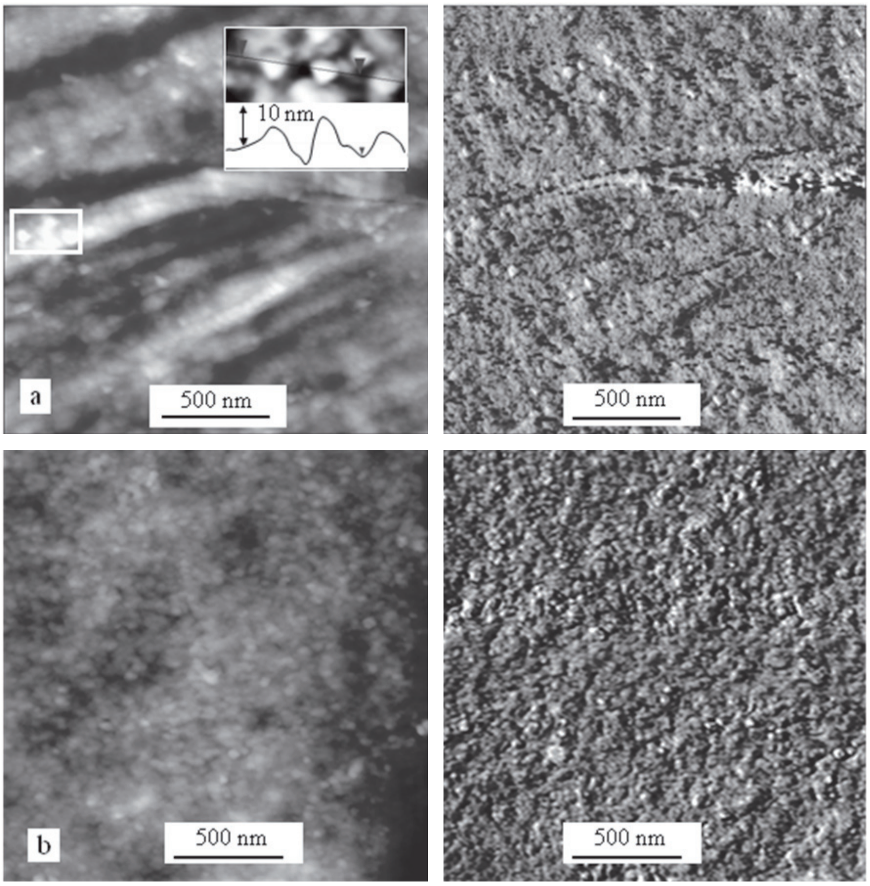

Figure 3. *AFM images (left height image, right phase image) of cotton fiber surface (a) and polyester fiber surface (b).*

by the chemical bonds of cotton fibres. Such bonds should be formed between the unhydrolizable functional glycidoxy groups in the sol layer deposited, resulting from the open epoxy ring of the GPTMS precursor during sol synthesis, and the hydroxyl groups in the cotton fibre surface layer.

To examine the structure of xerogel coats obtained in this way, these were also prepared in the form of a film on a smooth glass plate. AFM observations allowed one to confirm the presence of numerous Al_2O_3 particles with a size of about 15 nm, regularly distributed in the SiO_2 modified matrix forming a continuous coat on the film surface (***Figure 1***). Hybrid modified SiO_2/Al_2O_3 sol synthesised in this way and diluted with water (1:20) was used for padding PET/CO fabric under the above mentioned conditions [29]. The fabric was then dried at 60 °C, followed by its thermal treatment at 160 °C for 1 min., assuming that the use of the highest permissible temperature (causing no fibre destruction) will intensify the cross-linking of the xerogel coat and consequently increase its hardness and abrasion resistance. This should positively influence the formation of chemical bonds between the coat and cotton fibre surface, thereby increasing the extent of the coat-fibre combination.
The fabrics treated were subjected to SEM and AFM examinations, as well as to an abrasion Martindale test and fuzz and pilling test according to the modified Martindale test.

