

## PREPARATION AND PROPERTIES OF HIBRYD ORGANIC-INORGANIC COMPOSITES BACED ON POLY- TiO<sub>2</sub>\*\*

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### ABSTRACT

Optically transparent hybrid organic-inorganic copolymers based on the poly-TiO<sub>2</sub>, vinyl monomers and lactide or glycolide have been prepared. Optical and physical-mechanical properties of composites are depended with the ratio of components have shown. Hybrid copolymers possess photochromic properties. By the UV light excitation reversible darkening of the samples due to the transition  $Ti^{4+} \leftrightarrow Ti^{3+}$  had observed. The speed of transition depends on the copolymer composition.

**Key words:** poly-TiO<sub>2</sub>, hydroxyethyl methacrylate, lactide, glycolide, hybrid organic-inorganic copolymers, nanocomposite, reversible photochromic properties, solid-state

### INTRODUCTION

In recent decades, research to develop new polymer composites containing nanoparticles metals or their oxides, as well as nanostructured hybrid organic-inorganic composites has been in rapid progress. Interest to these objects is very strong because of by the transition from micro- to nanoparticles a qualitative change in many physical and chemical properties have taken place. Often this materials show complex of unique properties such as structural, catalytic and biological.

Among the hybrid organic-inorganic polymer composites particular interest represent the copolymers poly-TiO<sub>2</sub>. Gels of poly-TiO<sub>2</sub> have demonstrated unique optical properties. By the UV light excitation observed reversible conversion  $Ti^{4+} \leftrightarrow Ti^{3+}$  which accompanied by darkening - the enlightenment of samples. However the instability and absence of shape of this gels determine the need in synthesis of solid-state samples which can withstand mechanical

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handling. In this regard the synthesis of hybrid copolymers contained poly-TiO<sub>2</sub> component which stabilized by polymeric matrix organic nature are promising.

For particular interest to create optical data storage devices are composite materials based on organic-inorganic copolymers containing metal nanoparticles. Additional introduction of metal nanoparticles can change the optical properties of the samples. Copolymers containing silver nanoparticles were synthesized.

### **METHODS OF SAMPLE MANUFACTURING AND ANALYSIS**

In this work, two-stage method of synthesis samples has been used: at first - hydrolytic polycondensation  $Ti(OPr^i)_4$  in organic monomer - hidroxyethyl methacrylate (HEMA) or mixture of HEMA - lactide (glycolide), and then by low-temperature radical polymerization. The components were mixed in different molar ratios. In the compositions was added dopant –  $AgNO_3$  for the formation nanoparticles. Mixture was poured into forms between the panes with a calibrated distance between them. The resulting composition was left to form a polymeric inorganic matrix. On completion of this process was judged visually by the loss of fluidity of the samples. The next stage was the polymerization for the formation of organic polymer at  $70^\circ C$  in an air thermostat.

#### *Investigation of physical and mechanical properties of hybrid models*

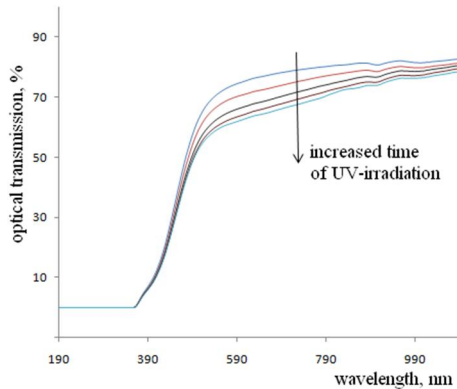
The resulting hybrid copolymers should have dimensional stability and withstand handling. The strength and ductility of the samples with different ratio of organic and inorganic components was investigated. Studies carried out on tensile testing machine ZWICK / Roell Z005.

#### *Investigation of changes in optical density of the hybrid composites under UV exposure and during relaxation*

The samples were irradiated with a mercury lamp of high and medium pressure DRT-400. The process of change in optical density due to the transition of  $Ti^{4+} \rightarrow Ti^{3+}$ , monitored on a spectrophotometer Shimadzu UV-1650PC. After the end of UV exposure, the samples were left at room temperature and monitored for changes in the relaxation spectra of light transmission.

