Nanostructured polymer–titanium composites and titanium oxide through polymer swelling in titania precursor

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Abstract Polymer (XAD7HP)/Ti⁴⁺ nanocomposites were prepared through the swelling of polymer in titanium (IV) ethoxide as a titanium dioxide precursor. The nanocomposite beads exhibit relatively high porosity different than the porosity of the initial polymer. Thermal treatment of composite particles up to 200 °C in vacuum causes the change of their internal structure. At higher temperature, the components of composite become more tightly packed. Calcination at 600 °C and total removal of polymer produce spherically shaped TiO₂ condensed phase as determined by XRD. Thermally treated composites show the substantial change of pore dimensions within micro- and mesopores. The presence of micropores and their transformation during thermal processing was studied successfully by positron annihilation lifetime spectroscopy (PALS). The results derived from PALS experiment were compared with those obtaining from low-temperature nitrogen adsorption data.

Keywords Composite · Titanium dioxide · Positron annihilation lifetime spectroscopy (PALS)

Introduction

In recent years, titania dioxide have attracted a great interest due to many real and potential applications. In these applications, titanium dioxide is used as a component of various types of composites of some significance in production of pharmaceuticals, cosmetics or paints [1, 2], drug delivery systems with controlled release [3–5], solar cell [6–9], chemical sensing [10–12], luminescent material, and photocatalyst for, e.g., water purification [13–16]. In the wide field of organic–inorganic composite materials, titanium dioxide is a popular filler of organic matrices. The combination of TiO₂ with polymer results in new and often unique properties, unapproachable for the individual components.

Direct mixing is the simplest way to produce polymer–TiO₂ nanocomposites [17–22]. However, the achievement of uniform dispersion of the hydrophilic inorganic phase in a hydrophobic organic polymer causes a lot of problems. The host–guest interactions are in this case very weak and based only on hydrogen bonds and van der Waals forces. A high surface energy of inorganic particles is responsible for their tendency to aggregate. In most cases, surface modification of the inorganic phase is an important part of the procedure. A way to reach stronger chemical bonds and reduction of aggregation is the use of the sol–gel process [22–26]. This process is based mainly on titanium alkoxide which, after hydrolysis and condensation, produces the desired crystal structure of TiO₂.

The dispersed phase morphology can be controlled by modification of the hydrolysis/polycondensation parameters, titanium dioxide precursor type and host–guest interaction nature. A frequent polymer–TiO₂ synthesis route is in situ emulsion polymerization, which leads to a good dispersion of the inorganic phase [27–29]. Titanium dioxide encapsulation in polymer, often results in a core–shell morphology [30]. On the other hand, polymers may be used as a specific reactor for preparation of TiO₂ particles of...
dimensions mostly useful for specific applications [e.g., 31–33]. The performance of TiO₂ microparticles in applications requires modeling of their morphology and porosity by controlling the parameters that influence the growth of oxide particles.

Recently, we applied preformed polymer particles as a support for synthesis of SiO₂ mesoporous particles [34–36]. Silica particles were obtained by calcination and removal of polymer template from the polymer–silica nanocomposite being the product of swelling of pure polymer in silica precursor. In the present paper, a similar approach is applied for preparation of Ti⁴⁺/polymer and TiO₂ materials.

**Experimental**

**TiO₂ preparation**

The composite samples were prepared by swelling of the commercial Amberlite XAD7HP (a nonionic aliphatic acrylic ester, Rohm and Haas, today Dow) beads (0.2–0.5-mm fraction) in a solution of ethanol (99.8 % EtOH solution supplied by Polish Chemical Reagents, POCH) with titanium (IV) ethoxide (Sigma-Aldrich, 98 wt.%). A similar procedure was recently applied for preparation of polymer–silica composite using Amberlite XAD7HP or TRIM as a polymer and tetraethyl orthosilicate (TEOS) as a silica source [34–36]. Initially, the polymer beads were thoroughly washed with distilled water as the manufacturer suggests. Then the washed polymer XAD7HP was wetted with alcoholic solution of titanium (IV) ethoxide (70 %). The amount of the titania precursor was adjusted so that the beads started to stick together, preserving a loosely packed structure. The resulting polymer/titania (IV) ethoxide ratio was 0.5 w/w. It can be assumed that part of the added titania precursor takes part in filling pores, and a part in the swelling process. Next, the Amberlite XAD7HP particles saturated with alcoholic solution of titanium (IV) ethoxide were transferred into aqueous ammonium hydroxide solution (15 cm³ of 25 % NH₄OH solution supplied by Polish Chemical Reagents, POCH per 15 g of sample) and kept at room temperature for 24 h for gelation and ageing. The solid product in the form of spherically shaped particles was filtered, washed with deionized water, and dried at 110 °C under vacuum. No aggregation of these particles was observed. The drying procedure was performed for 12 h. The dry composite sample obtained in the aforementioned manner was denoted as XADTi-B. In order to prepare pure TiO₂, being the inorganic component of the composite, part of the base sample XADTi-B was calcined in air at 600 °C for 12 h. The remaining incombustible residue was denoted as Ti-B.