From the microscopic observations, it follows that hybrid modified SiO_2/Al_2O_3 sols can be deposited on both PET and cotton fibres in the form of thin elastic xerogel coats, which completely and uniformly cover the fibre surface, as is clearly seen in the SEM images (***Figure 2.a***) and AFM images (***Figure 3***) at a higher magnification. The high elasticity of these xerogel coats on PET fibres (***Figure 2.a***) and cotton fibres (***Figure 2.b***) can be observed in the SEM images. These images prove that hybrid modified SiO_2/Al_2O_3 sols show good film-forming properties and form uniform and elastic coats on both types of fibres, whose stretched fragments are visible between fibres with no cracks or fractures. This high coat elasticity also facilitates fibre replacement to a limited extent, which should positively influence their abrasion resistance and tensile strength. The good covering of the cotton fibre surface by the

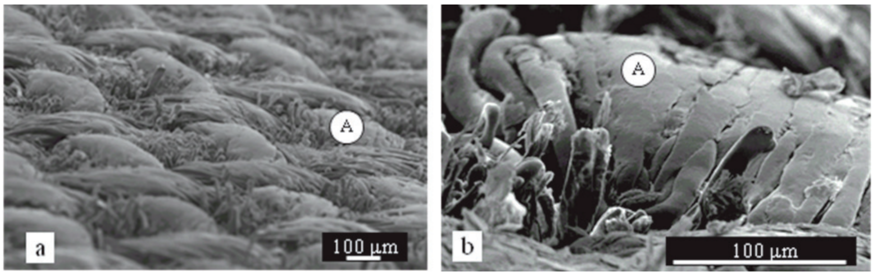

Figure 4. *SEM images, taken at an angle of 10 degrees, of cotton fabric coated with modified SiO_2/Al_2O_3 sol after abrasion tests. Area 'A' shows the good condition of coats deformed by abrasion.*

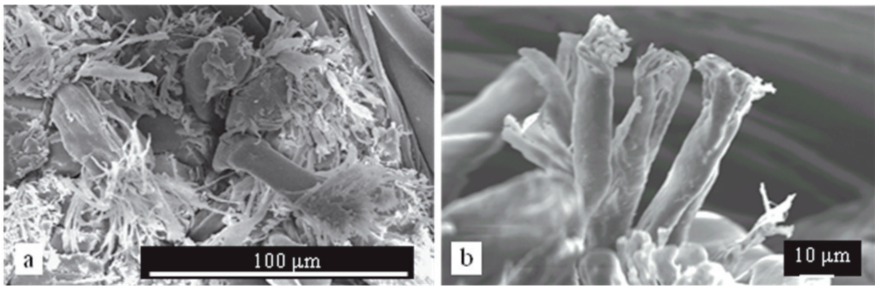

Figure 5. *SEM images of fabrics after abrasion tests: (a) unmodified cotton fabric (clear fibrillation of fibers), (b) cotton fabric coated with modified SiO_2/Al_2O_3 sol (no fibrillation of cotton fibers).*