### **RESULTS AND DISCUSSION**

The optical properties of hybrid organic-inorganic polymer composites with different initial ratio of organic (HEMA) and inorganic (-TiO<sub>2</sub>-) copolymer have been studied. All the composites were characterized by optical transparency, the amount of light transmission depending on the ratio of the components reaches  $\sim 85\%$  at  $\lambda = 700$  nm. Hybrid polymers are transparent in the visible spectrum and fully absorb light in the UV region (*fig.1.*).



**Fig.1** – Change spectra of transmittance for the hybrid copolymer with UV irradiation for 3 hours

For the performance of the copolymers is important to obtain samples with various and regulate plasticity. However, the samples consisting of poly-TiO<sub>2</sub> and poly-MEG are very fragile. A third component - glycolide or lactide in different ratios was added in two-component mixture to increase the flexibility of the samples. Physical-mechanical properties of composites based on a three-component mixture were investigated (*Table 1*).

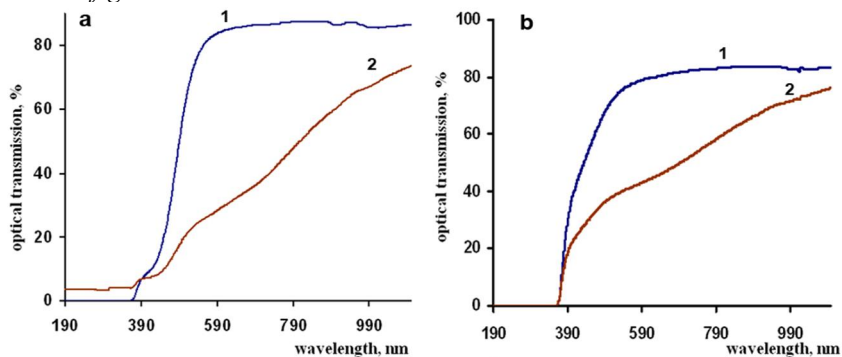
*Table 1.* Physical and mechanical properties of hybrids containing glycolide and lactide

[Ti(OPr <sup>i</sup> ) <sub>4</sub> ]/[MEG]/[x], mol	[x] = glycolide		[x] = lactide	
	stiffening σ <sub>cp</sub> , MPa	deformation, ε <sub>cp</sub> , %	stiffening σ <sub>cp</sub> , MPa	deformation ε <sub>cp</sub> , %
1:4:0	3,92	2,18	3,92	2,18
1:4:1	5,23	5,51	-	-
1:4:2	4,14	45,80	3,43	51,8
1:4:3	1,40	113,72	1,18	73,1
1:4:4	1,29	136,47	0,79	103

The data in *Table 1* shows that the intake of a third component - glycolide – lead to reduction of the damaging voltage of the system from 5.23 MPa to 1.29 MPa and an increasing the deformation of the samples up to 136%. It can be concluded that the links are internal plasticizer glycolide, which are built into the structure of the copolymer and decrease the intensity of interaction between macromolecules, facilitating the mobility of their segments.

It should be noted that the transparence of samples is stay in the order of 87 % with modification of physical- mechanical properties.

The spectra of transmittance for ternary organic-inorganic copolymers containing units of TiO<sub>2</sub>, HEMA and glycolide; TiO<sub>2</sub>, HEMA and lactide are shown in *fig.2*.



**Fig. 2** – The absorption spectra of the hybrid copolymer composition (a) [Ti (OPr)<sub>4</sub>] / [HEMA] / [glycolide] = 1:4:4 mole; (b) [Ti (OPr)<sub>4</sub>] / [HEMA] / [lactide] = 1:4:4 mole under UV irradiation of the sample: curve 1 - 0 min UV curve 2 - 3 hours of UV

