A COMPARISON BETWEEN ACRILIC RESIN AND BUTANETETRACARBOXYLIC ACID USED TO BIND TiO_2 NANOPARTICLES TO COTTON FABRICS.

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ABSTRACT

In order to apply finishing particles onto fabrics, several methods such as, padding, bath exhaustion, spraying and foaming can be used. In this research, spray treatment is compared to padding when applying TiO_2 nanoparticles onto textile. Cotton fabrics´ surfaces were observed by scanning electron microscopy (SEM) and characterized by Fourier Transformed Infra Red (FT-IR) spectroscopy and energy dispersive using X-Ray (EDX). EDX technique showed that it was a suitable method to detect the presence of Ti particles on the fabric surface. We confirm that the fabric treated by padding procedure contained a higher quantity of Ti particles than the one treated by spraying. On the other hand, we compared two different auxiliary products to bind the particles onto the fibers, an acrylic resin and the polycarboxilic acid 1,2,3,4-butanetetracarboxylic acid (BTCA) in the presence of sodium hypophosphite (SHP). We used EDX to evaluate the effectiveness of both binders after washing . We improved the presence of TiO_2 particles on the fibers when using an acrylic resin, and observed that when BTCA, is used to fix the particles, there was no increase in the quantity of titanium on the fabric after 5 washing cycles compared to the sample without binder treatement.

KEY WORDS

Polycarboxilic acid

Acrylic Resin

Binder

INTRODUCTION

UV-blocking agents have been developed to improve the UV-protective function of textiles. There are both organic and inorganic blockers. The organic blockers are also called UV absorbers because they mainly absorb UV rays. Inorganic UV blockers are usually certain semiconductor oxides such as TiO_2, ZnO, SiO_2, Al_2O_3 and other related products (Chen et al. 2010; Montazer and Seifollahzadeh 2011, Yang and Zhu 2004).

Recently, the use of nano titanium dioxide (TiO_2) to improve the absorption of ultra-violet irradiation on fabrics´ surface has been studied in many works (mainly Chen et al. 2010; Montazer and Seifollahzadeh 2011; Yang and Zhu 2004; Ibrahim et al. 2010; Nazari et al. 2009; Sunderesan et al. 2011), due to its good photocatalytic properties, low cost, high stability and efficiency (Kuo et al. 2011). UV protection is a natural attribute of TiO_2, which can be explained by the band theory of solids. The band gaps for rutile and anatase are 3.0 eV and 3.2 eV, respectively, corresponding to the absorption bands of 413 nm and 388 nm. (Chen et al. 2010; Mo and Ching 1995). The absorption band centred on 413 nm is in the visible light range. This is the reason why TiO_2 has photocatalytic activity under UV radiation and visible light (Chen et al. 2010).

Several methods can be used to apply finishing materials onto fabrics, such as, padding (Dehabadi, et al. 2012; Cheema et al 2010; Wang and

Chen 2006; Martel et al. 2002), bath exhaustion (Bonet et al. 2012, Mongkholrattanasit 2014), spraying (Miró et al. 2010), and foaming (Sarier and Onder 2012). But when treating the textile with TiO_2 padding is the most commonly used method (Chen et al. 2010; Ibrahim et al. 2010; Nazari 2009; Sunderesan 2011; Dong et al. 2007; Colleoni et al. 2012; Dong et al. 2007; Pan et al. 2006). Several articles have studied the use of TiO_2 with some auxiliary products such as polycarboxylic acids (Montazer et al. 2011; Nazari et al. 2009; Montazer et al. 2012; Karimi et al. 2010; Wanga and Chen 2005) to improve durability during washing or handling. Carboxylic acids have been used to modify the TiO_2 nanoparticles as well (Qu et al. 2010).

Cotton fabrics are generally treated with crosslinking agents in combination with phosphorus-containing catalysts to impart anti-crease and durable press properties (Yang 2001). This is due to the fact that crosslinkers react with the hydroxyl groups in cellulose molecules with primary chemical bonds (Lam et al. 2010; Trask-Morrell et al. 1994; Sricharussin et al. 2004; Dehadabi 2012; Peng 2012). Previous studies have shown that the crosslinking agents can interact with nanoparticles of titanium dioxide to improve the adhesion between cellulose molecules, but these carboxylic acids need to have at least two free carboxylic groups to be able to bind to both cotton and TiO_2 (Montazer et al 2012; Karimi et al. 2010). Butanetetracarboxylic acid (BTCA) with a sodium hypophosphite (SPH) catalyst has been recognized as having excellent performance including durability in repeated laundering (Kim, Y.H., et al 2003).

