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PREPARATION OF POLYMER MATERIALS CONTAINING TITANIUM COMPOUNDS

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Abstract

Titanium compounds in view of their physicochemical properties constitute interesting materials applied in chemical synthesis. They are used for preparation of antifungal agents as well as for production of self-cleaning coatings. Moreover, mentioned inorganic compounds are characterized by a capability of neutralizing of unpleasant odor. Those all characteristics make these substances useful in many fields. In the framework of presented research series of polymer materials modified with titanium and titanium oxide have been obtained by means of photopolymerization. In the further step, studies on such synthesized materials have been conducted with particular emphasis on determining a mechanical properties and wettability. Hardness of prepared polymers have been tested by means of Shore durometer. Based on the research it can be concluded that addition of titanium compounds to the polymer matrix resulted in the improvement of mechanical properties as well as in an increase of hydrophobicity. It is worth mentioning that it is possible to manipulate properties of the obtained compositions by the introduction of an appropriate amount of additive into their matrices.

Keywords: Titanium, polymers, antifungal properties, wettability, mechanical properties

INTRODUCTION

Chitosan binders (or chitosan hydrogels) are flexible polymer materials of natural origin that are widely used in different areas of industry. Their main feature is the high water absorption, which results in the great interest in these substances on the polymer market. On the chemical market they have been around for a long time, so they are the subject of many studies. In the present work special attention is paid on their application in foundry and medicine. Furthermore, their biocompatibility with human tissue, biocompatibility, capability of controlled drug release as well as to the great sorption capacity make the mentioned materials applicable also as binders in medicine (e.g. in tissue engineering). Based on the many studies it was stated that titanium and titanium dioxide affect the improvement of bactericidal properties as well as have a positive impact on the adhesion of the binder to bone tissue. An additional advantage in both cases of hydrogels' applications is the fact that binders on the basis of chitosan are biodegradable, therefore they do not affect the environment. One of the main purposes of searching new solutions in the foundry industry is to get rid of unfavorable environmental molding molds. Main purpose of the research involves preparation of polymers modified with titanium compounds as well as characteristic of their properties such as swelling ability, behavior in simulated body fluid and impact of incubation in such fluid on the structure of the tested materials, wettability, surface morphology and hardness.

MATERIAL AND METHODS

Preparation of hydrogels materials was conducted by dissolving an adequate amount of chitosan and gelatine in 0.05% acetic acid solution in volume ratio of 3 and 2% respectively – that mixture was a base solution. Such prepared hydrogels were modified with an adequate amount of titanium or titaniuim dioxide. In order to crosslink the polymer materials crosslinking agent (diacrylate poly(ethylene glycol), Mw = 700) and photoinitiator (2-hydroxy-2-methylpropiophenone, Darocur 1173) were added to the previously prepared mixture and the whole was poured down on a Petri dish and treated with UV radiation (as its source lamp Medilux 436 HF was used). In **Table 1.** and **Table 2.** compositions of materials obtained are presented.

Prepared materials were subsequently subjected to the studies aiming at characterization of their poperties. Results of conducted studies as well as discussion are shown in the section below.

Table 1. Composition of polymers containing titanium dioxide.

Sample	Base solution, ml	Titanium dioxide, ml	Photoinitiator, ml	Crosslinking agent, ml
1	10	0.2	0.1	1.6
2	10	0.6	0.1	1.6
3	10	1.0	0.1	1.6
4	10	1.4	0.1	1.6

Table 2. Composition of polymers containing titanium.

