

Investigation of supramolecular structure of the rare and rare-earth elements nanoparticles carrier when modified using microwave irradiation

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Abstract. In this paper, we present an IR and XRD study of the polypropylene fibrous nanoparticles carrier when its surface modified with rare and rare-earth elements nanoparticles using microwave irradiation, by the example of SnO₂/TiO₂ hetero-nanoparticles. The paper shows that the smectic mesomorph structure of the non-modified polypropylene fibrous carrier transforms into the monoclinic α -crystalline due to microwave irradiation. At the same time, the carrier material remains stereoregular and keeps its helical structure.

1. Introduction

Nowadays, polymer melt-blown fibres are widely used for the manufacture of textile goods, insulation materials and fibre composites, absorbents of oil, petroleum and heavy metals, filtering materials for water and air treatment or as nanoparticles carriers [1-3]. Spheres of its application are determined by physical properties, chemical constitution of polymers, structure and redox properties of surface. Among these materials, the polypropylene (PP) melt-blown webs have substantial advantages [4]. An extensive base of raw materials, constant developing of new methods of modification, and a valuable set of physical properties create supportive environment for the manufacture development and application of products produced on the basis of these webs. Application of these materials, as the filtering and absorbing elements in the water purifying systems, is especially relevant [5-7].

Nanosized particles attached to the polymer fibre surface can be used for the transformation of organic water pollutants, such as phenols, aromatics, surface-active reagents, and nitro compounds, into the compounds safe for humans [3, 8 and 9]. At recent time, a lot of success is achieved in the developing the filtering materials – the polypropylene fibres, whose surface is modified with active nanoparticles, such as the systems named as “nanoparticles (TiO₂, SnO₂, TiO₂/SnO₂) – polypropylene fibrous carrier”.

Attached to the carrier surface hetero-nanoparticles are most advantageous in case of developing effective photocatalytic systems on account of generating more free radicals due to spatially separation of electron-hole pairs [10, 11]. Structure and properties of modified materials and, consequently, the functional features and application sphere largely depend on methods of their obtaining. Thus, arises a



need of thorough study all the materials which were obtained using new methods. This work is aimed at using the IR spectroscopy technique to investigate the changes in the chemical structure of the polypropylene melt-blown web, when modified with $\text{SnO}_2/\text{TiO}_2$ hetero-nanoparticles.

2. Materials and methods

The PP melt-blown webs as a carrier for $\text{SnO}_2/\text{TiO}_2$ nanoparticles were obtained by the direct aerodynamic formation, a kind of the melt-blowing process, from melting of isotactic polypropylene (iPP) [12]. Such raw materials as the commodity polypropylene 21060-16 and 21080-16 grades issued in accordance with TU 2211-016-05796653-95 were used in the research. The selection of samples was provided according to the GOST 10213.0-2002. "Staple fibre and tow chemical. Acceptance rules and the method of sampling." The phase composition, crystallite size, and internal elastic strain ($\Delta d/d$) of the resulting materials were determined by X-ray diffraction (XRD) on an XRD-6000 diffractometer with CuK_α radiation. The surface microstructure of the modified fibers was examined by transmission electron microscopy (TEM) on a JEOL JEM_100CXII. Formation the $\text{SnO}_2/\text{TiO}_2$ hetero-nanoparticles – carrier systems was provided by a mutual precipitation of the stannic and the titan chlorides hydrolysis products to the polypropylene carrier surface.

The starting material for the synthesis of $\text{SnO}_2/\text{TiO}_2$ photocatalytic nanoparticles was water solutions of the stannic chloride (II) and the titan chloride (IV) with the chemical purity. 1 gram of the carrier was placed in a container with the prepared stannic chloride (II) and titan chloride (IV) solution, kept for 15 minutes at room temperature, then withdrawn from the solution, and subjected to the microwave radiation to produce the $\text{SnO}_2/\text{TiO}_2$ nanocrystals attached to the fibre surface. The irradiation was conducted in a laboratory microwave oven with an output power of 650 W and a frequency of 2.45 GHz. The working chamber was a rectangular resonator with a standing wave and a rotating sample holder continuously rotating by 360° . The exposure time to the microwave radiation was 3 minutes.

