Catalysis Today 161 (2011) 15–22

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Photocatalytic evaluation of TiO_2/nylon systems prepared at different impregnation times

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ARTICLE INFO

Article history:
Available online 20 October 2010

Keywords:
Impregnation time
Photocatalysis
TiO_2/nylon
Methanol photodegradation

ABSTRACT

TiO_2/nylon fabrics were investigated for methanol degradation under UV light irradiation. TiO_2 Degussa P-25 was supported on nylon by immersing the nylon in sol–gel TiO_2 and silicone. The TiO_2 layers on the nylon were explored as a function of the time of immersion, impregnation agent and the type of nylon fabric used. The energy diffuse spectroscopy (EDS) and infrared spectroscopy (ATR-FTIR) confirmed the presence of TiO_2 bonded to the nylon fabrics. Optical microscopy (OM) and scanning electron microscopy (SEM) show a more uniform distribution of TiO_2 on nylon fabrics prepared by immersion in sol–gel as compared to the silicone method. The most suitable photodegradation of gaseous methanol by TiO_2/nylon samples was obtained by sol–gel samples prepared by 24 h immersion time.

1. Introduction

Methanol is a VOC's type gaseous emission from numerous industries. It is widely used as industrial solvent, raw material in the manufacture of formaldehyde, as antifreeze in vehicles, fuel for camping-gas canisters, and in the preparation of dyes, resins and adhesives [1]. At 20 °C it is harmful in the air leading to irritation of eyes, skin and respiratory problems within a short exposure. Higher doses lead to unconsciousness and death [2,3].

Heterogeneous photocatalysis is a promising technology for the removal of VOC's, by the use of supported TiO_2 to abate pollutants in the gas phase [4]. Photoactive systems TiO_2/textile fibers are promising supports for TiO_2 due to their low cost, high surface area, flexibility and relative stability [1]. Studies of TiO_2 coated fabrics for pollutant degradation [5–7], self-cleaning [5,8,9] and bacterial inactivation have been recently reported, and show a potential for large scale application [5,10,11].

Two immersion–diffusion methods for the catalyst preparation by dip coating were evaluated at different impregnation times [12,13] focusing on the immersion time of the nylon in the TiO_2 suspensions. The first method used silica sol–gel as the TiO_2 binder and the second method used silicone as the binding agent. The photocatalytic degradation was investigated as a function of the type of binder, the immersion time and the type of nylon used.

2. Experimental

2.1. Materials

Two types of 100% nylon fabrics were used: the first type, nylon NT is a commercially ready for use in the form of a cohesive yarn containing lubricants, bleaching agents and stabilizers [1,12]. The second type, nylon NC, is a fabric that has not the finishing process [12]. Both types of nylon were provided by local textile industries.

2.2. Nylon textiles prepared using TiO_2–SiO_2 sol–gel

The sol–gel of SiO_2 to impregnate the nylon was prepared using 15 mL of tetraethyl orto-silicate (TEOS), 2.4 mL of distilled water, 25 mL of isopropyl alcohol (ISO) and 0.1 mL of HCl 3 M. All chemicals were reagent grade (p.a.). The hydrolysis of TEOS leads to the substitution of OR groups linked to silicon by silanol Si–OH groups (Fig. 1a and b). These groups react to form Si–O–Si (siloxane), leading to a three-dimensional network (Fig. 1c). The isopropyl alcohol and ethanol formed during the process remained within the pores of the network (Fig. 1d) [12,13].

After ageing for 24 h, the silica structure was formed. Then, TiO_2 Degussa P-25 (3.6 g) was added and was trapped within the pores of silica matrix (Fig. 1d). The TiO_2 enters the SiO_2 matrix and remains catalytically active as observed during the degradation of methanol.

Subsequently the nylon sample of 9 cm^2 of area was immersed into this TiO_2–SiO_2 suspension and left for 11 or 24 h for the

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doi:10.1016/j.cattod.2010.09.005

