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SEM/EDS and Raman Micro-Spectroscopy Examination of Titanium-Modified Polypropylene Fibres

Abstract

In order to impart photo-catalytic properties to fibres, one can modify them by means of titanium dioxide. Such a modification should provide the best effectiveness with no deterioration in the basic properties of the fibres modified. Accordingly the modifiers should be deposited on the surface of fibres instead of adding them to the whole mass of the fibre-forming polymer. To characterise polypropylene fibres (PP) modified with titanium dioxide doped with nano silver (TiO₂/Ag), Raman micro-spectroscopy and SEM/EDS micro-analysis were used. The combination of both techniques in the analysis of the fibre surface and cross-section allows qualitative and structural assessment of the distribution of titania modifier in the fibre.

Key words: polypropylene fibres, TiO₂/Ag, SEM/EDS analysis, Raman mapping.

Introduction

Increasing requirements concerning the functional properties of textiles result in the development of studies on new-generation fabrics meeting such expectations. Added value can be imparted to fibres with no deterioration in their basic properties by means of various methods, one of which is their surface modification, especially with the use of the nanotechnology [1]. On account of photo-catalytic properties and the advantages of nano-scale, it is nano-titanium dioxide (TiO₂) that has been more and more often used as a modifier for that purpose [2 - 4]. Fibre modification based on nanoparticles requires the use of modern analytical tools for the assessment of the effects obtained. The analysis and identification of modified fibres are carried out with the use of both spectroscopic [1, 5 - 7] and microscopic methods [8 - 10]. The use of such non-invasive research methods allows one to obtain an image of the surface tested and provide information about its composition and the modifier arrangement on the surface analysed. Raman micro-spectroscopy merges vibration spectroscopy together with microscopy, and owing to the possibility of Raman mapping allows one to analyse a specified surface and assess, e.g. the shape or size of the surface modifiers [11, 12] or dye distribution in an elementary fibre [13]. The SEM/EDS technique is also a method avoiding visible damage of the surface tested that can be applied for morphological studies and chemical composition analysis. A modern scanning electron microscope (SEM) enables to obtain surface images even within the range of magnification of 1,000,000×, with an accessible resolution

of 3 - 3.5 nm and high depth of focus. In combination with EDS, it allows one to characterise materials by analysis of the chemical composition, including light elements starting from beryllium [14]. The aim of the study presented was to assess the effects of TiO₂/Ag modification of PP fibres by means of two microscopic techniques combined with the following tools of instrumental analysis: Raman micro-spectroscopy and scanning electron microscopy with X-ray micro-analysis (SEM/EDS).

Experimental details

Materials

Polypropylene fibres (PP) with a diameter of 23.1 μm, made of Moplen HP462R granulated polymer, with a flow rate factor, according to ISO 1133 (230 °C/2.16 kg), of MFI = 25 g/10 min, from Basell Orlen Polyolefins Ltd. (Poland) were used.

The fibres were spun with the use of a spinning machine with a Barmag extruder, spinning head and pump with a yield of 1.2 cm³/revolution, a chamber of side air blow, and a godet collector with a wind-up apparatus from Neumag allowing for a fibre take-up rate of 500 - 1300 m/min.

PP fibres were modified with titanium dioxide doped with silver (TiO₂/Ag) from TJ Technologies & Material Inc. (TJTM), China, with characteristics given in **Table 1**.

As titania standards TiO₂ anatase and rutile (Aldrich, Germany) were used.

The modification was performed by depositing TiO₂/Ag ethanol dispersion (150 g/dm³) during the final fibre drawing on a laboratory stand with a roll system and tray for liquid medium, cooperating with an EKS 9 winder. The drawing ratio was 3.5 and the drawing rate 10 m/min.

Characterisation methods

The surface and cross-section of the modified PP fibres were analysed by means of a Raman dispersive spectrometer: Renishaw InVia Reflex with Leica microscope (Renishaw, GB) and excitation source (λ = 785 nm) and a VEGA 3 electron microscope (Tescan, Czech Republic) with an EDS INCA Energy micro-analyser (Oxford Instruments Analytical, GB) equipped with a monocrystalline silicon Li-activated detector for the detection of the elements of composite material surfaces from beryllium (Be) to uranium (U) with the maximal spectral resolution 128 eV for Mn (Kα) lines were used.

The analysis by Raman technique was carried out in a closed microscope chamber of the spectroscope, with samples being placed on the microscope plate.

Table 1. Characteristics of the TiO₂/Ag powder according to its manufacturer.

Assay, wt%	99.2
Average Granule Diameter, nm	30 - 50
Loss on drying, wt%	0.34
pH value (1:10)	7.4
Ti, wt%	30 ± 1
Ag, wt%	3.1
Zr, wt%	5 ± 1
Zn, wt%	5 ± 1
As, mg/kg	≤ 1
Heavy metal (as Pb), mg/kg	≤ 10

