

**ANATASE TiO₂ NANOWIRES AS A MODIFIER OF CHITOSAN BLENDED
WITH A FLUORINATED POLYMETHACRYLATE: EFFECT ON HEAT
RESISTANCE, PERMITTIVITY AND MICROBIAL INHIBITION**

Rustamov Uktamjon Raxmatjon ugli

Researcher of the department of organic synthesis and bioorganic chemistry,
Institute of Biochemistry Samarkand State University named after Sh. Rashidov /
University bvld-15, Samarkand city, 140104, The Republic of Uzbekistan

Ibrohim Erol

Doctor of chemical sciences, professor of the department of organic synthesis and
bioorganic chemistry, Samarkand State University named after Sh. Rashidov /
University bvld-15, Samarkand city, 140104, The Republic of Uzbekistan

Abstract

This paper describes nanocomposites in which TiO₂ nanowires, prepared by a hydrothermal route, are dispersed in a matrix of chitosan and poly(4-(trifluoromethyl)benzyl methacrylate) (PTFBMA). The filler content was 3, 5 and 7 wt%, and the mixtures were treated hydrothermally at 120 °C. The materials were studied by FTIR, NMR, XRD, SEM-EDX, TGA/DSC, contact angle measurements and dielectric spectroscopy, and their activity against *E. coli*, *S. aureus* and *C. albicans* was checked by the disc diffusion method. TiO₂ raised the glass transition temperature from 118 to 131 °C and the dielectric constant from 2.8 to 7.4. The water contact angle decreased from 64.09° to 50.99°, so the surface became more hydrophilic. The composite with 7 wt% TiO₂ showed the largest inhibition zones against all three microorganisms.

Keywords

chitosan; titanium dioxide; nanowires; hydrothermal synthesis; nanocomposite; dielectric properties; antimicrobial activity.

Introduction. Natural polymers attract attention in medicine, packaging and agriculture because they are renewable, biocompatible and degrade without harm to the environment [1, 2]. Chitosan, which is obtained by deacetylation of chitin, is among the most studied of them. Its amino and hydroxyl groups allow chemical modification, and the positive charge of the protonated amino groups gives the polymer a noticeable antibacterial effect [3, 4]. For practical use, however, chitosan alone is often not sufficient: its heat resistance is moderate and its antifungal action is weak.

One way to improve these properties is to introduce inorganic nanofillers. Titanium dioxide is chemically stable, non-toxic and able to generate reactive oxygen species, and its anatase form is known for photocatalytic and antimicrobial behaviour [5]. One-dimensional nanostructures such as nanowires have a large surface area and can form many contacts with the polymer chains, so they are especially attractive as fillers. A second modification used in this work is the addition of a fluorinated polymer. The trifluoromethyl groups of PTFBMA are hydrophobic and change how the material interacts with water and with cells.

The aim of the present study was to prepare PTFBMA–chitosan nanocomposites containing TiO_2 nanowires by a hydrothermal method and to evaluate how the filler content affects their structure, thermal stability, surface and dielectric properties and antimicrobial activity.

Experimental

Materials. 4-(Trifluoromethyl)benzyl chloride and sodium methacrylate were obtained from Sigma-Aldrich, AIBN and the TiO_2 precursor from Merck. Low molecular weight chitosan with a degree of deacetylation of 85 % was used. Ethanol and acetonitrile were of analytical grade.

Synthesis of TFBMA and PTFBMA. The monomer was prepared by nucleophilic substitution between 4-(trifluoromethyl) benzyl chloride and sodium methacrylate in

acetonitrile at 80 °C under an inert atmosphere, with stirring at 600 rpm for 24 h. The product was extracted with diethyl ether and crystallized from ethanol. Free radical solution polymerization with AIBN was carried out at 65 °C under nitrogen for 36 h in an oil bath, and the polymer (PTFBMA) was purified with n-hexane.

Synthesis of TiO₂ nanowires. Five grams of TiO₂ were mixed with 50 ml of 10 M NaOH and sonicated for 15 min. The suspension was kept in a Teflon-lined autoclave at 150 °C for 20 h. After cooling, the solid was separated by decantation, washed with distilled water until neutral pH, stirred in 100 ml of 1 M HCl (ultrasound for 15 min and then 4 h of stirring), washed again and calcined at 300 °C.

Preparation of nanocomposites. Two grams of chitosan were dissolved in 15 ml of 2 % acetic acid at 50 °C for 3 h (500 rpm). Two grams of PTFBMA dispersed in water were added slowly, and the mixture was stirred at 1200 rpm for 3 h. TiO₂ nanowires were then introduced at 3, 5 and 7 wt%, followed by 3 h of stirring and 1 h in an ultrasonic bath. The dispersions were treated in Teflon-lined autoclaves at 120 °C for 24 h, and the resulting solids were dried and ground.