Before and after surface modification with metal nanoparticles, the samples of the carrier were submitted to an FTIR analysis to find out the transformation in their chemical structures [13]. All spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer using the standard technique in the wave number range of $4200 - 400 \text{ cm}^{-1}$. The samples for IR spectroscopy were completely dried as a result of 21 day keeping in an air-tight glass weighing capsule in the presence of P_2O_5 .

3. Results and discussion

Assuming that the spectroscopic properties of the nanoparticle carrier (NC) do not change in the process of the nanoparticles attachment, it is worthwhile to begin analysing the IR spectrograms of NC before modification and to check up the changes afterward. The spectrograms of a non-modified carrier in the wave number range of $1200\text{--}800 \text{ cm}^{-1}$ show several strong and medium absorption bands that correspond to the stretching vibrations of CH group, symmetric bending vibration of CH_2 group ($\nu=1435 \text{ cm}^{-1}$), antisymmetric bending vibration of CH_3 group ($\nu=1454 \text{ cm}^{-1}$ and 1460 cm^{-1}), and symmetric bending vibration of CH_3 group ($\nu=1380 \text{ cm}^{-1}$). The IR spectra of the non-modified NC also show the clearly pronounced absorption bands 1366, 1328, 1302, 1258, 1224, 1103, 1045, 998, 975, 899, 842, and 810 cm^{-1} that give evidence of isotactic structure of the carrier material. Optical micrograph of the fibrous carrier is presented in figure 1.

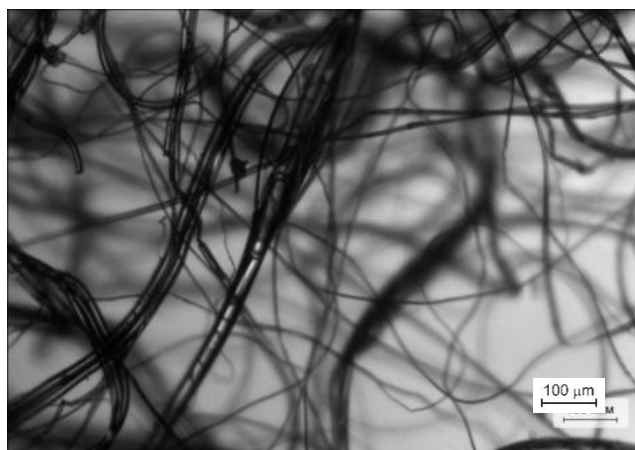


Figure 1. Optical micrograph of the fibrous carrier

The appearance of the 975 cm^{-1} band is caused by an interaction of the methyl group rocking vibration and the stretching vibration of the $-\text{CH}-\text{CH}_2-$ group. The band at 975 cm^{-1} is slightly related to the vibrations of the CH_2 group and $-\text{CH}-\text{CH}_2-$ groups adjacent to a molecular chain and does not depend on the conformation of macromolecules. The band at 998 cm^{-1} is caused by an interaction of the methylene group rocking vibration and stretching vibration of the $-\text{CH}-\text{CH}_3$ group. The power of this interaction depends on the conformation of macromolecules and, consequently, on the isotacticity degree. The degree of isotacticity is considered to mean the ratio of the intensities of the absorption bands 998 and 975 cm^{-1} in the IR spectra. The ratio of intensities of these bands is 0.86 . According to [14], the band at 840 cm^{-1} , typical of the polypropylene spectra, defines the number of molecular chains which consist of the sequenced trans-gosh-conformers $(\text{T}-\text{G})_n$ $n > 10$. The band at 975 cm^{-1} defines a content of conformers $(\text{T}-\text{G})_n$ $n > 4$ in the amorphous areas of a high-molecular crystallising polymer. The presence of segments with helical conformation is proved by the band at 998 cm^{-1} . The coiled conformation, which can be identified by the band at 1155 cm^{-1} , is absent. The ratio of intensities of the absorption bands 975 and 840 cm^{-1} shows that the structure of NC is represented mainly by the long segments ($n > 10$) in a helical trans-gosh-conformation, which lead to the formation of a long-length lamellar structure [15]. Hence, we can conclude that before the modification, the material of the nanoparticle carrier is isotactic polypropylene with high degree of isotacticity.