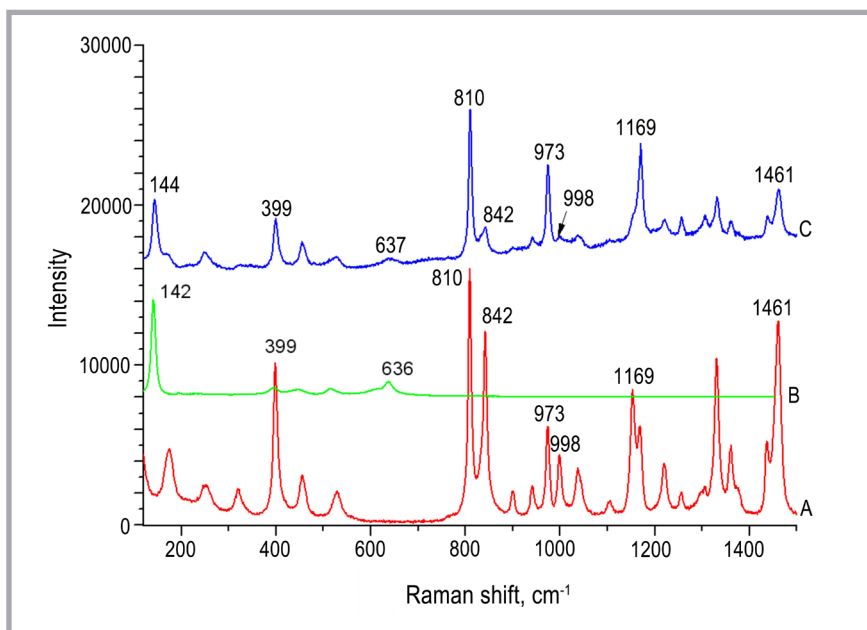


Figure 1. Raman spectra: A) PP fibre, B) TiO₂/Ag, C) PP fibre surface-modified with TiO₂/Ag.

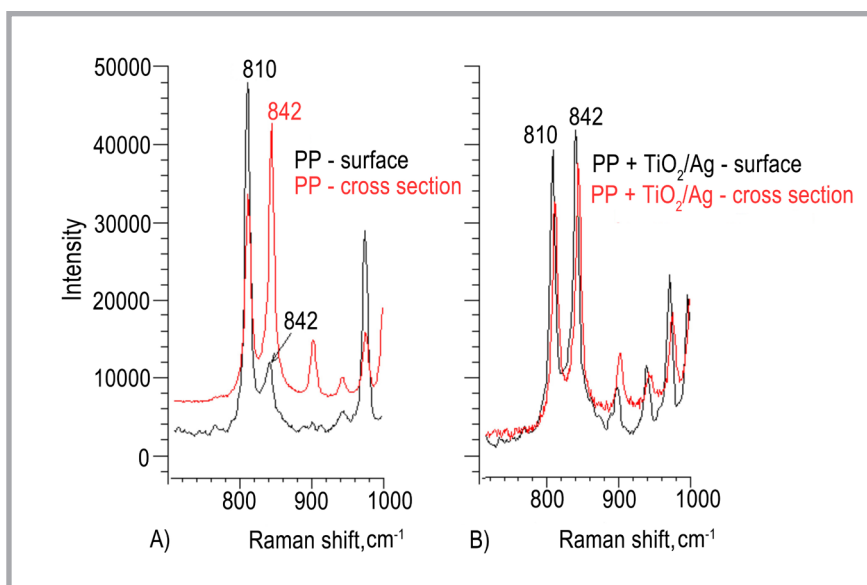


Figure 2. Raman spectra of PP fibre surfaces and inside the fibre bulk. A) unmodified PP fibre, B) PP fibre modified with TiO₂/Ag.

Samples were positioned in the laser light focus by means of a microscope (magnification 50×) with CCD camera. The recording of spectra and Raman maps was carried out by means of Renishaw WIRE 3.2 software. Spectra processing were done with the use of Microcal Origin 8.0 software.

Microscopic observations were made using magnifications of 8000× and 10,000× under the following conditions: operating mode under a high vacuum, electron beam energy 20 keV, and a detector with the highest resolution of low-energy

secondary electrons emitted by a sample, responsible for the topographic contrast.

The surface of each specimen was gold sputtered by means of a vacuum sputter (Quorum Technologies Ltd., GB) X-ray micro-analysis of the surfaces investigated was performed under a low vacuum (specially dedicated air pressure 40 Pa) using electron beam energy: 20.00 keV, without sputtering, at magnification 8000×. The percentage content of the given element was determined with an accuracy of 1% by means of the INCA program using the ZAF correction procedure.

Results and discussion

Analysis of PP fibre surface by the Raman technique

Raman spectra of PP fibres before (A) and after surface modification (C) as well as powder of the TiO₂/Ag modifier (B) are shown in **Figure 1**. Raman spectra of the TiO₂ anatase and rutile standards are presented in **Figure 3.B**.

Figure 1 shows the spectrum (line A) with bands characteristic of PP [15 - see also **Table 2**] at 810 cm⁻¹, 842 cm⁻¹, 973 cm⁻¹, 1169 cm⁻¹ and 1461 cm⁻¹ corresponding to C-C stretching vibration (810, 973), CH₃ wagging vibration (1169), CH₂ rocking vibration (842) and CH₂ bending vibration (1461) [15-17]. On account of the strong characteristic Raman effect of nonpolar groups, the skeleton C-C vibrations of PP are conjugated and sensitive to conformation effects [16, 17], which is observed when the spectrum of pure PP (line A) is compared to that of modified PP (line C).