Characterization. FTIR spectra were recorded on a Nicolet iS5 spectrometer (KBr pellets, 4000–500 cm⁻¹). ¹H and APT ¹³C NMR spectra were measured in DMSO-d₆ on a Bruker AVANCE III 400 MHz instrument. XRD patterns were obtained on a Bruker D8 Advance diffractometer (Cu Kα, 40 kV, 30 mA, 2θ = 10–80°, step 0.02°). TEM images were taken with a Hitachi HT7800 at 100 kV, and SEM-EDX analysis was performed on a NanoSEM 650. TGA (30–600 °C, 20 °C/min) and DSC (30–250 °C, 10 °C/min) were run in nitrogen on a Shimadzu 60 series analyzer. Contact angles of water and diiodomethane were measured and used to calculate the surface free energy. Antimicrobial activity against *E. coli*, *S. aureus* and *C. albicans* was assessed by the disc diffusion method; inhibition zones were measured after 24 and 48 h, with three replicates for each sample.

Results and discussion

Monomer and polymer. The FTIR spectrum of TFBMA contains the ester C=O band at 1722 cm^{-1} , vinyl C=C at 1638 cm^{-1} and C–F and C–O–C bands in the $1325\text{--}1018\text{ cm}^{-1}$ range, and a band at 826 cm^{-1} typical of a para-substituted benzene ring. In PTFBMA the carbonyl band moves to 1734 cm^{-1} and the vinyl absorption disappears. The NMR spectra agree with this: the vinyl protons at 5.6–6.2 ppm and the vinyl carbons are no longer present after polymerization, whereas the ester carbon (166 ppm in the monomer, 168 ppm in the polymer) and the aromatic signals remain. The polymerization therefore proceeded to completion without damage to the aromatic and CF_3 groups.

TiO₂ nanowires. The XRD reflections at $2\theta = 25.3^\circ, 37.8^\circ, 48^\circ, 54^\circ$ and 62° belong to anatase, and the Scherrer crystallite size was about 20 nm. SEM showed long thin wires, roughly 20 nm in diameter and up to several micrometres in length, arranged more or less in parallel. EDX detected only titanium and oxygen, which points to a pure product, and TEM confirmed single-crystalline wires without amorphous clusters.

FTIR and XRD of the nanocomposites. The ester carbonyl band of PTFBMA is found at $1738\text{--}1731\text{ cm}^{-1}$ in all composites and shifts slightly with the TiO_2 content, which indicates physical interaction between the filler and the matrix. Bands at $1327\text{--}1166\text{ cm}^{-1}$ belong to C–O–C and C–F, and a band at 534 cm^{-1} corresponds to Ti–O–Ti stretching; its intensity grows with the filler content. The diffraction pattern of the PTFBMA–chitosan matrix has a broad maximum near 20° , attributed to short-range order in chitosan. When TiO_2 is added, this maximum becomes weaker and shifts a little, so the matrix is even more amorphous, while the anatase peaks ($25.3^\circ, 37.8^\circ, 48.0^\circ, 53.9^\circ, 55.1^\circ, 62.7^\circ$) appear against the amorphous background and are strongest in the 7 wt% sample.

Morphology. At 3 wt% TiO_2 the surface is dense and uniform, with only a few white dots of nanowire clusters. At 5 wt% more distinct particles and partial

agglomeration are seen, and at 7 wt% the surface is heterogeneous, with voids and unevenly distributed aggregates, rougher and more porous. The titanium content measured by EDX increased from 1.34 wt% (0.36 at%) at 3 wt% to 3.40 wt% (1.22 at%) at 5 wt% and to 15.21 wt% (8.11 at%) at 7 wt%. Fluorine from PTFBMA and nitrogen from chitosan were present in all samples.

Thermal properties. All composites decomposed in three stages. The first stage (30–120 °C, 3–5 % of mass) is the loss of adsorbed water and volatile substances, the second (250–400 °C) is the main decomposition of chitosan and PTFBMA, and the third (400–600 °C) is the breakdown of carbonized residues. TiO₂ shifted the main stage to higher temperature, and the residue at 600 °C grew from 22 % (3 wt%) to 25 % (5 wt%) and 28 % (7 wt%), since the oxide itself does not decompose. The decomposition temperature of the 7 wt% sample reached 334 °C. The glass transition temperature obtained by DSC rose steadily (Table 1). This is explained by hydrogen bonds between the OH and NH₂ groups of chitosan and the hydroxyl groups on the oxide surface, which reduce the mobility of chain segments, and by the barrier effect of the filler.