In addition, the IR spectrogram contains the following bands: a weak band at 1720 cm^{-1} belonging to the stretch vibration of $\text{C}=\text{O}$ group that gives evidence of the oxygen-containing groups formation and absorption bands in the range of $2500\text{--}3700\text{ cm}^{-1}$ with the maximum of absorption at $3400\text{--}3460\text{ cm}^{-1}$, which correspond to the stretch vibrations of OH groups in accordance with the results published in literature [16, 17]. See table 1. The appearance of these bands can be explained by the fact that when the melt of PP is blown, free radicals are formed due to the presence of the methylene groups in the PP macromolecular chains with low bond energy containing hydrogen at the tertiary carbon atom. In the presence of the air oxygen, thermal destruction goes by the radical-chain mechanism with the formation of the peroxide radicals and peroxides. It leads to the formation of the structure defects in the material including the unsaturated and oxygen-containing functional groups, not typical of initial polymer, such as hidroperoxides, carbonyl, ether, etc. [18]

Table 1. Absorption bands for initial polypropylene melt-blown web.

Wavenumber (cm^{-1})	Intensity	Absorbing group and type of vibration
809	weak	$\gamma_r(\text{CH}_2)$
842	average	$\gamma_r(\text{CH}_3)$
975	average	$\gamma_r(\text{CH}_3); \nu(\text{C}-\text{C})$

998	average	$\gamma_r(\text{CH}_3)$; $\nu(\text{C}-\text{CH}_3)$
1155	average	$\nu(\text{C}-\text{CH}_3)$
1168	average	$\gamma_r(\text{CH}_3)$; $\nu(\text{C}-\text{C})$
1380	strong	$\delta_s(\text{CH}_3)$
1435	average	$\delta_s(\text{CH}_2)$
1460	average	$\delta_a(\text{CH}_3)$
1645	weak	$\nu(\text{C}=\text{O})$
1720	weak	$\nu(\text{C}=\text{O})$
2720	weak, narrow	$\nu(\text{OH})$
2838	average	$\nu_s(\text{CH}_2)$
2879	average	$\nu_a(\text{CH}_2)$
2921	very strong	$\nu(\text{CH})$
2950	very strong	$\nu_a(\text{CH}_3)$ symmetric to $\text{H}-\text{C}-\text{CH}_3$ plane
2959	very strong	$\nu_a(\text{CH}_3)$, antisymmetric to $\text{H}-\text{C}-\text{CH}_3$ plane
3400	weak, broad	$\nu(\text{OH})$

The presence of oxygen-containing groups on the NC surface makes it possible to carry out its modification by the method that includes the smearing of the carrier surface with an active component obtained as a result of the tin-salts hydrolysis. The active component is stabilized on the carrier surface due to the bonding of the metal cations by carboxylic groups coupled with the formation of hydrogen bonds between the carboxylic group hydroxyl hydrogen and the hydrolysed tin salt oxygen. These processes take place only at low pH. Formation and immobilisation of the tin dioxide nanoparticles on the NC surface occur due to the microwave irradiation. [19]. The results of an XRD study indicate that the supramolecular structure of the non-modified polypropylene fibrous carrier is represented by 33% of the smectic mesomorph phase, which can be identified by the presence of two wide peaks, situated at the $2\theta = 14.8^\circ(5.99)$ и $21.4^\circ(4.19)$ (figure 2.1). Furthermore, the supramolecular structure of the modified NC is represented by 42% of the monoclinic α -crystalline phase (figure 2.2).