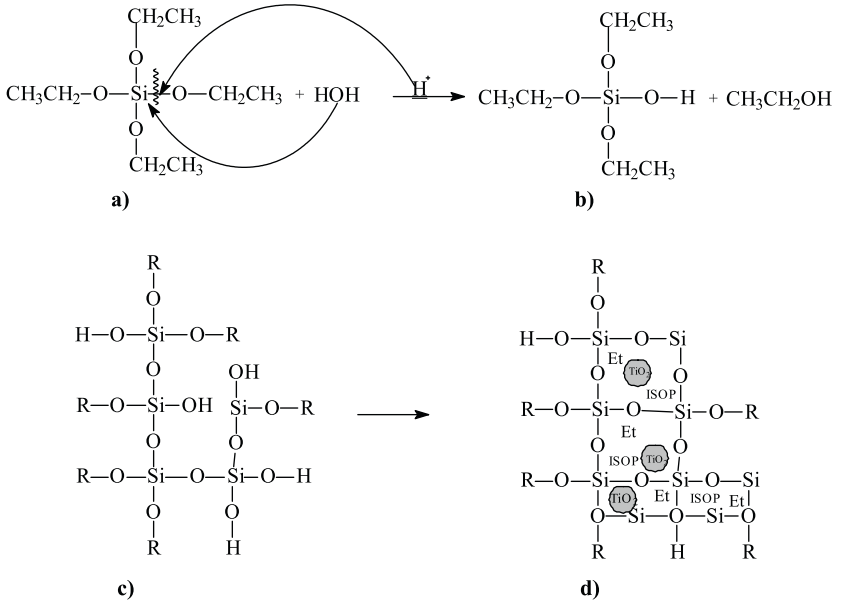


Fig. 1. Mechanism of silica matrix formation by sol–gel method and addition of TiO_2 Degussa P-25 (in the figure, a bi-dimensional view is displayed). a and b) Substitution of OR groups linked to silicon by silanol Si–OH groups, c) Si–OH groups react to form Si–O–Si (siloxane) bonds, and d) isopropyl alcohol (ISOP) and ethanol (ET) formed during the process remained within the pores, additionally TiO_2 Degussa P-25 is trapped within the pores after its addition.

suspension to diffuse into nylon. Coated samples were washed and dried at 100 °C for 1 h as noted in the scheme shown in Fig. 2. The silica added on the nylon served as a binder for TiO_2 and protected the nylon from the H^+ attack during light irradiation.

2.3. Nylon samples prepared with TiO_2 using silicone

In the second method, the silicone dispersion was prepared by diluting 0.84 g of silicone in 50.4 mL of dichloromethane under magnetic stirring. Then, 3.5 g of TiO_2 was added to the dispersion. Nylon fabrics were immersed in the dispersion for 11 or 24 h. Then, the coated samples were dried in oven at 100 °C for 1 h and washed thoroughly. Fig. 3 shows the schematic of the coating process using silicone. The poly-silicone has been widely reported as a binding agent [1].

Nylon samples impregnated with silicone presented a yellow color unlike the sol–gel coated with SiO_2 fabrics that were observed to be white. The coloration of the fabrics is due to the oxidation of silicone leading to colored functional groups [14,15].

2.4. Characterization of samples

Scanning electron microscopy (SEM) analysis of the coated fabrics was carried out in scanning electron microscope (JEOL JSM 5910LV) provided with a BS-SE-detector. An X-ray detector type EDS (energy dispersive spectrometer) was used for the surface chemical composition analysis. Optical microscopy images of the impregnated TiO_2 surface were made using a NICO E200 microscope in a transmittance mode.

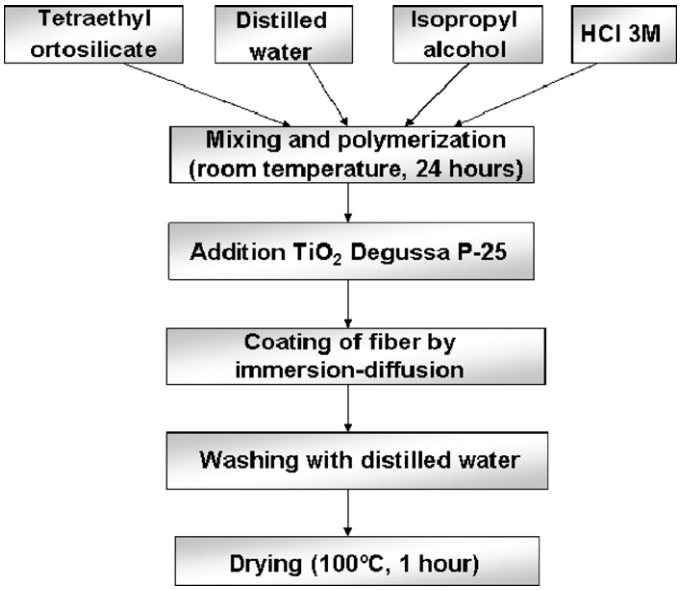


Fig. 2. Schematic of the sol–gel coating.

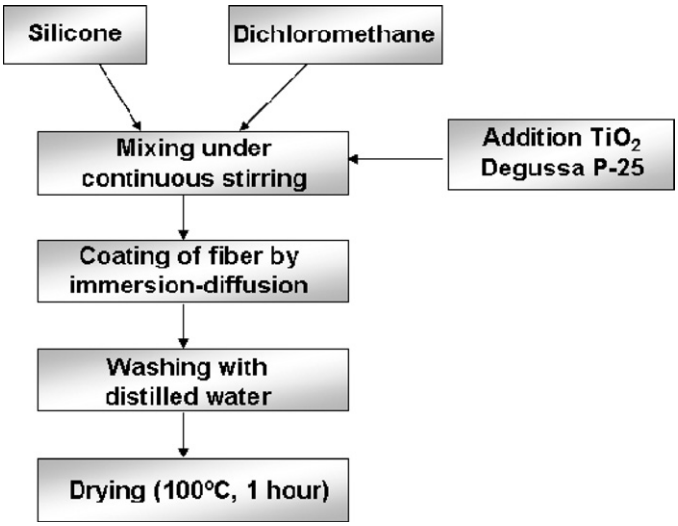


Fig. 3. Schematic of the coating process using silicone.

