

Surface modification of TiO_2 and SiO_2 nanoparticles for application in polymeric nanocomposites

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Introduction

Nanoparticles show a strong tendency to agglomerate due to the electrostatic forces [1]. Therefore, in order to eliminate this effect, chemical and physical modification is usually applied [2], and in a consequence, nanoparticles if used a reinforcing phase in polymer matrix [3], do not agglomerate and can be more uniformly distributed in a polymer matrix. As a result, improved mechanical or surface properties of resulting nanocomposite, can be obtained.

Surface modification of silica oxide or titanium oxide nanoparticles [4,5] or other metallic oxides can be realized by chemical or physical process. When chemical methods are applied, different organic or inorganic compounds of low molecular masses are used or polymer grafting is performed. The most common modifying agents are silane promoters of adhesion terminated with functional groups capable to hydrolysis. Their general structure can be presented as RSiX_3 , where X is a hydrolyzable group, i.e. chloric, ethoxyl or methoxyl, while R is an organic group of different functionality. The X group is capable to react with hydroxyl groups from silica or titanium surface, while alkylene residue can react with polymer matrix. In this way, hydrophilic surface of nanoparticles is converted into hydrophobic nanoparticles. The $-\text{OH}$ group on silica surface allow to bond covalently different trialkoxyorganosilanes functionalized with amine ($-\text{NH}_2$) or mercaptyl ($-\text{SH}$) groups. The amine surface modification gives a high yield and uniform distribution of nanoparticles. The amine group can also be easily converted into carboxylic group. Another efficient method for surface modification is surface grafting with polymers, what leads to hydrophobization of silica or titania dioxide nanoparticles, and in a consequence, increase of interface interactions in polymeric nanocomposites.

Physical modification is usually performed with surfactants or macromolecules adsorbed on the surface of metal oxide nanoparticles. The polar groups of surfactants are selectively adsorbed on nanoparticle surface due to electrostatic interactions. Surfactants can decrease the particle-particle interactions thus diminishing the agglomerates formation due to the decrease of physical forces, and separated nanoparticles can easily be introduced into polymer matrix [2].

In this work, the results of spectroscopic investigations of titanium dioxide and silica dioxide nanoparticles modification with the use of alkylsilane and fatty acid in order to produce nanoparticles with diminished tendency for agglomeration are presented.

Experimental part

Surface modification of nanoparticles

Titanium dioxide nanoparticles (Aeroxide P25, Evonik) of 21 nm size were heated for 6 hours under 3-aminopropyltriethoxysilane (APTES) reflux in toluene and methylizobutylketone (MIBK). Modified nanoparticles were washed out with toluene or MIBK and ether, and then centrifuged and dried. Silica dioxide nanoparticles (Aerosil R972 – hydrophobic and Aerosil I30 - hydrophilic) of 16 nm size were heated for 6 hours under APTES reflux in MIBK, then washed out with MIBK and ether, finally centrifuged and dried. Silica dioxide nanoparticles were also modified with oleic acid (OA) in n-hexane,

by heating them for 4 hours in reflux, then modified nanoparticles were washed with water/ethanol (3/7 vol.%) mixture and dried.

Sample preparation for IR spectroscopy

Titanium and silica dioxide nanoparticles (5wt%) were mixed with KBr and dried at 40°C in vacuum oven. Prepared mixtures were pelletized to 3 mm tablets. IR spectra were performed SPECORD M80 CARL ZEISS JENA spectrometer.

Sample preparation for UV-Vis spectroscopy

Unmodified and modified nanoparticle dispersions in ethanol were prepared at 0.02 wt%, then spectra at transmitted light were collected with SPECORD M40 CARL ZEISS JENA spectrometer. The neat titanium dioxide nanoparticles were also investigated at reflected mode with UV-VIS V-650 Jasco spectrometer.

Results and discussion

IR spectroscopy

• Surface modification of titanium dioxide

Figure 1 presents the infrared spectra of modifying agent APTES (1), unmodified TiO_2 (2) and TiO_2 after modification (3), and MIBK (4). At spectrum (2) of non-modified TiO_2 , the peak at 700 cm^{-1} is ascribed