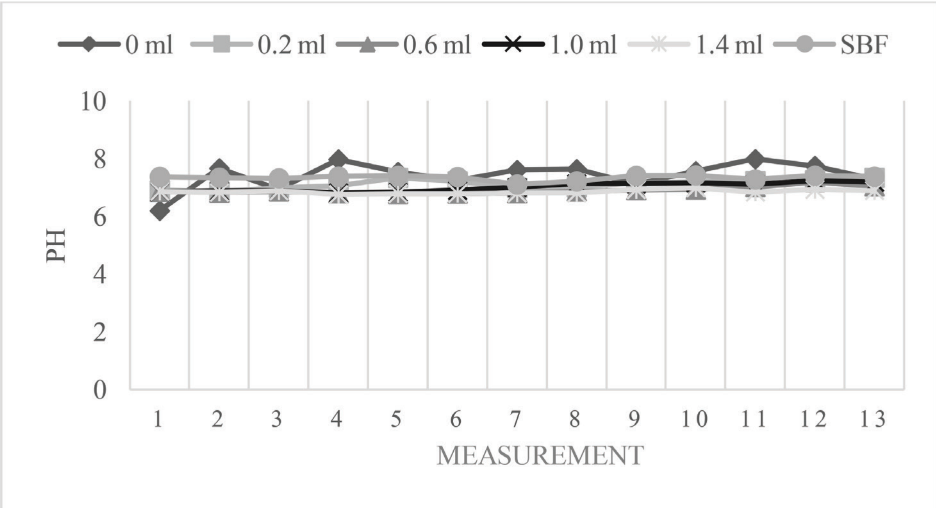
Próbka	Base solution, ml	Titanium, ml	Photoinitiator, ml	Crosslinking agent, ml
1’	10	0.2	0.1	1.6
2’	10	0.6	0.1	1.6
3’	10	1.0	0.1	1.6
4’	10	1.4	0.1	1.6

RESULTS AND DISCUSSION

Incubation studies

Research was carried out in order to determine a tendency of prepared chitosan binders to degradation in fluid which compositions are similar to those occuring in human body i.e. SBF *(Simulated Body Fluid)*. Study consisted in measurements of pH values of solutions containing tested materials for a period of 30 days. Results are shown below in **Figure 1**.

In case of polymers modified with titanium pH values of the examined solutions do not differ significantly from each other. On the basis of such observation it can be stated that binders containing both titanium and titanium dioxide are characterized by good buffering properties. Any rapid changes in pH values of SBF solution (without immersed sample, refference solution) as well as solutions containing samples without additives are not observed. pH results of all tested solutions maintained at a similar level during the whole incubation period. Even at the end of the study, measured pH values did not diverge widely from the initial values. Based on this phenomenon it can be concluded that prepared materials did not degrade in the tested environment. It is also important that introduction of titanium compounds did not change a behavior of the tested materials in SBF.



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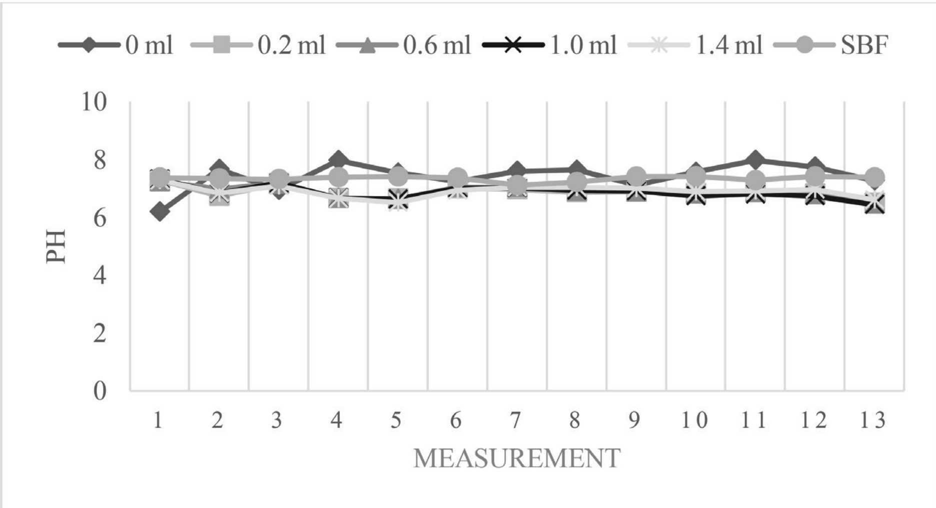

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Figure 1. Changes of pH values of SBF solutions containing polymers containing: a) titanium, b) titanium dioxide.