In spectrum A, one can observe a strong band at 842 cm⁻¹ and a band at 998 cm⁻¹ that are weakly visible in spectrum C. A change in the intensity ratio of bands 810 and 842 cm⁻¹ is clearly seen. According to previous studies on PP [16, 17], these bands are connected with the crystallinity of PP. The band at 810 cm⁻¹ is characteristic of the crystalline phase. The band at 842 cm⁻¹ is present due to the non-crystalline phase and/or the low molecular weight content in the polymer. PP crystallinity also affects the ratio of bands at 973 and 998 cm⁻¹ and a difference in the relative intensity between both bands in spectra A and C was also observed.

Figure 2 presents fragments of Raman spectra of unmodified and titania modified fibre surfaces and fibre cross-sections. In the case of unmodified PP fibre (**Figure 2.A**) the relative intensity between bands 810 and 842 cm⁻¹ gives a ratio of ca. 4.1 for the fibre surface, whereas the same relation is ca. 0.7 for the cross-

Table 2. Characteristic bands of polypropylene [15].

Frequency, cm ⁻¹	Assignment
1461	δ _b (CH ₃), δ _a (CH ₃),
1169	v _b (C-C), r _a (CH ₃), w (CH)
998	r _b (CH ₃),
973	r _a (CH ₃), v _b (C-C)
842	r (CH ₂),
810	v _s (C-C), r (CH ₂),
399	v _b (C-C), δ (C-CH ₃)

section. For titania modified PP fibre (**Figure 2.B**) these band relationships are ca. 0.9 for the surface and 0.8 for the fibre bulk. Analysis of bands 810 and 842 cm^{-1} , responsible for crystallinity, as well as changes in their relative intensity for surfaces of unmodified and modified PP fibres (black lines on **Figures 2.A** and **2.B**) can suggest that the modification performed also causes changes in polymer crystallinity on the surface. However, differences in polymer orientation should also be taken into consideration [18], requiring separate in-depth study.

In the spectrum of modified PP fibre (C) two new bands are formed: at 144 cm^{-1} and 637 cm^{-1} , which are consistent with those observed in the titania modifier spectrum (B) - 142 cm^{-1} and 636 cm^{-1} (**Figure 1**). The other less intense bands in the region between 399 and 636 cm^{-1} present in spectrum B are not recognised in spectrum C due to low intensity and/or because of overlapping with more intense bands of PP appearing in the same region. In spectrum C, the baseline went up in relation to spectrum A, which most probably resulted from the diffusion of laser light due to the roughness of the modified surface. The linear map based on 21 spectra of TiO_2/Ag modifier (**Figure 3.A**) shows a homogeneous character of the titania powder, with characteristic bands at 142, 399, 519 and 636 cm^{-1} that correspond to the anatase TiO_2 , bands observed (**Figure 3.B**) and reported in the literature [19, 20]: 144 (E_g), 399 (B_{1g}), 519 (B_{1g}), and 639 (E_g). Raman spectra of the TiO_2 rutile standard (**Figure 3.B**) has characteristic bands at 142, 231, 448 and 609 cm^{-1} , which is compatible with rutile results previously reported [21]: a broad two-photon band at 231 cm^{-1} and two peaks at 448 (E_g) and 608 (A_{1g}). The rutile standard spectrum (**Figure 3.B**) is distinguished by a lower intense band at 142 cm^{-1} than in the anatase spectrum. In the spectrum of the powder tested (**Figure 3.A**), one can also observe weak bands at 235 and at 1090 cm^{-1} , which are most probably derived from other metal oxide constituting, according to the data listed in **Table 2**, impurities in TiO_2 , i.e. zirconium oxide [22] or in the case of band 1090 cm^{-1} - zinc oxide [23]. The band at 235 cm^{-1} could also be from rutile TiO_2 , but then it should be accompanied with a band at ca. 448 cm^{-1} . Thus analysis of the TiO_2/Ag modifier suggests that mainly the titania anatase form is present. Relative intensity differences among the titania modi-