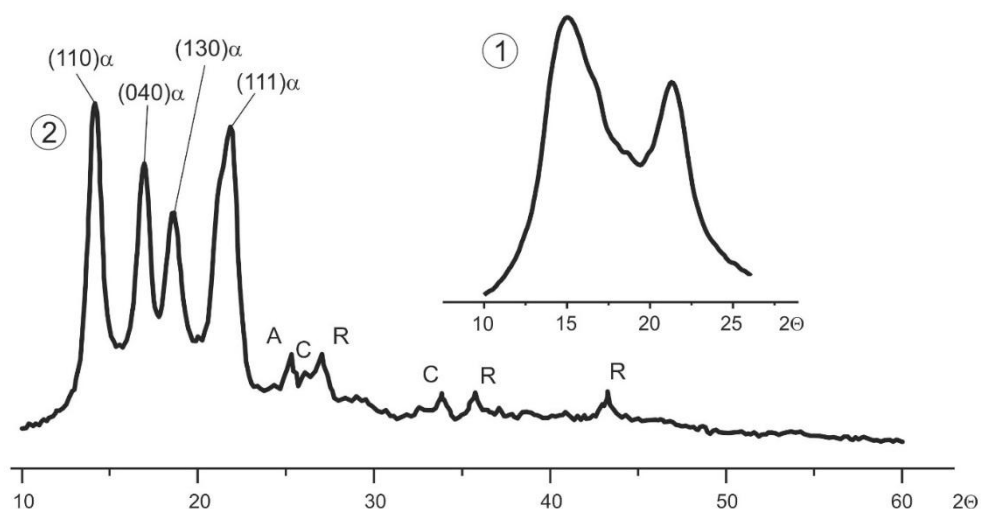


Figure 2. XRD spectra of polypropylene fibrous carrier before and after modification:
1 - non-modified NC; 2 - modified with $\text{SnO}_2/\text{TiO}_2$ nanoparticles NC

After modification, the IR spectra of NC samples demonstrate new absorption bands in the wave number range below 750 cm^{-1} . For the carrier material, weak bands located in this range are related to

the skeleton bending vibration and internal chain rotation. In addition, the authors of [20, 21] identified the absorption bands in this range as related to the SnO_2 nanoparticles. With respect to these works, we can recognise the bands at the 427 cm^{-1} , 530 cm^{-1} , and 679 cm^{-1} as related to the metal – oxygen stretch vibrations ($\nu\text{O-Sn-O}$), which can be identified as the Sn–O bonds vibrations with various coordination saturability of tin. Moreover, new absorption bands appeared at the 417 cm^{-1} and 519 cm^{-1} , which correspond to the titan dioxide in the rutile structure. The TEM micrograph (figure 3) shows microfibers with $(\text{TiO}_2/\text{SnO}_2)$ nanocrystals attached to their surface.

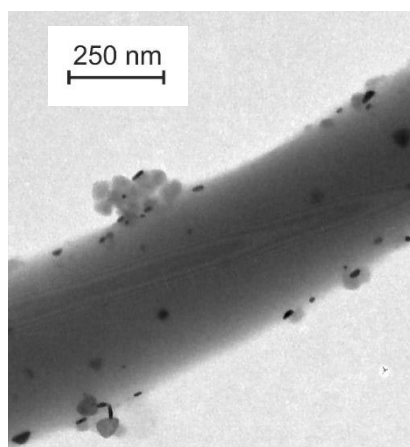


Figure 3. TEM micrograph of $\text{TiO}_2/\text{SnO}_2$ hetero-nanoparticles attached to the surface of a polypropylene fiber.

The spectra of the modified NC exhibit the clearly pronounced absorption bands 1366 , 1328 , 1302 , 1258 , 1224 , 1103 , 1045 , 998 , 975 , 899 , 842 , and 810 cm^{-1} that indicate that the structure of the carrier material is isotactic. The ratio of intensities of the absorption bands 975 and 840 cm^{-1} remains unchanged. Consequently, after modification, the structure of NC is still represented mainly by long segments ($n>10$) in a helical trans-gosh-conformation. This is indicative of the fact that the steric configuration is largely unchanged. Furthermore, modification of the carrier surface does not lead to the destruction of chemical bonds. The ratio of intensities of the absorption bands 975 and 998 cm^{-1} in the spectra of the modified NC remained the same – 0.86 . Thus, superficial modification of NC with the tin dioxide nanoparticles does not change its chemical structure.