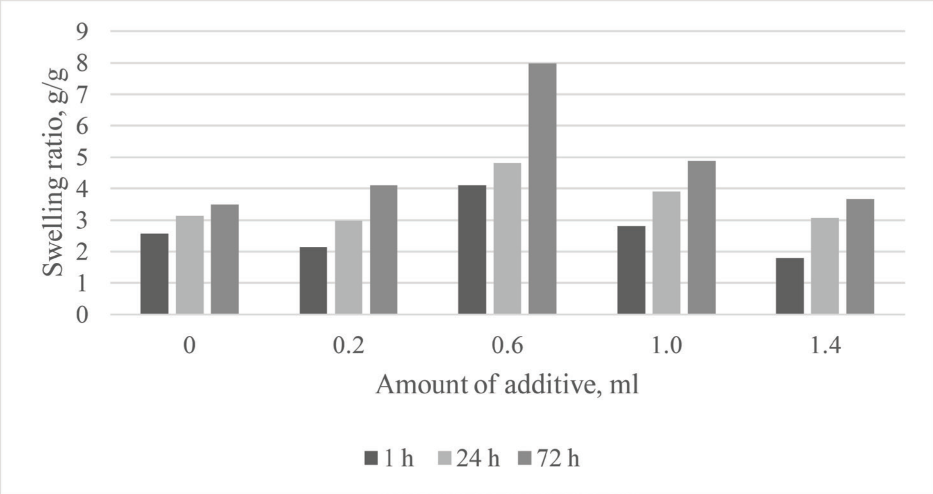
Study of sorption capacity

Properly prepared material was subjected to the process of sorption in distilled water and in SBF in order to define its swelling ability. Swelling ratio Q was determined using the following formula (1):

$$Q = \frac{m_1 - m_0}{m_0} \quad (1)$$

where:
m_0 – weight of a dry sample, m_1 – weight of a swollen sample.

Measurements of samples' weigth were carriet out after 1, 24 and 72 h respectively. Results of conducted studies are presented in **Figure 2.** and **Figure 3.**



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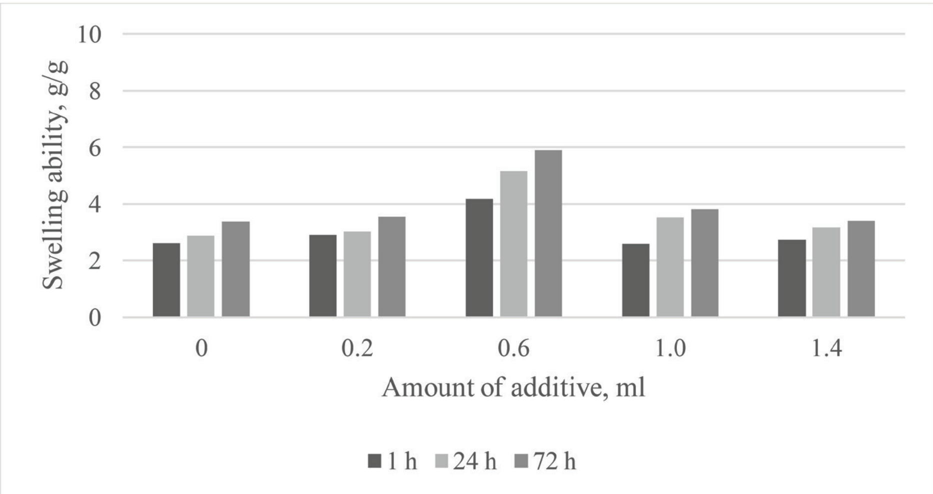

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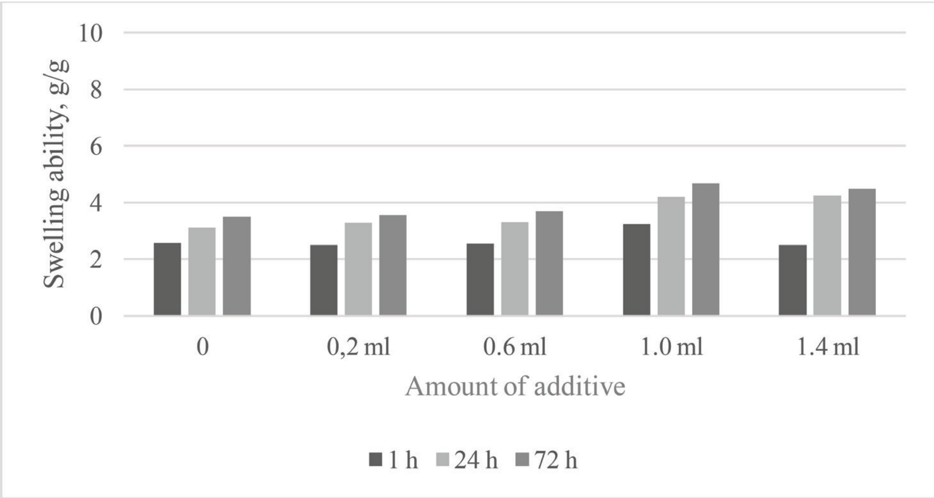
Figure 2. Swelling abilities of tested materials containing titanium in:
a) SBF, b) distilled water.