Table 1. Glass transition temperature of the samples

Sample	T _g , °C
PTFBMA–chitosan	118
+ 3 % TiO ₂	122
+ 5 % TiO ₂	126
+ 7 % TiO ₂	131

Surface properties. The values are given in Table 2. The matrix without filler has a water contact angle of 64.09°, and it decreases with each addition of TiO₂, down to 50.99° at 7 wt%; the contact angle of diiodomethane rises from 30.65° to 40.52°. The surface free energy goes up from 49.05 to about 53 mN/m. The polar hydroxyl groups of the oxide on the surface make it more hydrophilic, and a surface energy of about 50 mN/m or higher is useful for adhesion and wetting in coatings and sensors.

Table 2. Contact angles and surface free energy

Sample	Water, °	Diiodomethane, °	SFE, mN/m
PTFBMA–chitosan	64.09	30.65	49.05
+ 3 % TiO ₂	54.99	31.06	53.12
+ 5 % TiO ₂	52.67	38.92	52.40
+ 7 % TiO ₂	50.99	40.52	52.97

Dielectric properties. The real part of the dielectric constant decreased with frequency in all samples, as expected for dipolar polarization. The highest ϵ' was found for the 7 wt% sample (7.4), followed by 5 wt% (6.0), 3 wt% (3.5) and the unfilled matrix (2.8). A reasonable explanation is Maxwell–Wagner–Sillars polarization at the numerous interfaces between the conductive nanowires and the poorly conducting polymer. The imaginary part ϵ'' showed a Debye-type relaxation peak whose position moved to higher frequency with increasing TiO₂, and the largest maximum (0.92) was again observed at 7 wt%. At 1 MHz the AC conductivity was about 4.2×10^{-5} S/m for the matrix and 4.6×10^{-5} and 6.1×10^{-5} S/m for 5 and 7 wt% TiO₂ (3.2×10^{-5} S/m for 3 wt%). The series resistance of the 7 wt% sample fell from about $3.8 \times 10^5 \Omega$ at low frequency to $1.2 \times 10^5 \Omega$ at 1 MHz. High ϵ' together with moderate losses makes the composites suitable for film capacitors and sensor platforms.

Antimicrobial activity. The matrix itself already inhibited *E. coli*, and the effect was strongest for the 7 wt% composite, whose inhibition zone was 11.03 mm after 24 h and 11.38 mm after 48 h. For *S. aureus* the 7 wt% sample gave 10.57 mm (24 h) and 10.98 mm (48 h), and for *C. albicans* a zone of 11.22 mm. Overall, the composite with 7 wt% TiO₂ was the most active against all three microorganisms. Several effects probably act together: electrostatic interaction of the protonated NH₃⁺ groups of chitosan with the negatively charged cell membrane, formation of reactive oxygen species at the TiO₂ surface, and the hydrophobic CF₃ groups of PTFBMA, which change the contact between the surface and the cell. The thicker peptidoglycan wall of the Gram-positive *S. aureus* explains why its zones were somewhat smaller. The zones are smaller than those of conventional antibiotics, but the materials are biodegradable and safe, which is important for wound dressings and antimicrobial coatings.

Conclusions

PTFBMA–chitosan nanocomposites with 3, 5 and 7 wt% TiO₂ nanowires were prepared by the hydrothermal method, and the successful incorporation of the filler was confirmed by FTIR, XRD, SEM and EDX. TiO₂ improved the thermal behaviour (T_g from 118 to 131 °C, higher residue and decomposition temperature), increased the dielectric constant from 2.8 to 7.4 and the AC conductivity, and made the surface more hydrophilic with a surface energy of about 53 mN/m. The sample with 7 wt% TiO₂ had the best antibacterial and antifungal effect. At this loading, however, the nanowires begin to aggregate, so the optimum content should be refined in later work. The materials are of interest for wound dressings, antimicrobial coatings, sensors and dielectric films.

References:

1. C. P. Jiménez-Gómez, J. A. Cecilia. Chitosan: a natural biopolymer with a wide and varied range of applications // *Molecules*. 2020, 25(17), 3981. doi:10.3390/molecules25173981
2. M. Azmana, S. Mahmood, A. R. Hilles, A. Rahman, M. A. B. Arifin, S. Ahmed. A review on chitosan and chitosan-based bionanocomposites: promising material for combatting global issues and its applications // *International Journal of Biological Macromolecules*. 2021, 185, 832–848. doi:10.1016/j.ijbiomac.2021.07.023
3. I. Aranaz, A. R. Alcántara, M. C. Civera et al. Chitosan: an overview of its properties and applications // *Polymers*. 2021, 13(19), 3256. doi:10.3390/polym13193256
4. A. Khan, K. A. Alamry. Recent advances of emerging green chitosan-based biomaterials with potential biomedical applications: a review // *Carbohydrate Research*. 2021, 506, 108368. doi:10.1016/j.carres.2021.108368
5. Y. Khane, S. Albukhaty, G. M. Sulaiman et al. Fabrication, characterization and application of biocompatible nanocomposites: a review // *European Polymer Journal*. 2024, 214, 113187.