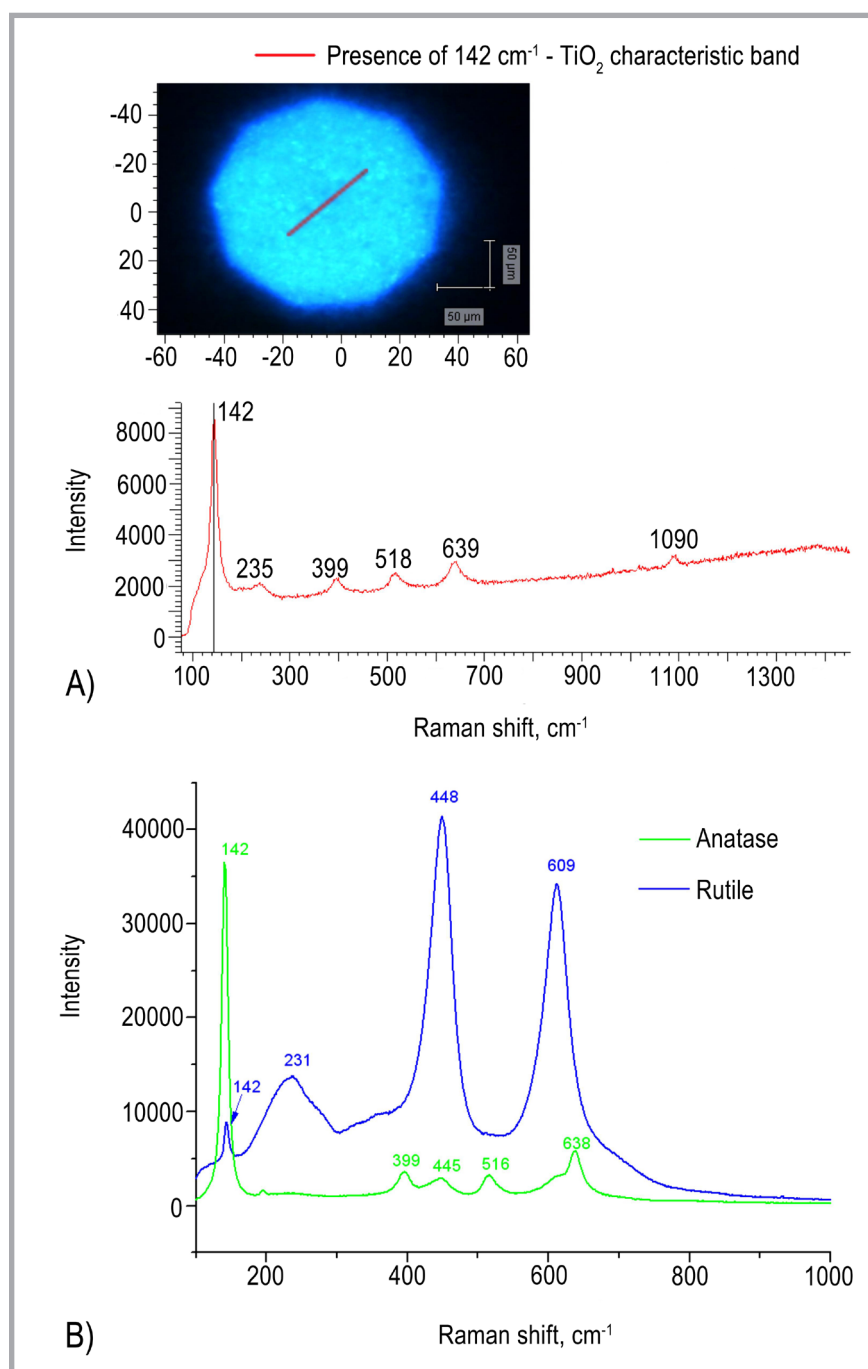


Figure 3. Raman spectra of TiO_2 : A) TiO_2/Ag powder used for the modification of PP fibre; B) TiO_2 standards.

fier's main band (142 cm^{-1}) and other bands explains why in the spectrum on the modified fibre surface (**Figure 1**) the band at 144 cm^{-1} is clearly recognisable as a new one, but the other bands are rather difficult to identify. The difference of 2 cm^{-1} between the Raman shift of the main titania band for the titania powder modifier and for the fibre surface could be the effect of intermolecular interaction.

The maps of modified PP fibre surfaces (**Figures 4.A** and **4.B**) represent a point map according to the band intensity at

144 cm^{-1} (**Figure 4.A**) and a 19×28 rectangle map (**Figure 4.B**). The point map was made on the basis of individual spectra (**Figure 4.C**) at 7 sites on the modified fibre surface. Green points show the places where the presence of TiO_2 was found. From **Figure 4.A** it follows that the presence of titanium dioxide was found in two points of the 7 sites tested. The rectangular map shown in **Figure 4.B** was made on the basis of spectra at 580 points, with an interval of 1 μm on a surface of 532 μm^2 . The green points show the spots where the presence of