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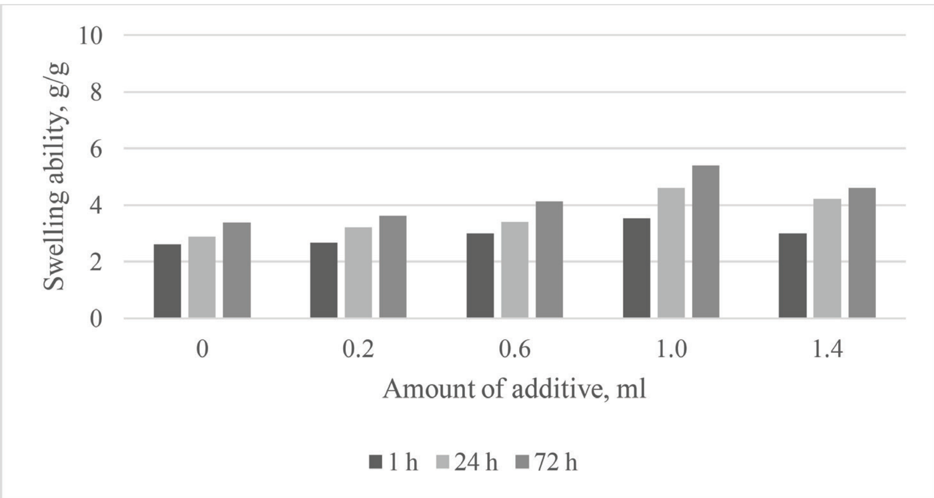


b)

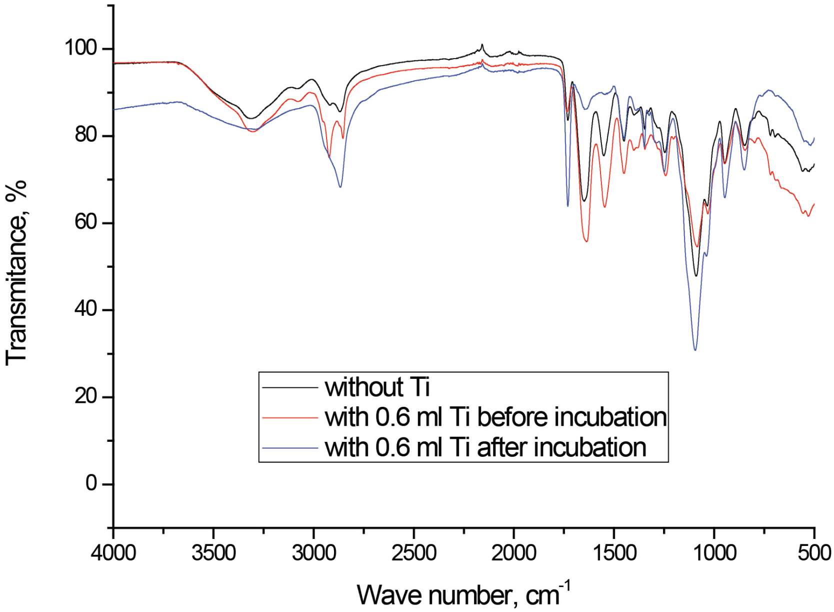
Figure 3. Swelling abilities of tested materials containing titanium dioxide in: a) SBF, b) distilled water.