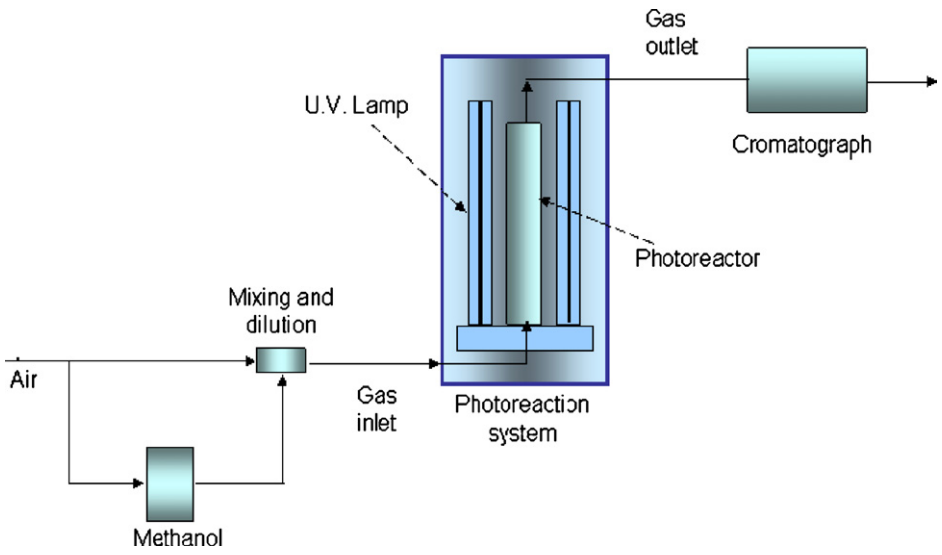


Fig. 4. Photodegradation unit of methanol.

The infrared spectroscopy was performed with an IR-Prestige-21/8400S Fourier Infrared Transform Spectrometer provided with an attenuated total reflectance (ATR-FTIR) attachment. The spectrum was taken in the range of 4000–500 cm^{-1}.

2.5. Photocatalytic evaluation of the fabrics

The photocatalysis was carried out by passing a methanol gas flow over TiO_2 coated nylon fabrics in a reactor provided with three UV lamps (365 nm, 4 W, Phillips). Plug flow tubular reactor made of Pyrex glass was used (9 cm length, effective volume 50 mL) and TiO_2 coated fabrics were positioned inside on the reactor wall.

The UV lamps were positioned around the reactor and aligned in a concentric axial geometry at 120° of each other. An average power of 4.6 W/m^2 and a temperature of 33 °C were measured in the reactor unit during the irradiation of the samples. The schematic diagram of the photodegradation unit is shown in Fig. 4. The airflow was split into two streams; the first flow