The focus of this work was to improve the UV protection activity of cotton fabrics finished with TiO_2 by increasing the presence of nanoparticles on the fabric. We compared the effectiveness of the treated cotton with TiO_2 by spraying or by padding, two commonly used industrial procedures. On the other hand, BTCA and an acrylic binder were selected to improve the particles durability on the fibres surface, it was evaluated their presence after 5 laundering cycles.

Surfaces of treated cotton samples were observed to evidence the presence of metal oxide on the fibre surface by Spectroscopy Electronic Microscope (SEM). Energy Dispersive X-ray (EDX) and Fourier transform infrared (FTIR) spectroscopy were used to know the amount of titanium on the fabric and to evaluate the loss of particles after 5 washes.

2.- MATERIALS AND METHODS

2.1.- Materials

The nano TiO_2 Degussa p-25 with 21 nm size was purchased from Evonik. BTCA with sodium hypophosphite monohydrate (SHP) and acrylic resin were employed to bind TiO_2 onto fabric. BTCA and SHP products were supplied by Aldrich Chemical Co., Alfa Aesar and Color Center, respectively.

The bleached 100% cotton twill fabric used, had the wrap density of 35 yarn/cm, the weft density of 20 yarn/cm and the fabric weight of 210 g/m^2.

2.2. - Preparation of TiO_2 fabrics

The nanoparticles dispersions were prepared with 2 g/L of TiO_2. The nano-particles of TiO_2 were applied to the surface of the fabric by padding or spraying. For padding, a horizontal foulard was used and its parameters were controlled in order to obtain a pick-up of around 88%. Concerning spraying method, the samples (2g) were sprayed on one side of the fabric. We controlled the amount of solution applied by gravimetric methods in order to get the same amount of solution by both spraying and padding.

Pad-dry-cure process was applied to the cotton fabric with TiO_2 with binders, acrylic resin or BTCA to compare the effectiveness of the products to adhere the nanoparticles onto cotton fibres. Samples treated with the acrylic binder were padded in a solution with 2 g/L of TiO_2 and 5g/L of the acrylic resin however; another cotton sample was treated using BTCA and SPH as crosslinking binder, employing 80 g/L and 40 g/L, respectively. Both samples were padded to obtain a pick-up of around 88-90%. Just immediately of padding procedure, samples were dried at 85ºC for 4 min and cured for 2 min, using different temperatures. The samples treated with an acrylic binder were cured at 110ºC. Previously, it had been demonstrated that this temperature was high enough to polymerise the binder (Monllor et al. 2010). The sample treated with BTCA were cured at 160ºC, temperature necessary to achieve the crosslinking and not to change the colour of the fibre considerably (Franklin et al. 1972; Socrates G 1997)

2.3. - Scanning electron microscopy

Changes in surface morphology were also observed with a scanning electron microscope FEI model Phenom (Fei, Oregon, USA). Prior to sample observation, samples were covered with a gold‐palladium alloy in a Sputter Coater EMITECHmod. SC7620 (QuorumTechnologiesLtd., EastSussex, UK). Samples were examined with suitable accelerating voltage and magnification. SEM pictures were taken of the tested samples to verify the existence of TiO_2 on the fibre surface.

2.4. - FT-IR Spectroscopy

A BRUKER IFS 66/S FTIR spectrometer and an attenuated total reflectance (ATR) accessory were used to analyse the spectrum and to obtain the amount of the TiO_2 on the fabrics. The resolution for the infrared spectra was 4 cm^{-1}, and there were 64 scans form each spectrum. Only treated samples by padding and spray, without some auxiliary products, were analysed.