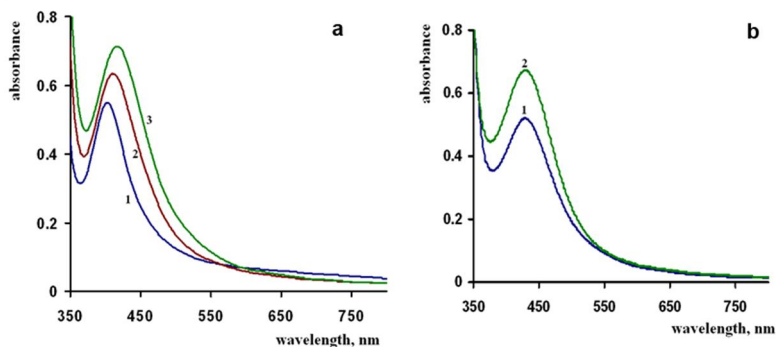
*Figure 2* shows that in the copolymers, which consist of three components, remains reversible electron transfer  $\text{Ti}^{4+} + e \rightleftharpoons \text{Ti}^{3+}$ , characteristic for gels of poly-TiO<sub>2</sub>. The appearance of broad absorption bands in the 400-800 nm was observed during UV irradiation of copolymers. Optical transmission of the sample of [Ti (OPr)<sub>4</sub>]/[HEMA]/[glycolide] = 1:4:4 mol after 3 hours of UV radiation varies from 82% to 37% at a wavelength of 700 nm, in copolymers containing lactide the light transmission is changed from 87 to 50%.

Thus, the totality of physical-mechanical and optical studies makes it possible to develop technology for organic-inorganic composite materials with controlled physical and mechanical characteristics while retaining the unique photochromic properties poly-TiO<sub>2</sub>.

Of particular interest to create optical data storage devices are composite materials based on organic-inorganic copolymers containing metal nanoparticles. Additional introduction of metal nanoparticles can change the optical properties of the samples. Copolymers were synthesized on the basis of HEMA and Ti (OPr)<sub>4</sub> containing the precursor – AgNO<sub>3</sub> - in different proportions (1-3%) by weight of Ti(OPr)<sub>4</sub>. Samples received a two-stage method which was described earlier.

Reducing of Ag<sup>+</sup> by UV irradiation is observed in samples. There is the emergence and growth of the absorption maximum in the region of 380-420 nm, corresponding about plasmon absorption of silver nanoparticles (*Fig. 3*).

From *fig. 3a* we can see that increasing the concentration of AgNO<sub>3</sub> shifts the absorption band at longer wavelengths, from 403 to 416 nm. That is give evidence about the formation of larger particles.



**Fig. 3** – The absorption spectra of hybrid composites, containing  $\text{AgNO}_3$ : a – composition  $[\text{HEMA}]/[\text{Ti}(\text{OPr})_4] = 4$ , with different concentrations of  $\text{AgNO}_3$  (% by weight of  $\text{Ti}(\text{OPr})_4$ ) after UV irradiation for 120 min, the curve 1 - 1% ( $\lambda_{\text{max}} = 403$  nm), 2 - 2% ( $\lambda_{\text{max}} = 411$  nm), 3 - 3% ( $\lambda_{\text{max}} = 416$  nm); b – Hybrid composites with initial concentration of  $\text{AgNO}_3$  3% (by weight of  $\text{Ti}(\text{OPr})_4$ ) and different molar ratios in the initial reaction mixture  $[\text{HEMA}]/[\text{Ti}(\text{OPr})_4]$ : curve 1 - 4 ( $\lambda_{\text{max}} = 416$  nm) curve 2 - 8 ( $\lambda_{\text{max}} = 429$  nm)

Changes in the ratio of organic and inorganic components at a fixed dopant concentration also leads to changes in the size of formed nanoparticles. The maximum absorption band shifts from 416 to 429 nm with doubling content of organic component (*fig. 3b*). Such an increase in the size of the particles may be due to the fact that the structure of the copolymer with low content of inorganic component is less cross-linked. This is facilitating the growth process of nanoparticles to larger sizes.

It should be noted that the hybrid copolymers containing silver nitrate, is far less effective darkening associated with the electronic transition  $\text{Ti}^{4+} + e \leftrightarrow \text{Ti}^{3+}$ . This may indicate that the  $\rightarrow$ priority process in these samples is the reduction of silver ions:  $\text{Ag}^+ + e \rightarrow \text{Ag}^0$ .

### CONCLUSIONS

The optically transparent hybrid organic-inorganic copolymers has been prepared. This copolymers retain unique photochromic optical properties of gels of poly- $\text{TiO}_2$ . By the UV light excitation observed reversible darkening of the samples due to the transition  $\text{Ti}^{4+} \leftrightarrow \text{Ti}^{3+}$  had observed. The speed of transition depends on the composition of components.

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