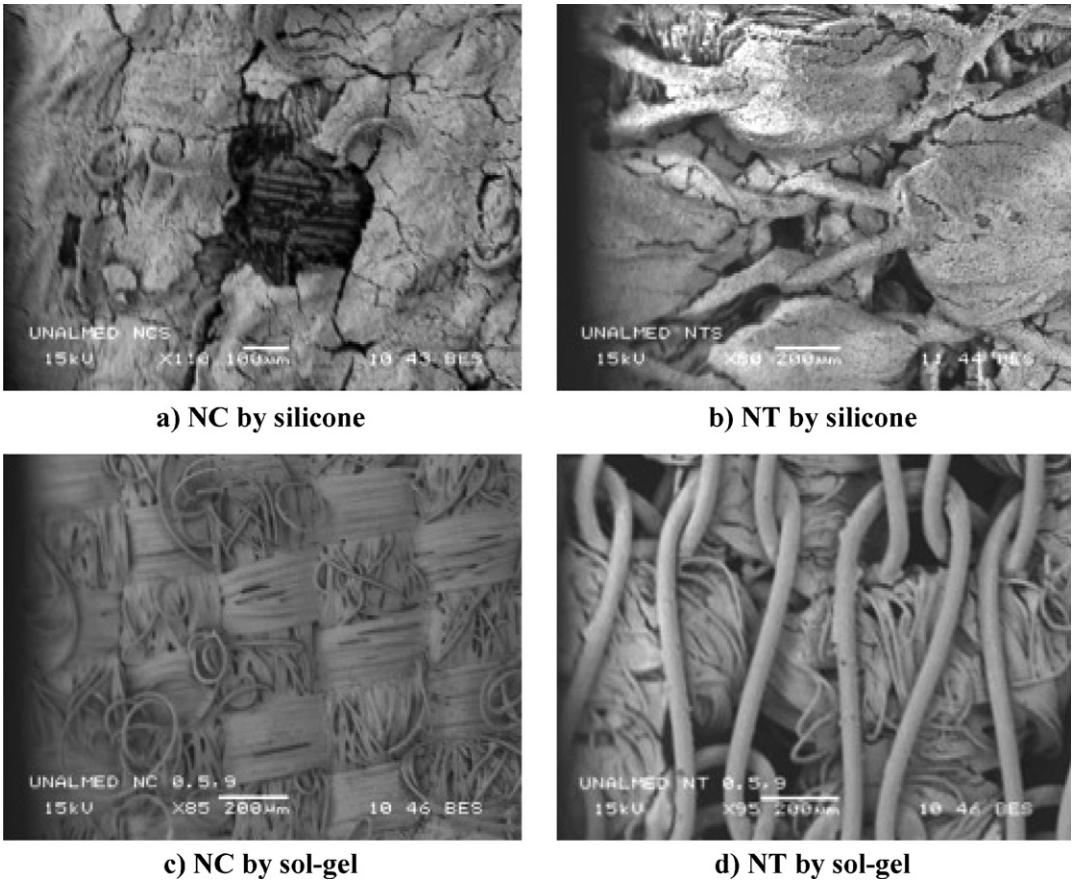
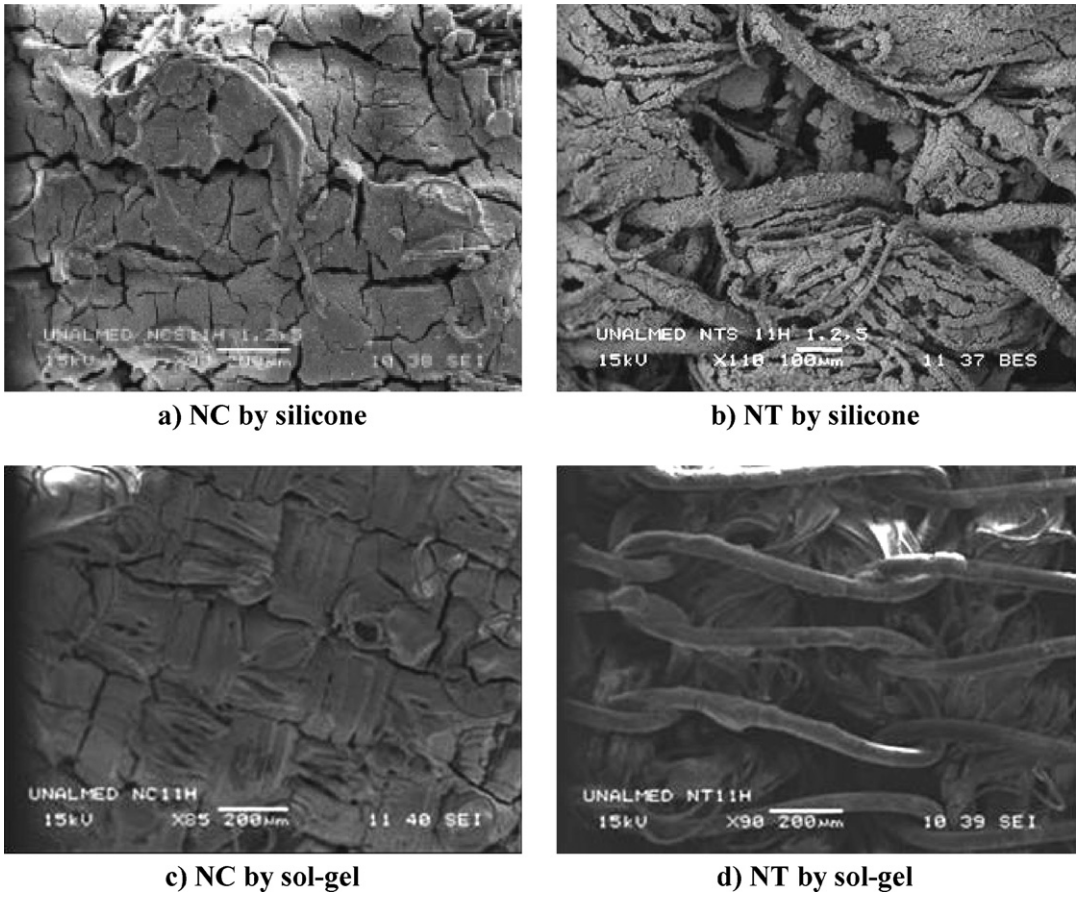


Fig. 5. SEM images of coated nylons with immersion time of 24 h by a and b) silicone and c and d) sol–gel.



a) NC by silicone

b) NT by silicone

c) NC by sol-gel

d) NT by sol-gel

Fig. 6. SEM images of coated nylons with immersion time of 11 h by a and b) silicone and c and d) sol–gel.

(carrier flow) allowed dragging the methanol into the photoreactor. The contaminant was kept at −13 °C in a cooling bath to control the spontaneous evaporation. The second airflow (the dilution flow) allowed diluting the methanol to reach the concentration range required for the experiments. 0.5 SCCM of carrier gas flow along 70 SCCM of the dilution gas flow were employed. This flow was introduced into photoreactor and the methanol degradation was measured by gas chromatography. The gas temperature in gas inlet was 24 °C and methanol concentration was 103 ppmv.