2.5.- Scanning electron microscopy/ energy dispersive using X-Ray

Energy dispersive X-Ray (EDX) analyses were conducted using a Scanning Electron Microscope JEOL JSM-6300. The samples had previously been covered with graphite in order to transform non conductive surface of fibres into a conductive one, graphite was selected to cover the fibres as a metal could interfere with the results. All the electron microscopy images were obtained with an accelerating voltage of 10 KeV. The EDX spectrums were also performed to verify the elemental composition of the deposited materials on the fibre surface. Analysis of this data allowed comparisons of TiO_2 nanoparticles at different locations on the fabric.

2.6.- Washing fastness

The washing fastness of samples with TiO_2 treated with BTCA and acrylic resin was tested by following UNE EN ISO 6330 method no. 2A. For each sample, 5 washing cycles were carried out.

3.- RESULTS

3.1.- SEM images

TiO_2 nanoparticles on cotton fibres are easily observed by SEM microscopy. Figure 1 shows SEM images with a suitable magnification of the cotton samples untreated and treated with TiO_2. Figure 1(a) shows the SEM micrograph of untreated sample, Figures 1(b) and 1(c) show the SEM micrograph of samples treated by spraying and padding, respectively.

The presence of a extraneous material can be observed in Figures 1b and 1c whereas it is not detectable in Figure 1a. This is due to the treatment with TiO_2, which allowed deposit of the nanoparticles on the fibre´s surface.

FIGURE 1 ABOUT HERE .

Regardless of the procedure used, we can observe that both treated samples show particles on the fibres' surface. If we compare images with different methods of application, it seems that the micrograph of samples treated by padding (Figure 1c) show more nano-particles than the ones treated by spraying (Figure 1b). Moreover, it is interesting to notice that the size of the TiO_2 particles on the fabric were different despite the fact it was the same product. The samples treated by padding seemed to have bigger particles than the ones observed on the samples treated by spraying, this may be due to the presence of aggregates of TiO_2 particles which had adhered to the cotton fibres.

3.2. - FT-IR Spectroscopy

To obtain the information on the reaction mechanism, ATR-IR measurements were carried out over 650-4000 cm^{-1}, as shown in Figure 2.

INSERT FIGURE 2 ABOUT HERE

Several works have demonstrated that the reaction mechanism of the TiO_2 is as follows: the pairs of free electrons and empty orbitals are formed in the conduction and valence band region of TiO_2 under the UV irradiation, which react with oxygen and absorbed hydroxyl groups to produce superoxide ($^{\bullet}O_2$) and hydroxyl radicals ($^{\bullet}OH$). (Karimi et al. 2010, Socrates 1997). For this reason, the wave peak in the 3600-3100 cm^{-1} range, associated with the peak of –OH groups of the cellulose, it is decreased when the cotton fabric is treated by TiO_2, due to the fact that TiO_2 has a high affinity towards hydroxyl groups (Socrates 1997).

It is noticeable that the presence of TiO_2 on fabric cannot be clearly appreciated by any specific peak, especially for Ti. However, we can see the loss of intensity of the hydroxyl group’s band. In order to standardise the results and avoid the influence of the signal in the measurement, the intensity of the band of OH groups was related to the presence of a band which is not modified by the treatment. It is the one related with –CH groups at 1317 cm^{-1}. The degree of consumption of –OH by the presence of TiO_2 was calculated from the proportional intensities of two wavelength's bands (-OH group 3336 cm^{-1}/-CH group 1317 cm^{-1}), bands which were described by Socrates (Socrates 1997). Moreover, the band at 1476 cm^{-1} corresponds to the symmetric stretching vibration of a bidentate carboxylate group with titanium atoms (Wu et al. 2009). To compare the amount of Ti atoms on the surface of the fibres, we calculated the ratio "band -O-Ti group 1476 cm^{-1}/ band -CH group 1317 cm^{-1}".

Table 1 presents the intensities of the bands at wavelengths of 3336 cm^{-1}, 1317 cm^{-1} and 1476 cm^{-1}, as well as both intensity ratios of these two wavelengths bands (3336 and 1476 cm^{-1}) normalized with the band at wavelength of 1317 cm^{-1} obtained from untreated and treated fabric with TiO_2 either by spraying or padding.