Based on the conducted research it is possible to conclude that chitosan binders modified with titanium exhibit sorption properties. In case of majority of examined samples value of swelling ratio defining the swelling ability of the binder increased in the course of the study. This proves maintaining good sorption capacity by prepared materials in the course of the entire study, i.e. for 72 h. The same conclusions can be drawn for binders containing titanium dioxide. However, it should be mentioned that the amount of the additive in the interior of tested binder has a considerable impact on its swelling ability. Despite the fact that samples in each tested solution retain the same upward trend in terms of sorption capacity the greatest swelling ratio is observed for a binder containing 0.6 ml titanium. After the introduction of a larger quantity of the mentioned additive imbalance of the tested material is observed and its sorption capacity decreases. Perhaps the addition of a greater amount of titanium in the form of suspension into the tested material results in the deposition of the additive in the spaces between the polymer chains. This in turn reduces the amount of the space available for the absorbed fluid, so the sorption capacity of the material is limited. What is also important, the swelling ratios calculated for all samples regardless of the type of introduced additive are greatest in distilled water. This is due to the fact that distilled water does not contain ions which could increase the degree of crosslinking of the tested binder. Similarly, in the SBF solution with the highest ion content, the swelling is clearly less intense. The introduction of titanium has a better impact on sorption capacity than the addition of titanium dioxide. The swelling ratio values for samples doped with titanium are higher.

Fourier transform infrared spectroscopy (FT-IR)

Samples with the lowest content of the additive and those characterized by the best properties reported on the basis of the previously conducted research were subjected to spectroscopic analysis. Its purpose was to identify the functional groups present in the obtained material as well as to determine the effect of immersion of binders in selected liquids on their structure. Samples were tested by means of a Nicolet iS5 spectrometer equipped with an ATR iD7 overlay. The obtained spectra are shown in **Figure 4.**

Based on the obtained FT-IR spectra it can be stated that the introduction of TiO_2 and Ti into the hydrogel matrix did not cause any changes in the structure of the tested material as indicated by the absence of new peaks on the spectrum deriving from the modified hydrogel in comparison to that one from unmodified sample. Furthermore, in case of hydrogels containing titanium any significant degradation caused by incubation was not observed. Any noticeable changes in intensity for most of observed spectra were not noticed. In the case of materials with TiO_2, a marked degradation of the tested samples occurred as evidenced by the fact that almost complete disappearance of the bands from the functional groups.



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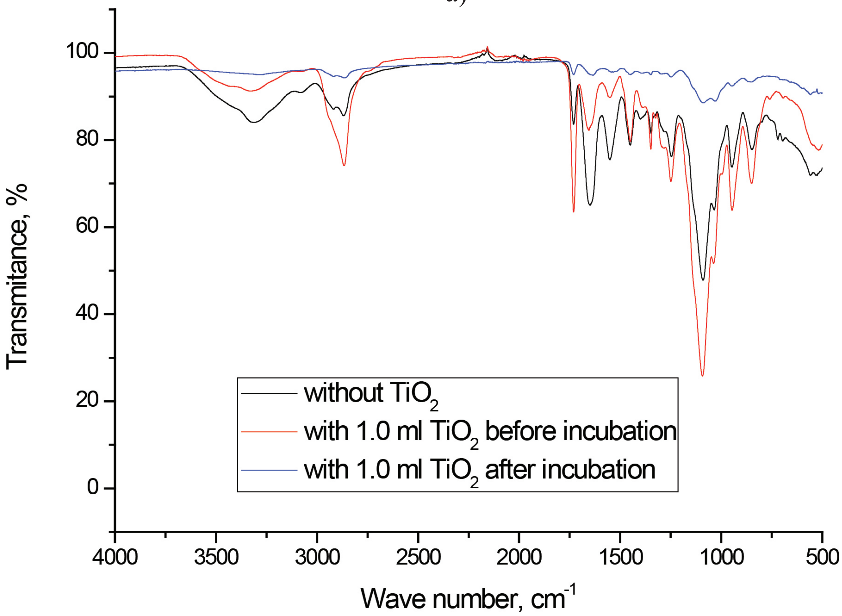
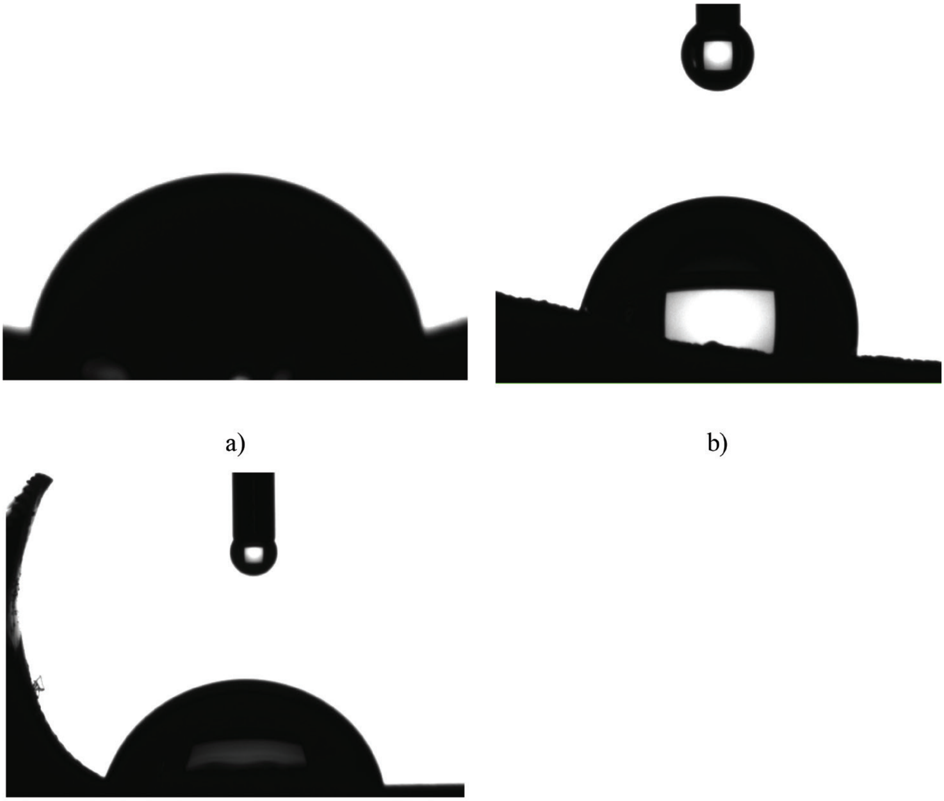