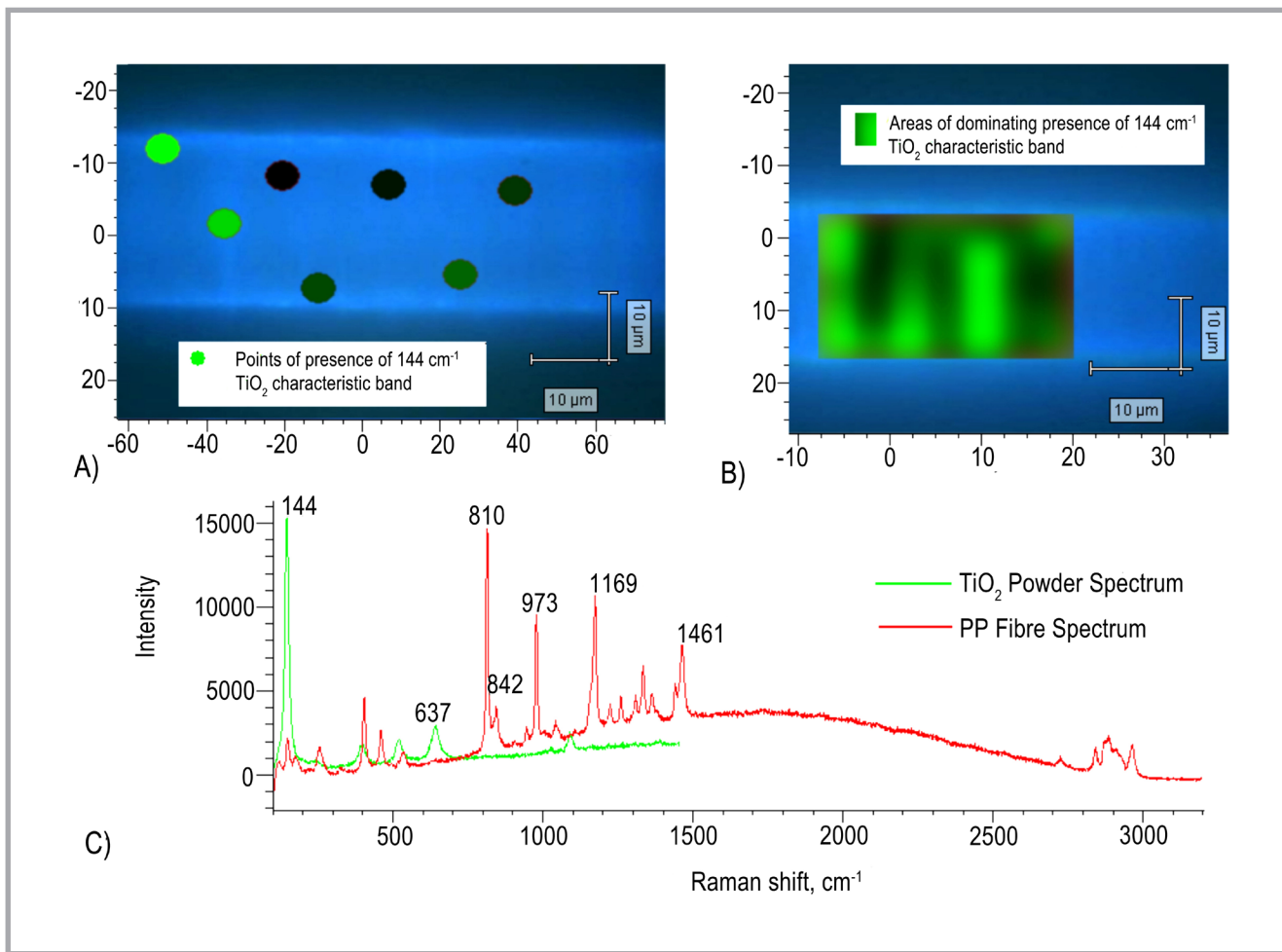


Figure 4. Map of the surface of PP fibre modified with TiO_2/Ag performed according to the intensity of band 144 cm^{-1} : A) Point map, B) Rectangular map, C) Spectra recorded on the surface tested.

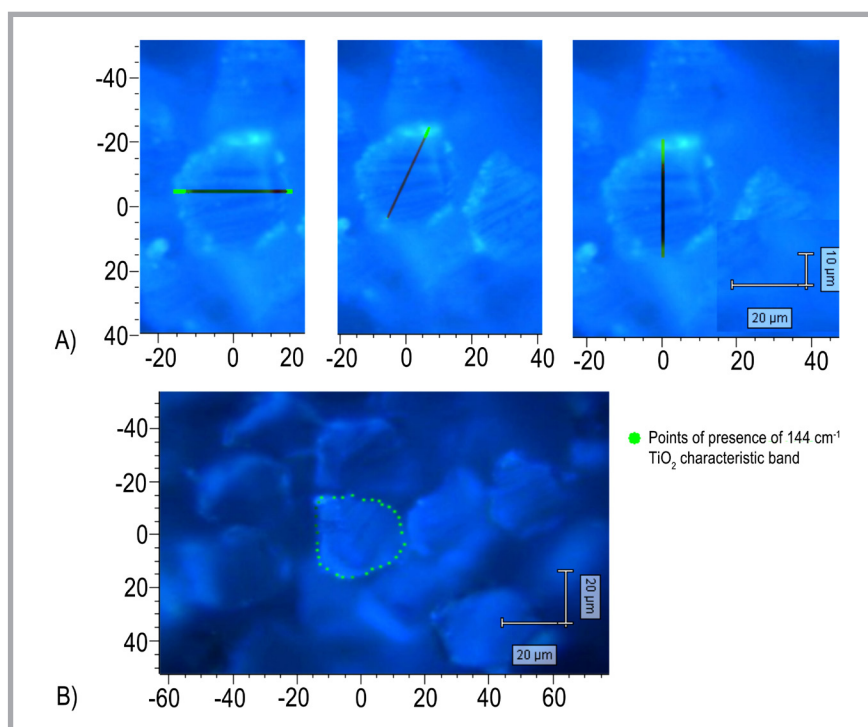


Figure 5. Map of the cross-section of PP fibre modified with TiO_2/Ag carried out according to the intensity of band 144 cm^{-1} : A) Linear map along the cross-section diameter, B) Point map made on the cross-section circumference.

TiO_2 was found, identified on the basis of the main titanium band at 144 cm^{-1} . As in the case of the point map, here it is also observed that the modifier is unevenly distributed on the fibre surface. These Raman maps made it possible to assess the presence of TiO_2 on a micro-scale on the fibre surface, while the images obtained (**Figures 4.A** and **4.B**) indicate differences in the TiO_2 distribution.

The technique of Raman spectroscopy also allows one to analyse the fibre cross-section (**Figures 5.A** and **5.B**). The fibre cross-section was examined along its diameter (**Figure 5.A**) and on the fibre circumference (**Figure 5.B**). Examination along the diameter shows the absence of the modifier inside the fibre and the presence of TiO_2 bands at the ends of the line examined, i.e. at the points belonging to the cross-section circumference. This observation is confirmed by the result of a test made point by point on the fibre circumference line (**Figure 5.B**). The examinations of the fibre surface and cross-section carried out by the Raman

spectroscopy technique prove that only the PP fibre surface was modified with titanium dioxide and the modifier did not penetrate across the fibre structure.