A similar procedure was applied to prepare the composite samples by hydrolysis and condensation of the titania precursor in distilled water (15 cm³ of distilled water per 15 g of sample). The dry water set was denoted as XADTi-N and its remaining incombustible part, after calcination in air at 600 °C was denoted as Ti-N.

**Samples characterization**

**Thermal analysis**

The mass loss TGA curves were measured using the Derivatograph C (MOM, Hungary) instrument. The samples were heated at the rate of 10 K/min⁻¹ from room temperature to 1,273 K in air flow.

**SEM**

SEM studies were conducted on a Quanta™ 3D FEG operating at a voltage of 30.0 kV.

**N₂ adsorption**

Textural characterization of the samples was carried out by the low-temperature nitrogen adsorption–desorption method. Nitrogen adsorption–desorption measurements were made at 77 K using a volumetric adsorption analyzer ASAP 2405 (Micromeritics, Norcross, GA, USA). The specific surface area, S_{BET}, of the investigated samples was evaluated using the standard Brunauer–Emmett–Teller (BET) method for the nitrogen adsorption data in the range of a relative pressure p/p₀ 0.05 to 0.25. The total pore volumes were estimated from a single point adsorption at a relative pressure of 0.985. The pore size distributions were obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) procedure [37].

**PALS experiment**

Positron annihilation lifetime spectroscopy (PALS) measurements were performed using fast–slow delayed coincidence spectrometer. The scintillator for detection of gamma quanta accompanying positron formation was ∅38 × 51 mm BaF₂, while annihilation radiation was detected by ∅38 × 38 mm BaF₂ crystal. As a positron source, 0.3 MBq²²Na enclosed in 8 μm Kapton foil was used. Background to signal ratio was about 6–7 %. Positron fraction annihilating in the foil with lifetime 374 ps was found [38] to be approximately 12 %. Wide energy windows, set in order to maximize 3γ annihilation radiation registration efficiency, allowed collecting 1.3 × 10⁶ counts per hour. On the other hand, the energy window setup resulted in a complicated time resolution function, which had to be approximated by three Gaussians with FWHM 0.28, 0.35, and 0.75 ns, and intensity of 69 %, 18 %, and 13 %, respectively. The spectra
collected during the 23 h (about $3 \times 10^7$ counts) were analyzed using MELT routine [39, 40]. Positron lifetime distributions were transformed to pore size distributions (PSDs) using the method described in [35, 41]. All measurements were performed in vacuum about 10$^{-3}$ Pa.

**XRD**

X-ray powder diffraction (XRD) patterns were measured on Diffractometer HZG 4AZ (Germany) using monochromatic CuKα radiation. The X-ray patterns were scanned in 2Θ range of 10° to 80° with a step of 0.05°

**Results and discussion**

On the basis of the previous studies, it is known that porous polymers including the commercial Amberlite XAD7HP easily absorb the silica precursor TEOS. The molecular structure of the composite samples, porosity and their physical appearance are affected by the synthesis conditions [36]. The Amberlite XAD7HP polymer wetted with titanium (IV) ethoxide swells also spontaneously. Wetting of swollen Ti$^{4+}$/polymer particles in water of adjusted pH causes hydrolysis of titania precursor followed by condensation and finally, similarly as in the case of silica, Ti$^{4+}$/polymer composite formation. The pure TiO$_2$ was obtained after composites calcination at 600 °C. The TGA thermograms (Fig. 1) for composite XADTi-N and pure TiO$_2$ (Ti-N) clearly indicate that the polymer component after the thermal treatment at 600 °C for 12 h is completely removed. The microscopic SEM pictures of the composites (Fig. 2a) and calcined samples (Fig. 2b, c) indicate that the investigated particles preserve the spherical shape of the initial polymer. Moreover, the images illustrate that the hydrolysis and condensation conditions (basic and inert) influence the visual appearance of Ti$^{4+}$/polymer composites and pure TiO$_2$ only slightly. The presence of cracks on the outer surface of particles is typical for samples after thermal treatment: Ti-N, Ti-B. Although the investigated samples preserve the spherical shape of the initial polymer, the pure TiO$_2$ particles have a more complex structure. The crushed titanium dioxide particle micrograph of Ti-B (Fig. 2c, d) demonstrates the core/shell structure.