4. Summary

Thus, this work has demonstrated the changes taken place as a result of the polypropylene melt-blown web superficial modification with the $\text{SnO}_2/\text{TiO}_2$ nanoparticles using microwave irradiation. These changes are manifested in an appearance of new absorption bands in the IR spectra. These bands do not overlap with the bands in the IR spectra of the unmodified carrier, and despite their weak intensity, can be surely identified as the bands of the $\text{SnO}_2/\text{TiO}_2$ nanoparticles. Having analysed the XRD analysis data, it has been concluded that the mesomorph structure of the carrier material transforms into the monoclinic α -crystalline due to microwave irradiation. Moreover, we have found out that the carrier material keeps its helical-chain conformation and remains stereoregular after modification. Therefore, the material of the carrier is not destructed under modification possessing the initial set of properties and attains new functional properties due to the presence of active nanoparticles attached to its surface.

Our findings lead us to the conclusion that a new opportunity appears of developing a new class of effective and safety filtering materials for the fresh and waste water purification using the polypropylene melt-blown webs modified with rare and rare-earth elements nanoparticles.

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References

- [1] Pinchuk L S, Goldade V A, Makarevich A V and Kestelman V N 2002 *Melt-Blowing: equipment, technology, and polymer fibrous materials* (Berlin: Heidelberg, New York: Springer)
- [2] Mohapatra H S, Chatterjee A and Kumar P 2013 *J. of Adv. and Nano Technol.* **1** 2347
- [3] Perepelkin K E 2009 *Fibre Chem.*, **41(1)** 9
- [4] 2003 *Handbook of Polypropylene and Polypropylene Composites, Revised and Expanded Ed.* Karian H G (Cleveland: CRC Press)
- [5] Shi L, Kang W M, Zhuang X P and Cheng B W 2011 *Adv. Mater. Res.* **332, 334** 1287
- [6] Kravtsov A G, Pinchuk L S and Goldade V A 2000 *Chem. Fibers* [in Russian] **6** 42
- [7] Zhukovsky M S, Lysak I A, Lysak G V, Vazhenin S V, Malinovskaya T D, Beznosjuk S A 2011 *Russ. Phys. J.* **54(7)** 739
- [8] Baoli T, Yu Q, Binbin H, Jiaruo S and Zuliang D 2012 *J. Mater. Res.* **27, 18** 2408
- [9] Lysak G V, Lysak I A, Shabalina A V, Izaak T I, Malinovskaya T D 2010 *Rus. J. Appl. Chem.* **83(12)** 2193
- [10] Lysak I A, Lysak G V, Malinovskaya T D, Tchaikovskaya O N and Artyushin V R 2015 *Adv. Mater. Res.* **1085** 107
- [11] Ungur G and Hruza J 2014 *Adv. Mat. Lett.* **5(8)** 422
- [12] Lysak G V, Lysak I A and Malinovskaya T D 2014 *Polzunovsky Almanah* [in Russian] **1** 30
- [13] 2012 *Advanced Aspects of Spectroscopy*, ed M A Farrukh (Rijeka: INTECH Open Access Publisher)
- [14] Barbara H S 2004 *Infrared Spectroscopy: Fundamentals and Applications* (New York: John Wiley & Sons Ltd.)
- [15] 1999 *Spectroscopy of Polymers*, 2nd edition, ed Koenig J L (New York: Elsevier Science Inc.)
- [16] Novoselova L Yu and Bordunov V V 2002 *Plastics* [in Russian] **6** 46
- [17] Gorohovatskii Yu A, Temnov D E, Chistyakova O V, Tazhenkov B A, Aniskina L B, Victorovich A S and Kojevnikova N O 2005 *Proc. of RSPU. Herzen: Scientific Journal: Natural and exact sciences* [in Russian] **5(13)** 91
- [18] Fridman M L 1982 *Technology for Processing Crystalline Polyolefins* (Moscow: Chemistry)
- [19] Lysak G V, Lysak I A, Malinovskaya T D and Volokityn G G 2010 *Inorg. Mater.* **46(2)** 183
- [20] Khan A F, Mehmood M, Aslam M and Ashraf M 2010 *Appl. Surf. Sci.* **256** 2252
- [21] Chacko S, Philip N S, Gopchandran K G, Koshy P and Vaidyan V K 2008 *Appl. Surf. Sci.* **254** 2179