INSERT TABLE 1 ABOUT HERE

Analysis of results show lower values for the ratio "-OH group 3336 cm^{-1}/-CH group 1317 cm^{-1}" from samples with TiO_2 and higher values for the ratio "-O-Ti group 1476 cm^{-1}/-CH group 1317 cm^{-1}". This can be seen for both sprayed and padded samples compared with untreated fabric. This may be due to the consumption of hydroxyl groups in the reaction between the TiO_2 and cellulose therefore, these results corroborate the higher presence of TiO_2 on cotton fabric treated by padding. Thus, demonstrates that TiO_2 has reacted with the hydroxyl groups. Both ratios studied; the ratio "-OH group 3336 cm^{-1}/-CH group 1317 cm^{-1}" and the ratio "-O-Ti group 1476 cm^{-1}/-CH group 1317 cm^{-1}"; are sensitive to the presence of TiO_2 on cotton fibres. When both treatments are compared, contrary to expectations, the padding procedure seems to increase the presence of TiO_2 on fabrics more than the spraying one.

3.3. Scanning electron microscopy/ energy dispersive using X-Ray

EDX was used to check if the particles seen on the surface of the fibres are TiO_2 and to assess the quantities of Ti atoms . EDX spectra of treated cotton samples are shown on Figure 3, where we can observe the characteristic titanium peak around 4,5 keV. This result confirms the presence of the particles shown by SEM images on cotton fibres. In order to assess the quantity of Ti located on the fabric, every sample was analysed over the same area (120x90 µm), we analysed the Ti atoms in each sample, and these results can be observed in Table 2.

INSERT FIGURE 3 AND TABLE 2 HERE

This analysis evaluates the amount of Ti deposited on the treated fabrics by different methods and enables a comparison to be established. We can observe a significant difference between both ratios. Results showed that padded samples contain more Ti particles than for the spaying method. This technical experiment corroborates the previous results found with

FTIR tests.

On the other hand, trying to improve the treatment durability during washing we used different auxiliary products, BTCA and SHP or an acrylic resin, to bind the TiO_2 particles onto the cotton fibres. Treated samples by TiO_2 with or without the use of auxiliary products were washed 5 times and these samples were evaluated by EDX. Table 3 and Figure 4 show % Weight Ti for each one of the samples after the washing cycles. It can be appreciated that the Ti particles deposited onto the cotton fabric are the same after the treatment, and the presence of auxiliary products to bind the particles onto the fibre does not show any influence.

INSERT TABLE 3 AND FIGURE 4 HERE

In Figure 4 shows the reduction in % Weight Ti when samples were washed for each sample , it can be observed that, as expected, the result decreased after 5 washing cycles. When the analysis is focused on the nature of the binder used, we can appreciate the stronger effect that the resin shows. Washed samples, which have been treated using acrylic resin, show higher values for % weight Ti, which implies that the fabric contains a higher quantity of TiO_2 than washed samples which had been treated using BTCA and SHP.

CONCLUSIONS

The effect of two different methods of applying TiO_2 onto a fabric, spraying and padding was studied. If padding treatment is compared with spraying using different techniques we can see that the sample treated by padding showed a higher quantity of TiO_2 particles on the cotton fibres' surface. SEM showed that the surface of fabric treated by padding presents a higher number of nanoparticles. The FT-IR analysis confirms this conclusion as the hydroxyl group decreases due to the reaction between TiO2 and cellulose hydroxyl groups . The EDX spectra confirm the presence of the titanium on the fabrics' surface. In order to compare the differences between the quantity of titanium on the fabric treated by different methods, we used the % weight Ti, which confirms that fabrics treated by padding contain a higher quantity of Ti particles. The results of this investigation showed that the EDX technique is a suitable analysis to detect Ti particles on a fabric´s surface. It must be remarked that the system for applying TiO_2, depends on the nature of the fabrics and the use they will have.

On the other hand, we used BTCA and SHP or an acrylic resin to fix the nano TiO_2 by pad-dry-cure. We studied the binders resistance to the washing process. Samples analysis by EDX evaluated the effect on TiO_2 durability. We analysed %weight Ti for unwashed and washed treated samples. We concluded that washed samples, which had been treated using acrylic resin, contained a higher quantity of TiO_2 on the fabric than those samples that had been treated using BTCA and SHP. This indicates that the acrylic resin is a good adhesive to bind this kind of particle onto the fabric.