Presumably, the core/shell structure of the TiO$_2$ particles is a result of the specific titanium (IV) ethoxide hydrolysis and condensation in the presence of a polymer template. When swollen, Amberlite XAD7HP particles are transferred into water solution of desired pH; the titania precursor present in the particle interior is partially excluded from these particles due to their shrinkage and condensation on the outer surface of the initial composite particle. Thus, it can be assumed that Ti$^{4+}$/polymer composite particles consist of two phases: Ti$^{4+}$/polymer, core and mesoporous pure Ti(OH)$_4$, shell. Further condensation of titania species takes place during calcination at 600 °C accompanied by thermal decomposition of the polymer template. In line with this deduction, the observed characteristic cracks on the outer shell and inner core are the result of the heat treatment and shrinkage of the whole particles. However, the interior of the Ti-N (Fig. 2e) and Ti-B (not shown) beads is rather smooth and consists of tightly packed spherical particles of TiO$_2$ sized from 11 to 20 nm. The shell is composed of significantly larger spherical TiO$_2$ particles (Fig. 2f). This clearly indicated that the sizes of the confined spaces in the polymer template have a great influence on the hydrolysis process and consequently on the size of the resulting TiO$_2$ particles.

The XRD experiment results for the pure polymer matrix XAD7HP, composites, and pure TiO$_2$ samples are shown in Fig. 3. No crystal peak was found prior to the calcination of the neutral and water set Ti$^{4+}$/polymer composite. Comparing these diffractograms, one can conclude that the introduction of a titanium precursor into polymer beads influences the arrangement of the hydrocarbon chains and reduces some regularity of the polymer matrix, what is visible as disappearance of broad peak at 2Θ=10–20°. The XRD patterns are practically identical for both calcined materials. The anatase structure is characteristic for Ti-N powder, while under the basic conditions, besides the anatase phase, a small amount of the rutile structure was found.

To determine the structure of nanocomposites as well as the final TiO$_2$ particles, low temperature adsorption studies of nitrogen were carried out. Figure 4 shows the relevant nitrogen adsorption and desorption isotherms for original Amberlite XAD7HP support, Ti$^{4+}$/polymer composites (XADTi-N, XADTi-B) and pure titania oxide samples after calcination and total removal of polymer matrix (Ti-N, Ti-B). As regards the composite samples, it is easy to observe that the shape of their nitrogen isotherms differs only slightly. A steep rise in the initial part of these isotherms, for $p/p_0<0.02$, suggests the presence of micropores with dimensions smaller than 2 nm. However, a wide hysteresis loop

![Fig. 1 TGA thermograms of composite XADTi-N and pure titanium dioxide Ti-N](image-url)
extending along the $p/p_0$ axis suggests a complex pore structure of these materials and the presence of mesopores of different dimensions. The different nitrogen adsorption of the composites and original Amberlite XAD7HP suggests that the titania precursor penetrated considerably the polymer pore network. In fact, the numerical parameters derived from the adsorption data presented in Table 1 show a substantial decrease of the total mesopore volume ($V_p$), average pore diameter ($D_p$) and BET surface area of the Amberlite after depositing the titania onto it under either basic (Fig. 4b) or neutral conditions (Fig. 4d). The decrease of these parameters suggests that TiO$_2$ phase is entrapped mainly in mesopores of the initial polymer.

For calcined samples, after the Amberlite support removal at 600 °C, the BET surface area ($S_{BET}$) substantially decreased, while the average pore diameter ($D_p=4V_p/S_{BET}$) and total pore volume ($V_p$) significantly increased as demonstrated by the data for Ti-B and Ti-N in Table 1. This may be caused by dissolution of smaller pore walls that leads to creation of bigger pores, which in fact represent free volumes occupied by the polymer before calcination.

The shape of isotherms for pure TiO$_2$ samples obtained by calcination of composites is quite different from those for the composites, and they are of type 4 according to the IUPAC nomenclature [42]. The initial micropore adsorption at $p/p_0<0.01$ became substantially lower for the calcined samples as it was for composites XADTi-B and XADTi-N. Moreover, the observed hysteresis loop with approximately parallel adsorption and desorption branches (Fig. 4c, e), is characteristic for porous solids composed of spherical nanoparticles. One can therefore assume that nitrogen adsorption isotherms primarily relate to the pore structure of the outer layer of TiO$_2$ particles.