Methanol degradation was determined by gas chromatography in an Agilent-6890N chromatograph, using TCD detector (thermal conductivity detector) at 105 °C, EC-WAX column of 30 m × 0.25 μm × 250 μm at 55 °C and splitless mode injector at 80 °C. The chromatographic readings were taken every 8 min.

The photocatalytic decomposition percentage of methanol ($\%M_{phot}$) was calculated by

$$\%M_{phot} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial concentration of methanol, and C is the residual photoreactor concentration of methanol after 140 min of photocatalysis. The initial concentration of methanol (C_0 concentration) was measured when the nylon was saturated. In this way, the methanol absorption effect on nylon during the photocatalytic degradation measurements was avoided and the decrease in the methanol concentration was only due to photocatalysis.

Absorption equilibrium was determinated by gas chromatography when the peak area of the methanol peak in the chromatographic spectra became stable.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

Fig. 5 shows the microscopy of fabrics NC and NT coated by two methods at 24 h. Samples prepared with silicone (Fig. 5a and b) present a rough non-homogeneous layer of TiO_2 and some cracks are visible. In the case of NC fabric, some delamination was observed. Fabrics impregnated by sol–gel at 24 h (Fig. 5c and d), show a thinner TiO_2 uniform surface layer than samples coated by silicone.

Samples coated for 11 h of immersion are shown in Fig. 6. TiO_2 film on fabrics impregnated by silicone (Fig. 6a and b) presents a similar structure and morphologic characteristic than those coated for 24 h. Fabrics impregnated by sol–gel at 11 h show a more uniform coating compared to samples obtained by sol–gel during 24 h (Fig. 6c and d).

3.2. Optical microscopy (OM)

Optical microscopy images of fabrics prepared by sol–gel and by silicone at immersion times of 24 and 11 h are shown in Figs. 7 and 8, respectively. A superficial film of TiO_2 was observed in the samples made with silicone; this film was not observed in fabrics coated by sol–gel where the coatings were thinner compared to the fabrics coated by silicone.

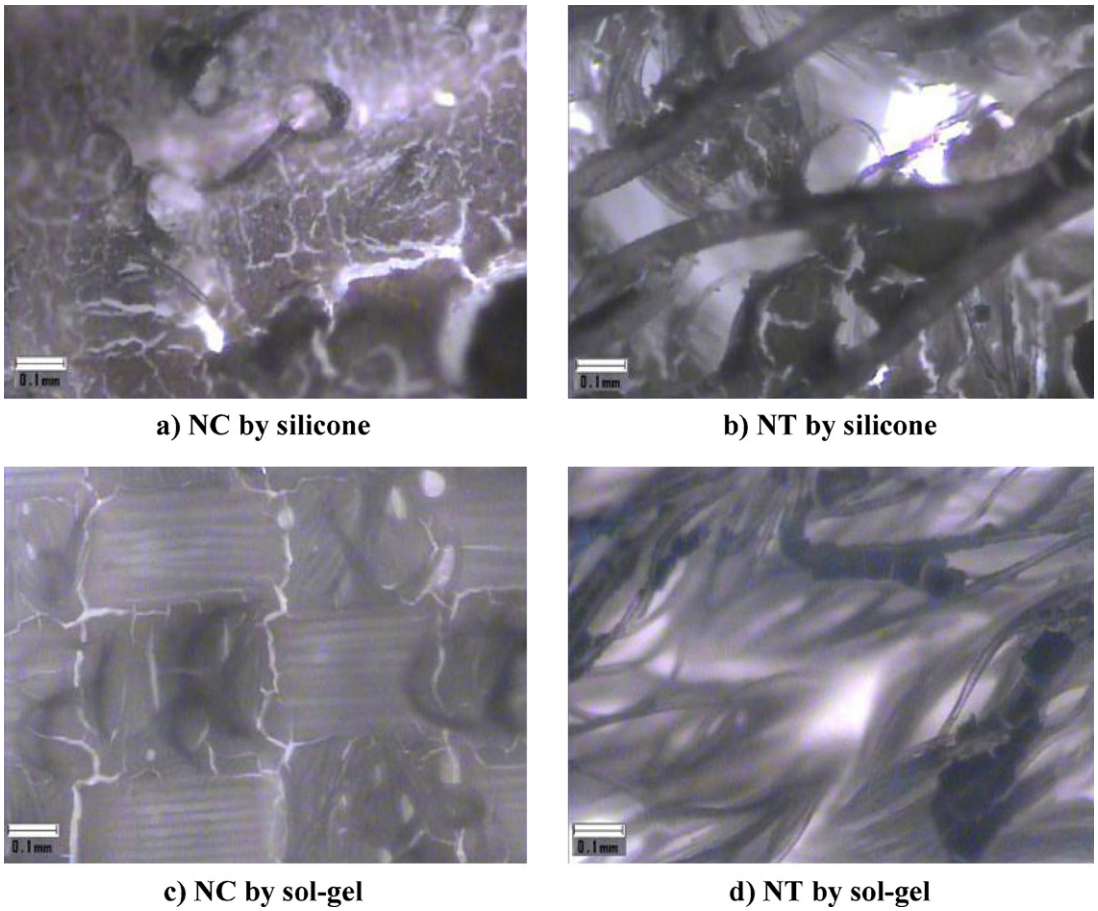


Fig. 7. Optical microscopic images with 5× of coated nylons with immersion time of 24 h by a and b) silicone and c and d) sol–gel.