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TABLES

Table 1 Intensity of the bands at the wavelengths 3336 cm^{-1}, 1317 cm^{-1} and 1475 cm^{-1} and the intensities for the untreated and treated cotton samples by spraying and padding methods.

Funtional group	Wavelenght (cm^{-1})	Intensity of bands		
		Untreated fabric	Sprayed fabric	Padded fabric
-OH	3336	0,5375	0,5189	0,4845
-CH	1317	0,1445	0,1438	0,1393
-O-Ti	1475	0,0559	0,0595	0,0614
-OH/CH	3336/1317	3,7183	3,6094	3,4776
-O-Ti/-CH	1475/1317	0,3870	0,4139	0,4404

Table 2 %Weight of titanium and oxigen for the untreated and treated cotton samples by spraying and padding methods

	Untreated sample	Sprayed sample	Padded sample
% Weight Ti	-	0,59	1,785

Table 3 %Weight of titanium for the treated fabric by TiO_2 without and with auxiliar products, acrylic resin or BTCA and SHP, as binders and evolution of this result to unwhased and washed cotton samples, 0, 1 and 5 washes.

	TiO_2 Fabric		
	0 washes	**1 wash**	**5 washes**
%Weight Ti	1,79	0,93	0,23
	TiO_2 and Acrylic Resin Fabric		
	0 washes	**1 wash**	**5 washes**
%Weight Ti	1,35	0,96	0,52
	TiO_2, BTCA and SHP Fabric		
	0 washes	**1 wash**	**5 washes**
%Weight Ti	0,27	0,78	0,35