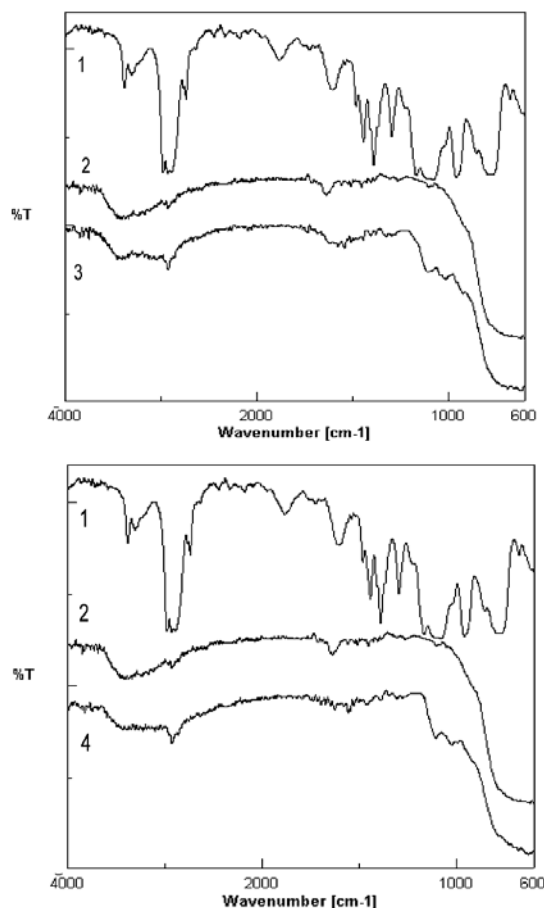


Fig. 1. IR spectra of modifying agent (1), titanium dioxide before (2) and APTES modification in toluene (3) and in MIBK (4)

to Ti-O i Ti-O-Ti bonds on the surface. Small peak at 1640 cm^{-1} and intense peak between 3400 and 3200 cm^{-1} is due to stretching vibrations of adsorbed water and -OH groups from nanopowder. After TiO_2 surface modification with APTES, a characteristic peak appears at 1540 cm^{-1} . It is ascribed to $-\text{NH}_2$ groups from aminosilane (spectra 3 and 4). Small peak at 1120 cm^{-1} indicates the formation of C-N bonds. Another peak at 3000 - 2923 cm^{-1} is referred to the presence of $-\text{CH}_2-$ groups, what is an evidence of efficient TiO_2 surface modification with APTES.

• **Surface modification of silica dioxide**

Figures 2 and 3 show transmission spectra of modifying agent, i.e. oleic acid (1), APTES (2), non-modified (3) and modified titanium dioxide in n-hexane (4) and methylizobutylketone - MIBK (5). As presented in Figure 2 and Figure 3, peak ascribed to Si-O-Si bonds on silica surface can be seen at about 1080 cm^{-1} (spectra 3, 4 and 5). The spectrum no. 4, Fig. 2 observed at 2936 cm^{-1} is indicating the presence of a long alkylene chain being an oleic acid (OA). The peak at 1705 cm^{-1} is characteristic for $-\text{COOH}$ bonds of a dicarboxylic group. The presence of additional peak at 3430 cm^{-1} (4) is an evidence of partial modification of TiO_2 surface of nanoparticles with oleic acid (OA).

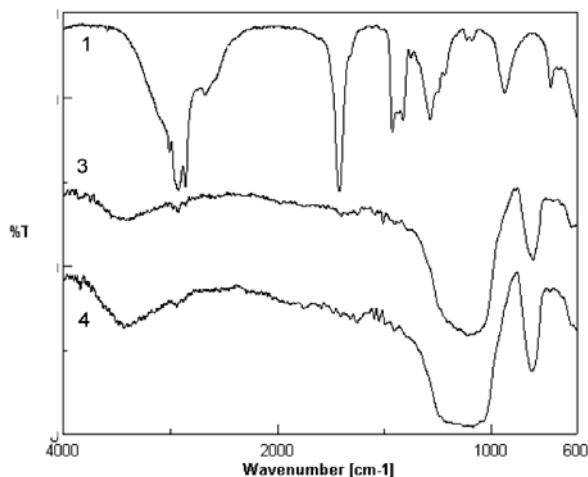


Fig. 2. IR spectra of modifying agent OA (1), APTES (2), silica dioxide (SiO_2 , Aerosil 130) before (3) and after modification (4) with OA in n-hexane, and APTES in MIBK (5)

Most probably, larger amount of OA as compared to SiO_2 , could lead to the total conversion of hydroxyl groups on silica dioxide surface. This peak is not present in Figure 3, what can be explained by different character of commercial silica dioxide. After surface modification with APTES in MIBK (see spectra 5), characteristic peak appears at 1540 cm^{-1} and it is ascribed to $-\text{NH}_2$ groups from

aminosilane. Small peak at 2923 cm^{-1} is characteristic for $-\text{CH}_2-$ groups on the surface, what is an indication for efficient surface modification with APTES.