Furthermore, TiO_2 films coated by silicone at 24 h of immersion (Fig. 7a and b) were less homogeneous and had higher crack density compared with NC and NT coated by sol–gel method at 24 h immersion time (Fig. 7c and d). A similar trend was observed in fabrics with 11 h of immersion (Fig. 8).

3.3. Energy dispersive spectroscopy (EDS)

Chemical analysis (EDS) showed TiO_2 presence in the coated samples (Fig. 9a and b) compared with non-impregnated nylon (Fig. 9c). These results indicate the TiO_2 presence on the nylon fabric. The presence of C and O in the EDS spectra is due to the nylon. The signal due to Si (from tetraethyl orto-silicate TEOS) was also observed in fabrics coated by sol–gel.

3.4. Infrared spectroscopy of TiO_2/nylon samples (ATR-FTIR)

Fig. 10a shows the ATR-FTIR spectrum of TiO_2/nylon samples prepared by sol–gel method at 11 h of immersion. The ATR-FTIR spectra shows TiO_2 band in the range of 800–500 cm^{-1}. The band at 940 cm^{-1} was assigned to the stretching vibration of Si–OH or Si–O groups. Furthermore, symmetric and asymmetric stretching bands of Si–O–Si were found at 1180 and 1050 cm^{-1}, respectively [16]. The presence of the later bands confirms that SiO_2 was formed during TEOS hydrolysis.

Characteristic bands of the nylon fibers were observed at 3300 cm^{-1} with an overtone at 3080 cm^{-1} due to the stretching of hydrogen bonded to the N–H and the N–H bending. The CH_2 symmetric and asymmetric stretching were found at 2930 and 2854 cm^{-1}, associated at ~720 cm^{-1} with the vibration of 4 or more $-CH_2$ groups in the polymer chain. The band at 1634 cm^{-1} is associated with the C=O stretching and the 1535 cm^{-1} band is due to a combination of the bending N–H band and the stretching of the C–N [17–19].

ATR-FTIR spectrum of TiO_2/nylon samples prepared with silicone (Fig. 10b) shows the TiO_2 band between 800 and 500 cm^{-1} and the characteristic bands of nylon. Silicone bands of the methyl silicone were also observed in Fig. 10b. The 1728 cm^{-1} band corresponds to C=O stretching of the ester-radicals of the silicone. The CH_3 asymmetric and symmetric stretching of $Si(CH_3–Si)$ were observed at 1365 and 1226 cm^{-1}, respectively, as well as the silicone bands at 1118 and 1018 cm^{-1} due to Si–O–Si stretching vibrations [20–22].

3.5. Photocatalytic methanol degradation

The concentration ratio C/C_0 vs. time of irradiation was plotted for the photocatalytic decomposition of methanol ($\%M_{phot}$) and it is shown in Fig. 11. Methanol concentration gradually decreased up to 120 min when the methanol concentration reaches a plateau. A similar trend was found for other TiO_2 catalysts on nylon mediating methanol photodegradation. Gas chromatography measurement showed that methanol degradation was not observed during photolysis.

Table 1 shows the $\%M_{phot}$ for fabrics impregnated by two immersion–diffusion methods. TiO_2 coated nylon obtained by sol–gel immersion reached higher percentages of degradation than