FIGURE 1

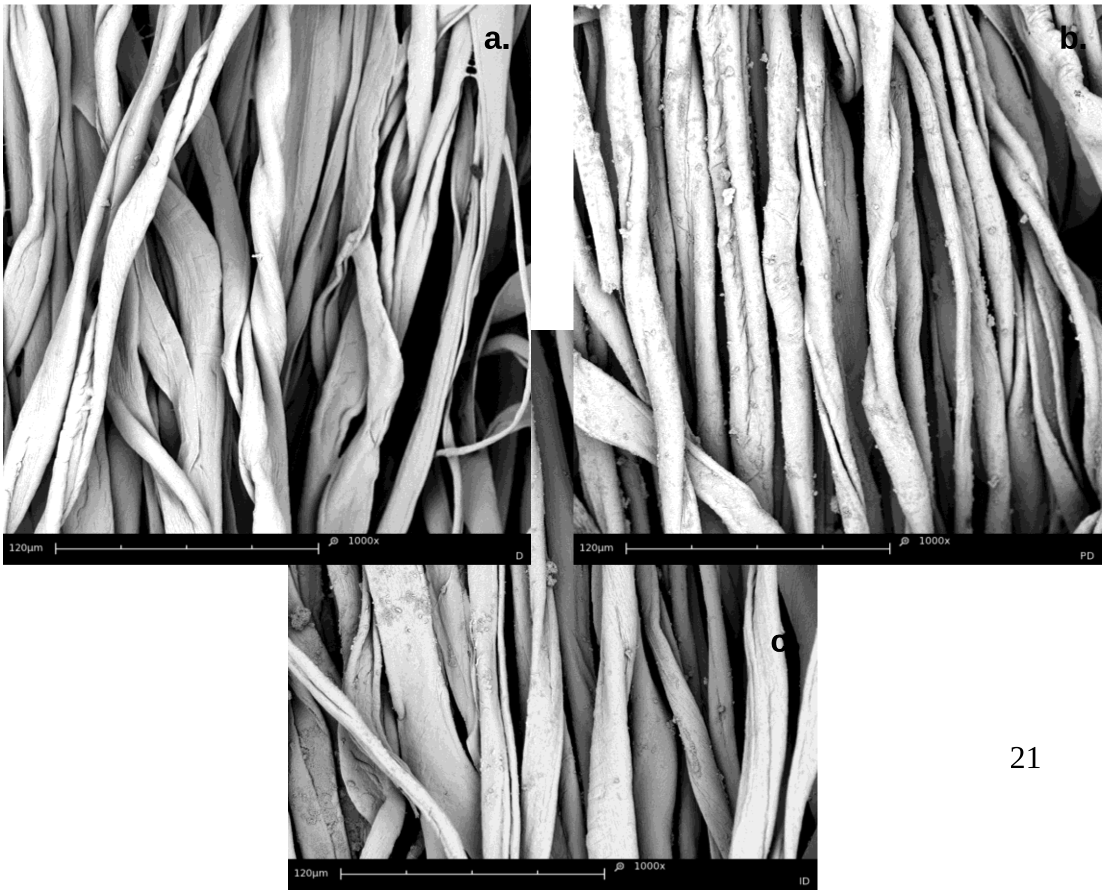

Figure 1. SEM images of the untreated and treated fabrics with TiO_2 nanoparticles by different methods at 1000 magnificatios: (a) untreated fabric (b) treated fabric by spraying, (c) treated fabric by padding.

FIGURE 2

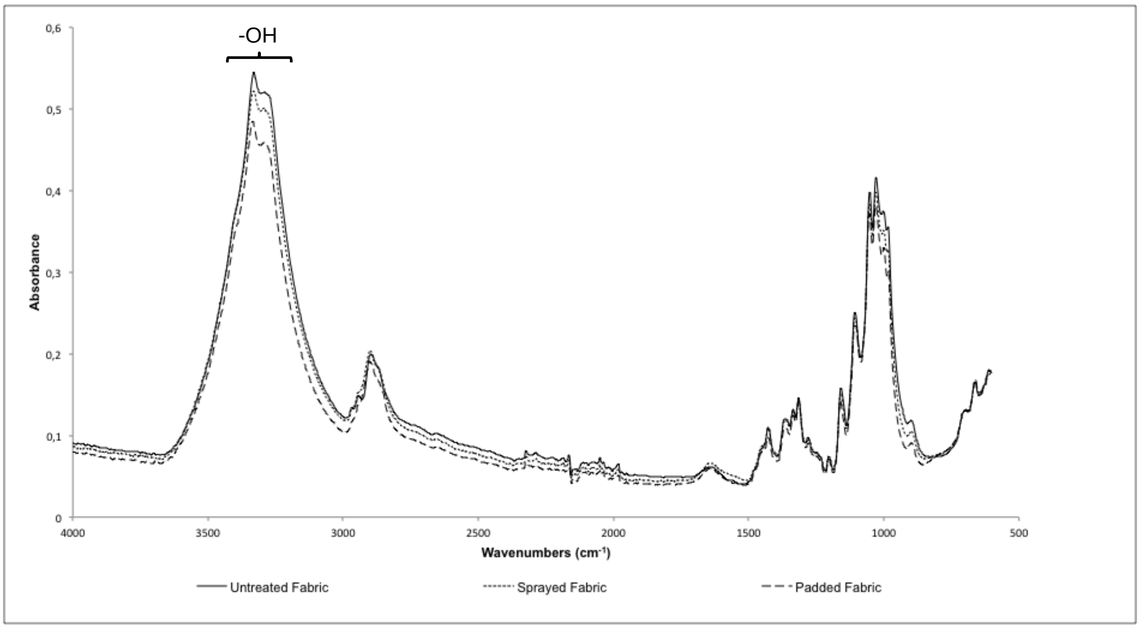

Figure 2. FTIR spectra of untreated and treated samples in the presence of TiO_2 (2 g/L) by padding and spray.