Analysis of PP fibre surface by the SEM/EDS technique

The examination of TiO₂/Ag powder by the SEM/EDS technique (**Figure 6**) confirms the presence of Ti, O and Ag as well as metallic impurities in the form of Zn and Zr declared by the manufacturer (**Table 1**). Moreover the presence of more than 15% of Si, Al, Na and C was observed. The presence of carbon in the powder analysed can indicate organic impurities. Analysing the weight proportions of the elements identified, one can observe a high oxygen content, amounting to 56.23%. The oxygen content percentage in titanium dioxide amounts to 40% (weight ratio of elements in TiO₂: Ti:O = 60:40). Thus if titanium dioxide were the sole compound with oxygen, the oxygen content should not exceed 40%. As the examination was performed under a vacuum, it should be assumed that the quantity of oxygen found during the examination results from the presence of other chemical compounds, most probably oxides such as SiO₂ (Si:O = 47:50), Al₂O₃ (Al:O = 53:47), and in a lower quantity ZnO (Zn:O = 80:20) or ZrO₂ (Zr:O = 74:26). Excess of oxygen can also derive from organic impurities.

SEM images of PP fibres presented on **Figure 7** show visual changes between the surface of unmodified fibre (A) and TiO₂/Ag- modified fibre (B). **Figures 8** and **9** present the results of SEM/EDS analysis of the modified PP fibre surface.

EDS examination (**Figure 8**) carried out in an area of 2,000 μm² showed the presence of the following elements and their distribution in the area analysed: carbon, titanium, oxygen, zirconium and silver. From among the elements identified carbon totally covers the surface tested, while oxygen, zirconium and silver are clearly distributed evenly, but their presence has a local character - they do not cover the whole surface under study.

EDS analysis performed with a magnification of 8,000× along a 40 μm line segment (**Figure 9**) confirmed the presence of oxygen, titanium, zirconium and silver and showed a uniform distribution of these elements on the segment tested. **Figure 9** also shows that along the sec-

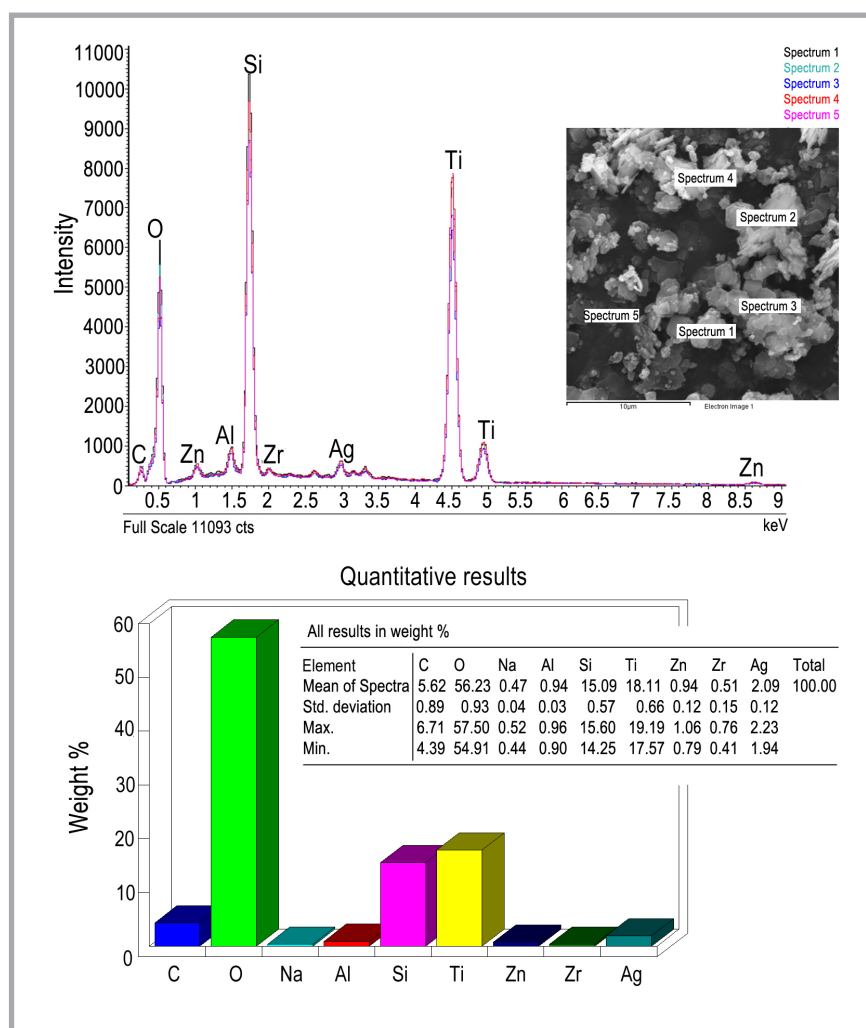


Figure 6. SEM/EDS of the TiO₂/Ag powder.