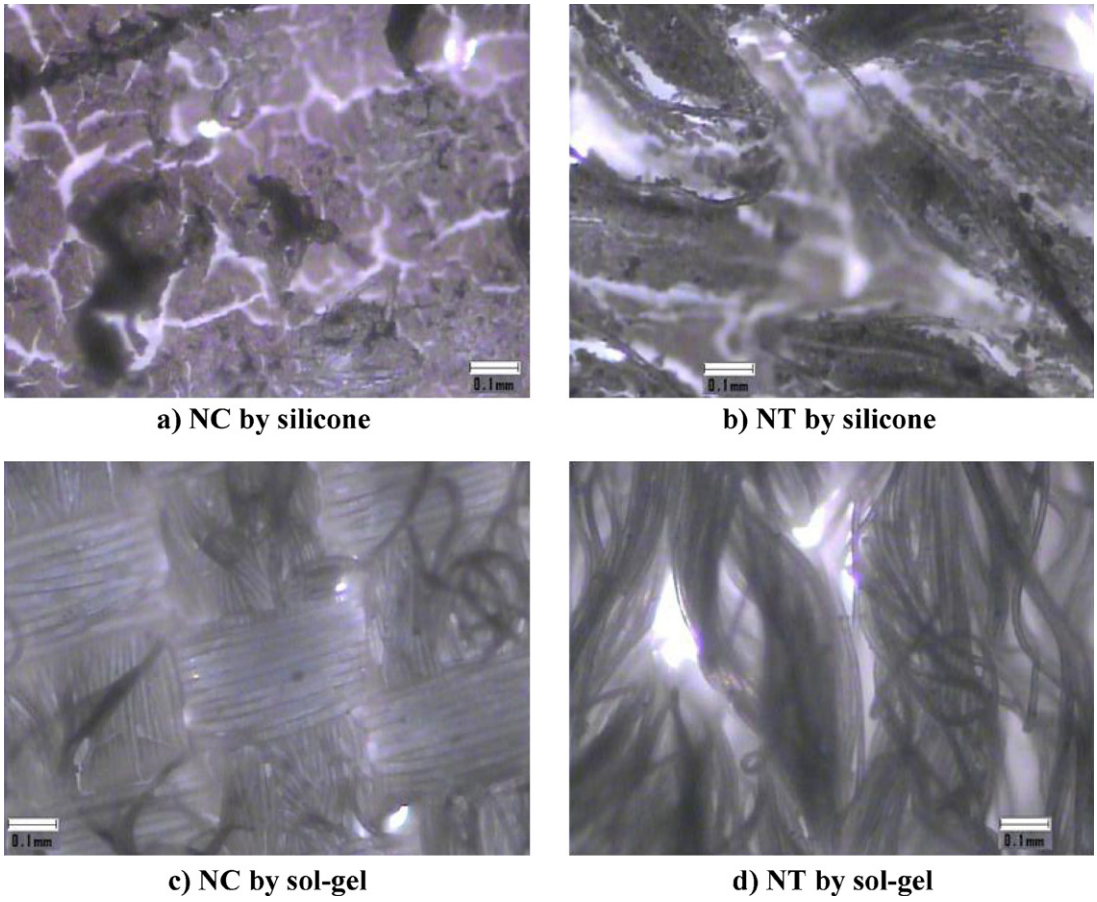
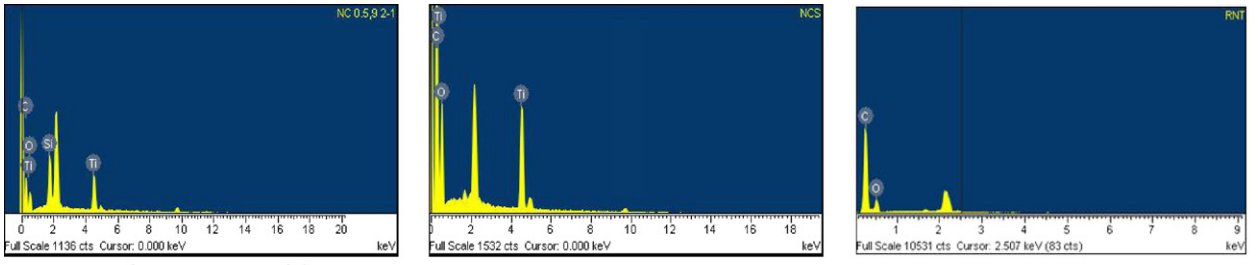


Fig. 8. Optical microscopic images with 5× of nylon coated by immersion time of 11 h: a and b) silicone and c and d) sol–gel.

that obtained by silicone. This result is consistent with SEM and OM analysis where coatings obtained by silicone present a higher density of cracks than the samples prepared by sol–gel immersion.

Additionally, six different methanol degradation cycles were carried out with a TiO_2/nylon sample coated by sol–gel. A good reproducibility during the methanol degradation cycles was found indicating the stability of the photocatalyst used.



Element	Weight%	Atomic%
C K	33.07	50.20
O K	28.13	32.05
Si K	11.08	7.19
Ti K	27.72	10.55
Totals	100.00	

Element	Weight%	Atomic%
C K	40.94	55.29
O K	36.59	37.10
Ti K	22.47	7.61
Totals	100.00	

Element	Weight%	Atomic%
C K	70.35	75.96
O K	29.65	24.04
Totals	100.00	

Fig. 9. EDS spectra of coated nylons with immersion time of 24 h by a) sol–gel, b) silicone and c) non-impregnated nylon.