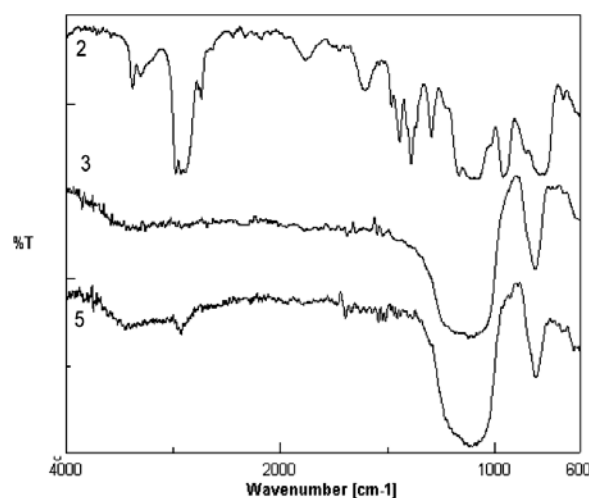
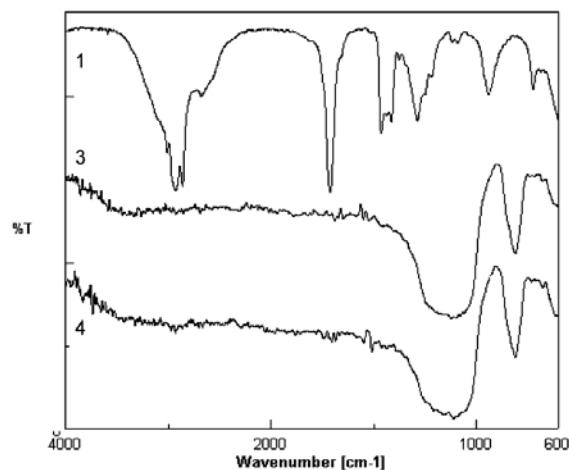


Fig. 3. IR spectra of OA (1) and APTES (2), silica dioxide (SiO_2 , Aerosil R972) before (3) and after modification in n-hexane (4), and APTES in MIBK (5)

UV-Vis spectroscopy

Figure 4 presents UV-VIS spectra recorded for non-modified (NM) and modified titanium dioxide in toluene and in MIBK as nanoparticles dispersion in ethanol. Figure 5 shows UV-Vis spectrum recorded at the reflection mode (samples were prepared as tablets). Both methods showed good correlation of the results. The absorbance limit was at 340 nm wave length for both methods. Surface modified TiO_2 nanoparticles showed larger decrease of absorption as compared to unmodified. The highest drop was observed for TiO_2 modified in MIBK.

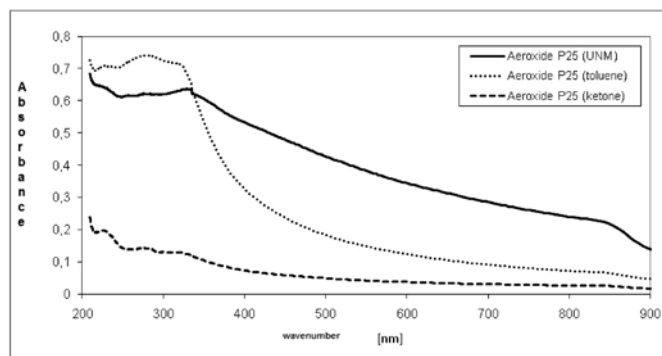


Fig. 4. UV-VIS spectra of TiO_2 before (UNM) and after modification with APTES in toluene and MIBK recorded at the transmitted light mode

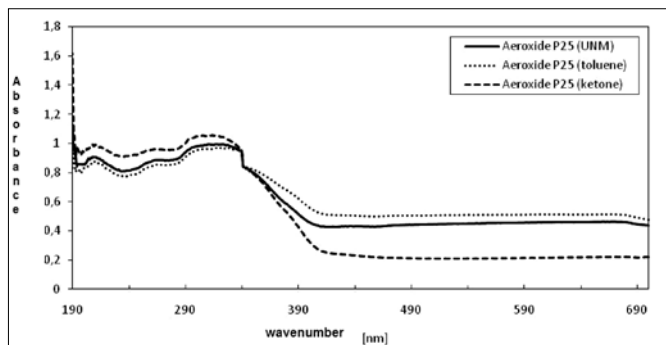


Fig. 5. UV-Vis spectra of TiO_2 before (UNM) and after modification with APTES in toluene and MIBK recorded at the reflected light mode

Conclusions

The results of surface modification of TiO_2 (Aeroxide P25, Evonik) and SiO_2 (Aerosil I30 – hydrophilic, and Aerosil R972 – hydrophobic) nanoparticles for potential application in polymeric nanocomposites were presented. IR and UV-VIS showed that the best results were obtained when APTES in MIBK was used as modifying agent. The effectiveness of the surface modification of nanoparticles will be checked by the preparation of polymeric nanocomposite with the use of modified and non-modified nanoparticles.

Acknowledgements

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English translation by the Author

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