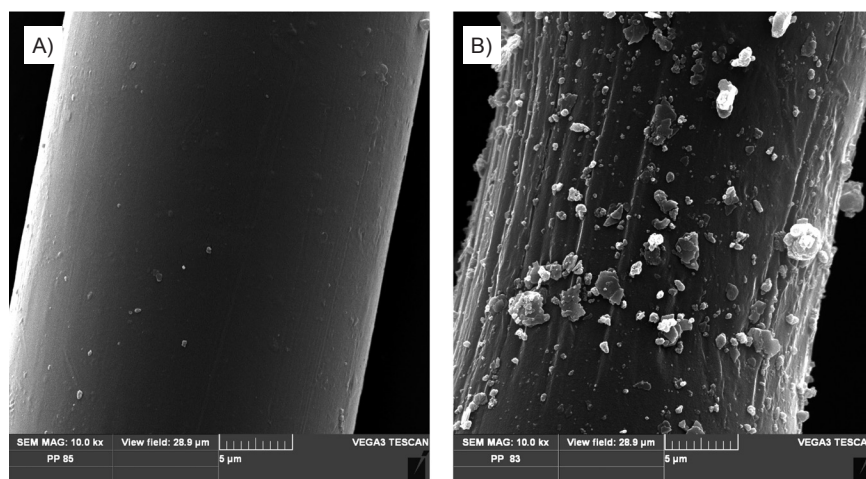


Figure 7. SEM image (magnification of 10000 ×) of PP fibre PP: A) unmodified, B) modified with TiO₂/Ag.

tion analysed the carbon content dominates, amounting to more than 86%. On account of the fact that carbon is the main component of polypropylene, one may conclude that this signal is derived from the fibre surface. Along the line analysed on the fibre surface, one can observe an

increase in the intensity of bands concerning titanium and zirconium within the ranges 13 - 14 μm and 23 - 40 μm with the maximum at 30 and 32 μm. The oxygen content along the line tested is constant up to about 30 μm, while in the segment of 30 - 40 μm, it is consid-

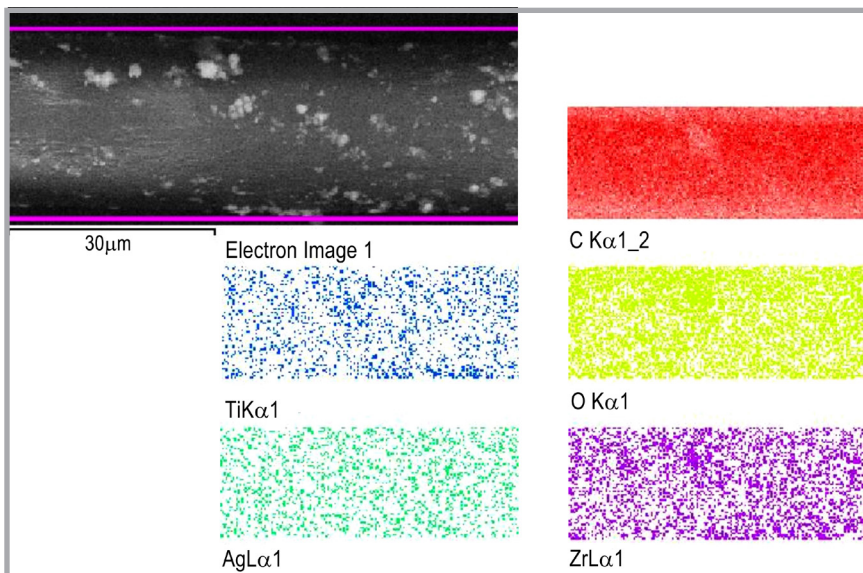


Figure 8. Distribution of elements on the PP fibre surface ($2000 \mu\text{m}^2$) modified with TiO_2/Ag .

erably increased. For this segment an increased content of titanium and zirconium is observed, which, also taking into consideration the Raman analysis results, allows one to assume that both titanium and zirconium are present in the form of oxides. Constant silver content observed along the whole segment analysed confirms the presence of element Ag. The distribution of elements on the modified PP fibre surface shown in **Figures 8** and **9** indicate a dominating content of titanium dioxide, while the contents of silver and zirconium are lower than those in the powder analysed. According to

the manufacturer's declaration (**Table 1**), the powder used in the modification contains 3% by wt. of silver and 5% by wt. of zirconium. SEM/EDS analysis of this powder showed that it contained 2% of silver and only 0.5% of zirconium. The band at 1090 cm^{-1} seen in the Raman spectrum (**Figure 3.A**) suggests that zirconium is present in the form of oxide [22] and the fact of detection of such small impurity in the Raman spectrum can be caused by the SERS effect connected with the presence of element Ag in the titania modifier [24]. Metallic elements, however fail to give a Raman

signal themselves; but noble metals are known to improve Raman analysis because of their ability to strengthen the Raman signal. Moreover, even though direct identification of silver is impossible by this technique, the presence of this element can be meaningful in the whole analytical study applying Raman spectroscopy. One should also take into account the local character of the analysis performed and the data obtained should then be treated exclusively in a qualitative way. It is particularly visible in the case of the analysis of the modified surface, where the dominating role is played by the component of the modified fibre surface, i.e. carbon. In this case, comparison of results of the composition of TiO_2/Ag before modification and those for the modified PP fibre surface indicates clear differences: a silver content of 0.17% and 2%, a zirconium content of 1.3% and 0.5%, for the finer surface and powder, respectively. The remaining powder components, Si and Zn, were not found on the fibre surface. These differences may result from both a high number of elements located on the modified fibre surface and the local character of the measurements performed.