Figure 4 also illustrates for all investigated samples the mesopore size distribution (PSD) derived from the N$_2$ desorption data using the BJH method. As it can be seen, the PSD for pure polymer XAD7HP is of bimodal character, whereas the broad PSD of the base XADTi-B and neutral set XADTi-N nanocomposites is of a very heterogeneous porosity character. The observed shape of PSD curves for composites is related to the process of the titanium source hydrolysis in the confined spaces of the polymer template. The created particles of TiO$_2$ in the polymer matrix are randomly packed causing the broad pore size distribution. However, for pure TiO$_2$ samples, both PSDs show practically one well-defined peak, which suggests a high uniformity of the mesopore size.

In order to get more precise information about the pore structure, the discussed samples were investigated by means of PALS. Positronium annihilation lifetime spectroscopy is a technique which allows investigation of any free volumes in the range of diameters from angstroms to tens of nanometers. This method allows for determination of pore size in solids,
including closed pores and the space between fine particles or molecules. Determination of pore size on the basis of o-Ps lifetime for radii larger than 1 nm is possible due to the Extended Tao-Eldrup (ETE) model [43]. The ETE model was successfully applied for characterization of several model silicas or glasses of controlled porosity [44–48]. Moreover, the PALS technique can be used in a wide temperature range. The use of any adsorbate molecules and cooling the solid to
low temperature, as is practiced by the conventional nitrogen adsorption method, are not required. This allows avoiding shrinkage of the solid pore network at a low temperature. This effect can be especially important for porous polymers and composites.

Figure 5 presents the pore size distribution of pure polymer, composite XADTi-N, and pure TiO₂ calculated on the basis of PALS measurements. The PSDs of XADTi-B composite and Ti-B are not shown for clarity but are almost identical with those presented in Fig. 5 for samples synthesized in neutral conditions. As can be seen in Fig. 5b, the introduction of titanium precursor into the polymer beads causes the disappearance of mesopores of diameter above 3 nm. The PSD for the composite sample XADTi-N exhibits the presence of at least four groups of pores within a wide dimension range of 0.3–2.5 nm. After calcination and total burning of the polymer matrix (Fig. 5c), these small pores disappear and one can observe the appearance of a new group of pores of PSD centered at 10 nm. The disappearance of the smallest pores group clearly indicates that they originate from the polymer constituent. The mesopores remaining in pure TiO₂ sample after calcination at 600 °C correspond probably to the free volumes between TiO₂ submicroparticles formed during condensation of Ti(OH)₄.

The interesting dependence of the free volume dimensions at different temperatures observed in composite samples is worth mentioning. Figure 6 presents pore volume distributions measured in vacuum for the composite obtained under neutral conditions at room temperature (Fig. 6a), at 200 °C (Fig. 6b) and after cooling again to room temperature (Fig. 6c). One can easily observe that the peak at \(D = 2.5\) nm disappears during heating of the composite up to 200 °C. The disappearance of the peak observed for the nanocomposite at room temperature testifies that simultaneously two processes take place during heating. Firstly, at about 200 °C, the Ti(OH)₄ condenses and amorphous TiO₂ starts to form. Additionally, at this temperature, the polymer matrix is more flexible and starts to stick more tightly to the incipient TiO₂ phase. This structure modification is preserved after cooling the sample down to room temperature. On the other hand, the high temperature does not influence substantially the pores of smaller size \(D < 2\) nm, which corresponds to the free volumes within the polymer matrix, indicating that the internal structure of the polymer remains almost intact at 200 °C.

**Conclusions**

The porous polymer/Ti⁴⁺ microspheres were prepared by polymer particle saturation with titanium (IV) ethoxide followed by its condensation. The obtained composites exhibit a relatively high porosity and preserved the spherical shape of the initial
polymer particles. Encapsulation of inorganic particles is a result of pore filling with tetraethoxy titania precursor and entrapment of the precursor molecules in the polymer matrix. Both specific surface areas and the total pore volume of the composite materials are slightly reduced as compared to pure polymer. Thus, polymer swelling in titania precursor allows us to control the particle dimensions of the composite and pure TiO₂ by using preformed polymer particles of tailored porosity. Thermal treatment of composites at 200 °C causes their structural reorganization and a tight packing of the polymer and titania component. After heat treatment at 600 °C and elimination of the organic component from Ti⁴⁺/polymer composite, a stable structure of TiO₂ particles was achieved. TiO₂ particles were composed mainly of anatase nanocrystals sized between 20 and 40 nm. Structural analysis of TiO₂ indicates a good dispersion of TiO₂ precursor within preformed polymer beads and well-developed mesoporosity of pure TiO₂ particles.

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