FIGURE 3

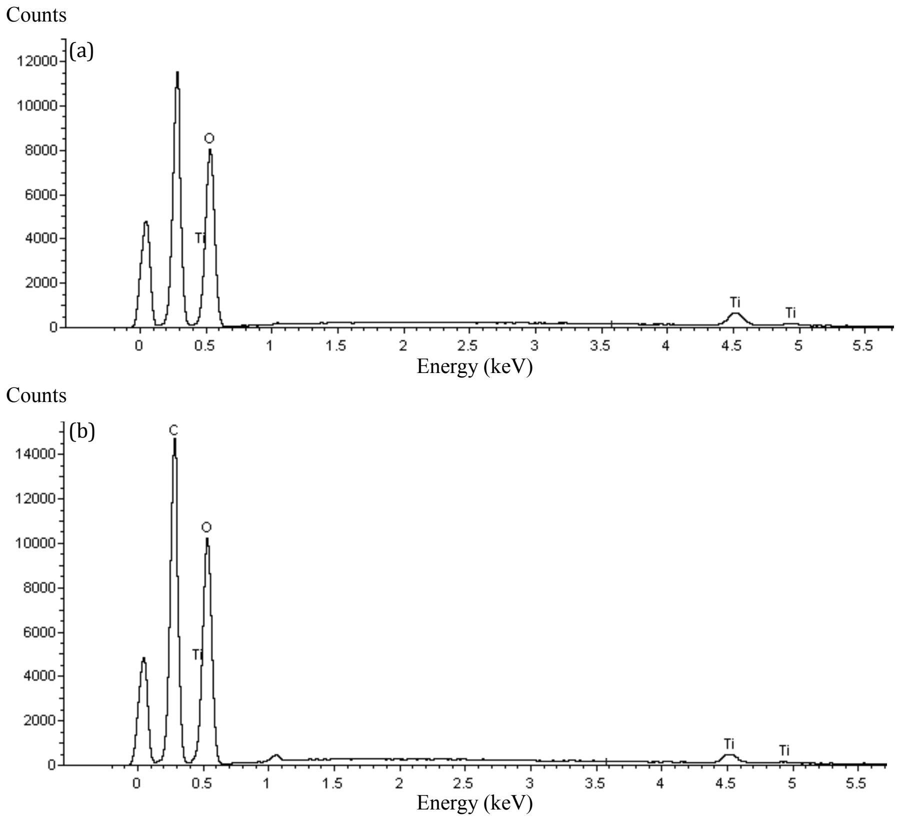

Figure 3 EDX spectra of treated samples in the presence of TiO_2 (2 g/L), (a) treated sample by padding, and (b) treated sample by spray.

FIGURE 4

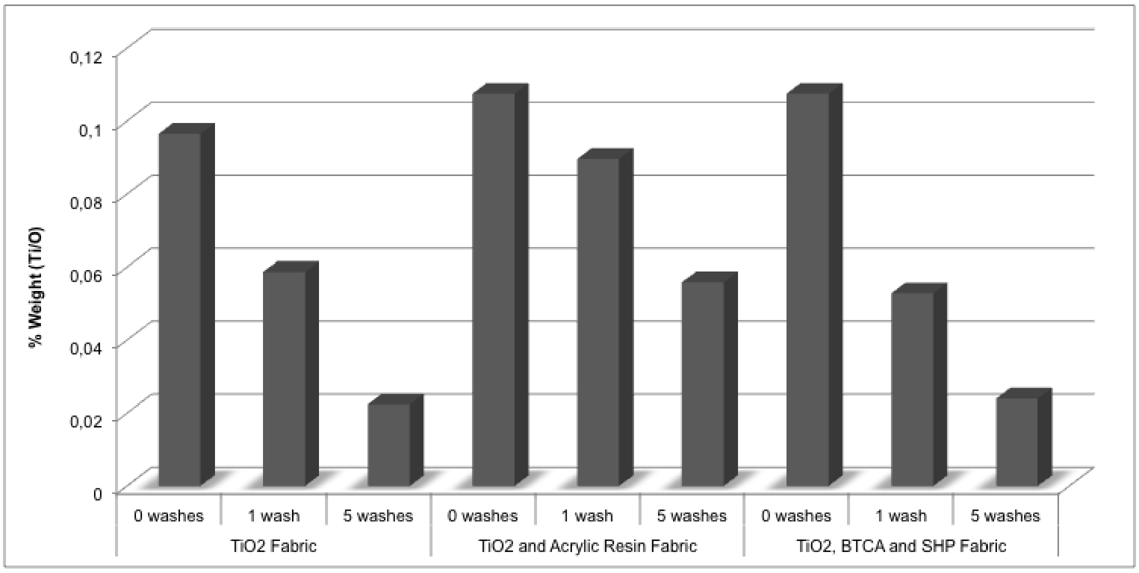

Figure 4 Comparative diagram of the %Weight Ti for the treated fabric by TiO_2 without and with auxiliar products, acrylic resin or BTCA and SHP, as binders and evolution of % weight Ti to unwhased and washed cotton samples, 0, 1 and 5 washes.