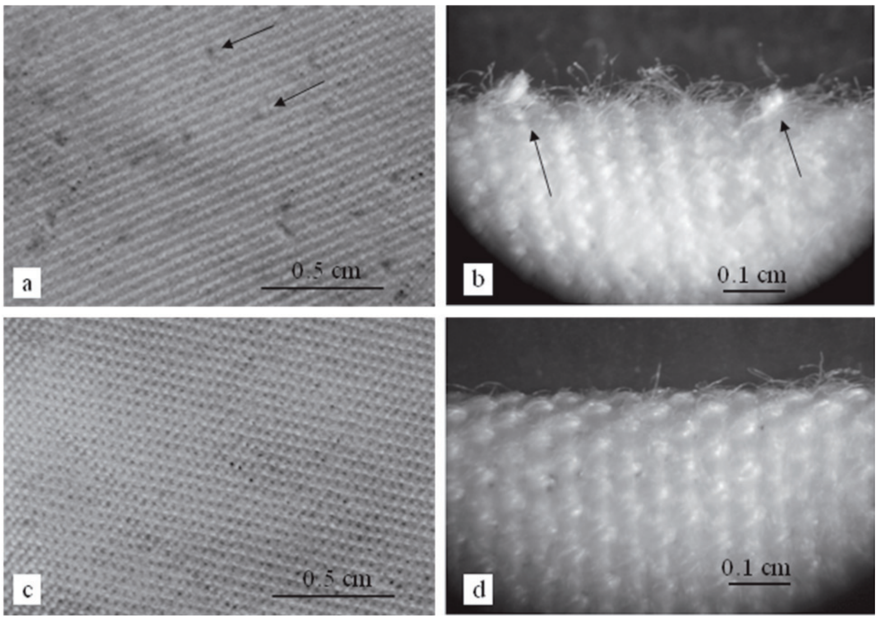

Figure 6. *Photos of fabrics after pilling tests: (a, b) untreated fabric (arrows indicate pills); (c, d) fabric coated with SiO_2/Al_2O_3 sol. Photos (b) and (d) show the edges of bent fabric taken under an optic microscope.*

xerogel coat is also visible in SEM images (***Figure 4***) showing the fibre surface after an abrasion test. Even after a prolonged action of the abrasive head (with a standard wool abradant), the protective xerogel coats remained undisturbed, undergoing only slight deformation – area "A" in ***Figures 4.a*** and ***4.b***. Moreover, if in the untreated fabrics clear cotton fibre fibrillation occurs (***Figure 5.a***) due to abrasion, as in the case of the fabrics finished with xerogel coatings, individual cotton fibres are enclosed by a stable protective coat and the fibre ends remain undamaged without any signs of fibrillation (***Figure 5.b***).

The abrasion tests performed confirm the protective action of xerogel coats. As a result of the coat finishing, the fabric abrasion resistance increased from 40 000 cycles to about 55 000 cycles, i.e. by about 38%, and this value remains unchanged after 5 washing cycles under standard conditions. It should also be noted that the increase in abrasion resistance of fabrics from PET/CO blends results first of all from the abrasion-proof soft cotton fibre occurring in a minority of cases (33%) and not from "hard" PET fibres, which, even without the xerogel coat, show a high abrasion resistance.

In addition to the considerable increase in abrasion resistance, the coat finishing used contributed to a very significant increase in fabric resistance to pilling. The tests performed show that this resistance of the fabrics coated was increased from the level 2 – 3 for untreated fabric to the highest level of assessment: 5, which indicates a smooth fabric surface without any signs of abrasive wear.

This very good resistance to pilling is also illustrated in the photos of fabric samples taken from the Martindale apparatus after the pilling test (7000 cycles) - ***Figures 6.a*** & ***6.b*** show untreated fabrics, and ***Figures 6.c*** & ***6.d*** show fabrics coated with SiO_2/Al_2O_3 sol.

Conclusions

1. The test results presented confirm the soundness of both assumptions of the synthesis of hybrid modified SiO_2/Al_2O_3 and the conditions of their application – the technology of depositing xerogel coats on polyester and cotton fibres.
2. The hybrid xerogel coats made on the fibre surface form a continuous and uniform covering thereof and are characterised by a high elasticity and resistance to chipping as well as by a very good combination with the fibre surface, as confirmed by the unchanged coat condition even after fivefold laundering under standard conditions.
3. The high resistance to abrasion and pilling of hybrid xerogel coat finishing and its durability in use and care conditions (after multiple washing processes), determined by Martindale tests, is confirmed by the results of the SEM and AFM examinations.
4. The synthesis of hybrid modified SiO_2/Al_2O_3 sol and the conditions of its deposition on fibres to form effective and durable xerogel coats increase the prospects of the industrial implementation of the coat finishing of PET/cotton textiles by the sol-gel

method for various applications, especially footwear and protective clothing materials.

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