Conclusions

The analysis of the fibre surface modified carried out by the technique of Raman micro-spectroscopy allows one to identify both constituents: fibre - polypropylene and the titania - surface modifier. Ap-

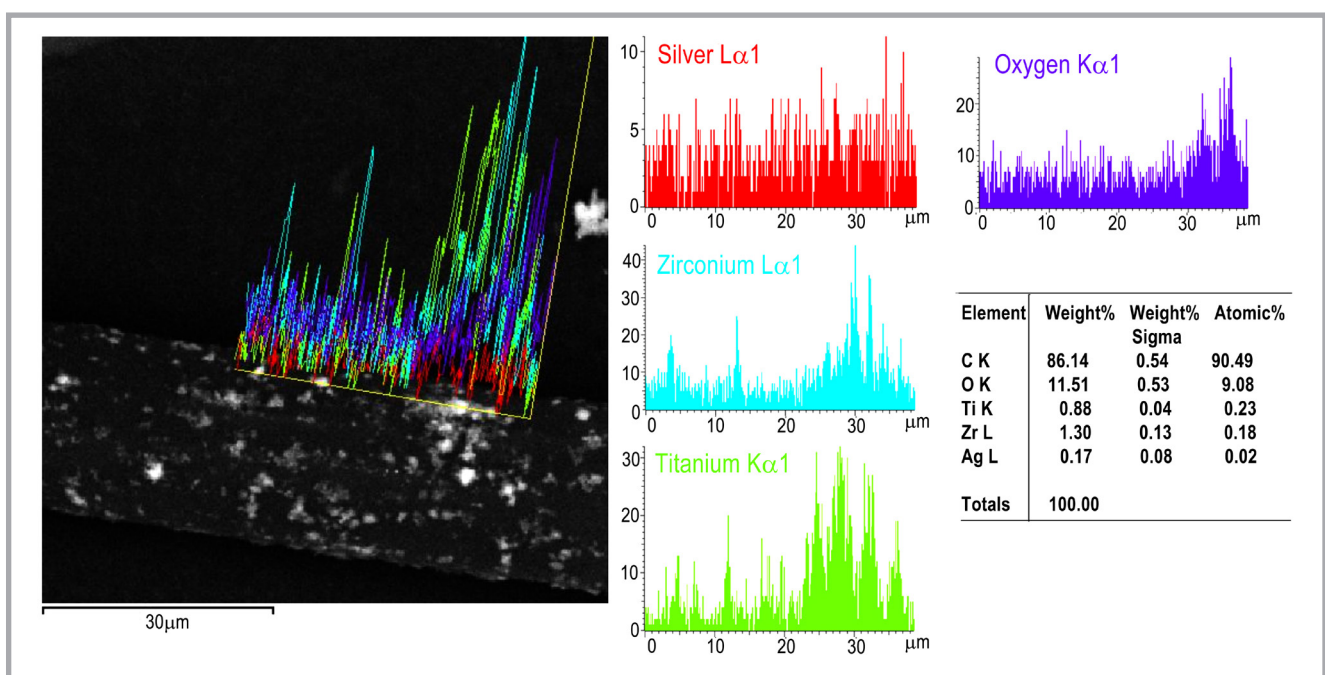


Figure 9. EDS distribution of elements along the set line on PP fibre modified with TiO_2/Ag .

plication of this technique enabled one to define the crystalline structure form of the titanium dioxide used. It is also possible to observe the effect exerted by the surface modification on the crystalline form of the fibre-forming polymer. Thanks to the use of the surface mapping system based on the identification of the main characteristic band of anatase titanium dioxide (144 cm^{-1}), it was possible to carry out qualitative analysis of the fibre's outer surface and fibre cross-section on a micro-scale. The modification only occurs on the fibre surface and the distribution of the modifier has a local character. The SEM/EDS examinations performed clearly confirm the modification of the fibre surface, showing the presence of titanium and oxygen, and also the fact that the modifier used is locally distributed on the fibre surface. The use of this technique makes it possible to very precisely assess the composition of elements on the fibre surface analysed, owing to which it is also possible to qualitatively assess the purity of both the modifier itself and the surface modified with its use.

The analysis of the PP fibre surface modified with TiO_2/Ag carried out by the techniques of Raman spectroscopy and SEM/EDS showed wide analytical possibilities of the combined application of both techniques. The technique of vibration spectroscopy allows one to identify characteristic bands of polypropylene as well as shows changes occurring in the crystalline form of PP under the influence of the modification. The maps of surfaces show the places where one can observe the presence of a peak representing a characteristic band of anatase TiO_2 . The SEM technique in combination with EDS makes it possible to visually assess changes in the fibre surface tested and the chemical analysis of elements located on it. The analysis of elements carried out by the EDS technique not only confirms the presence of titanium and oxygen on the PP fibre surface but also shows traces of metallic impurities. Examinations using the technique of Raman micro-spectroscopy provided information about the chemical structure and character of chemical combinations on the surface analysed, while SEM/EDS examinations enabled to obtain images of the surface tested as well as information about its chemical composition. Both techniques enriched with the mapping tool enabled to assess the uniformity of the modification.

Acknowledgments

The work was carried out within The Key Project - POIG.01.03.01-00-004/08 *Functional nano- and micro textile materials – NANOMITEX, supported by the European Community and The National Centre for Research and Development (Poland), Grant No. NN508440736 supported by the Ministry of Science and Higher Education (Poland) and Project WND-RPLD.03.01.00-00-001/09.*

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Received 18.11.2013 Reviewed 20.12.2013