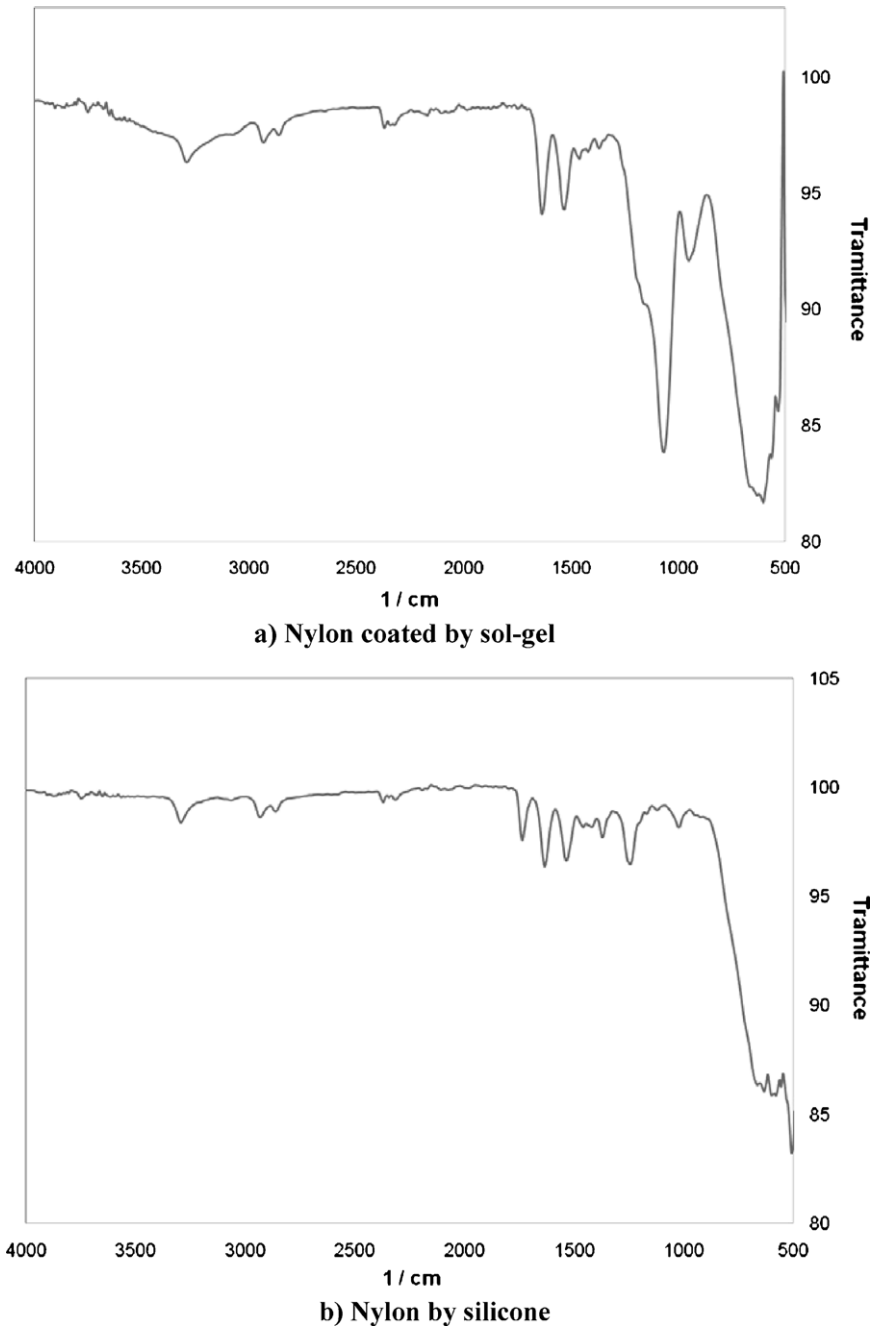


Fig. 10. ATR-FTIR spectra of TiO_2/nylon samples prepared by a) sol–gel and b) silicone after 11 h of immersion.

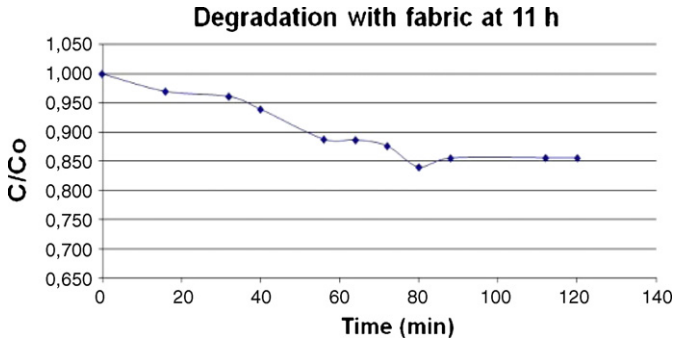


Fig. 11. Photocatalytic degradation of methanol vs. time using TiO_2/nylon prepared by sol–gel with immersion time of 11 h.

Table 1
Methanol degradation percentage related with immersion time and type of nylon.

Type of nylon impregnation method	$\%M_{phot}$ 11 h	$\%M_{phot}$ 24 h
NT (sol–gel)	15.93%	20.33%
NC (sol–gel)	13.07%	25.40%
NT (silicone)	10.04%	8.56%
NC (silicone)	10.68%	15.45%

4. Conclusions

- Results indicate that TiO_2/nylon supported photocatalysts prepared by immersion were useful on methanol photodegradation. A dependence was observed between the time of immersion and the TiO_2 film structure on the nylon.

- TiO_2/nylon showed photocatalytic activity leading to the elimination of gaseous methanol. A higher degradation was reached with samples prepared by sol–gel at 24 h. TiO_2/nylon coated using silicone leads to less effective methanol degradation.
- Sol–gel coatings were more uniform than the TiO_2 coatings applying silicone. The later ones showed more cracks and some TiO_2 was lost due to the gas flow in the photocatalytic reactor during methanol degradation.

Acknowledgements

The authors thank COLCIENCIAS and the University of Antioquia through the "Estrategia de Sostenibilidad de Grupos" program for financing the project.

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