b)

Figure 4. Impact of incubation on chemical structure of hydrogels modified with: a) Ti and b) TiO_2 determined on the basis of spectroscopic analysis.

Studies on samples' wettability

In order to determine the wettability of the material a drop of distilled water was applied on material's sample. The wetting angle of the applied drop to the sample of the tested material was determined using the geometric method. Measurements were carried out at a temperature of 22°C by means of the following apparatus: Kruss DSA 100M. Obtained results are presented in **Figure 5.**



a) b)

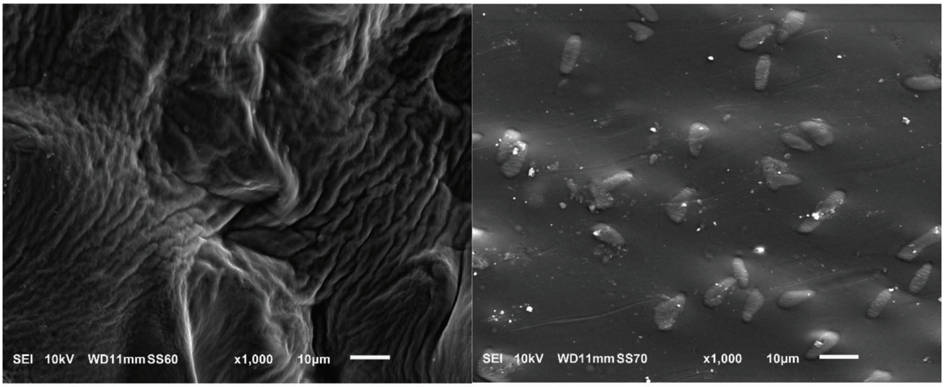
c)

Figure 5. Study of wettability of unmodified binder (a); modified with titanium (b) and modified with titanium dioxide (c).

On the basis of presented results it can be said that prepared binders are characterized by hydrophilicity (all angles are less than 90º). However, introduction of additives such as titanium or titanium dioxide into the hydrogel matrix resulted in reducing the hydrophilicity of obtained chitosan based binders that is important in view of the future application of the tested materials.

Study of surface morphology using Scanning Electron Microscopy (SEM)

Resulted binders were subjected to the analysis of their surface by means of scanning electron microscope. Attained microphotographs provide information about the external topography of the tested sample as well as about the nature of internal structure including porosity. Microscope Helios NanoLab H50HP FEI was applied for the above-mentioned research. SEM images were recorded at an accelerating voltage of 5 kV. Microphotographs of the tested materials are shown in **Figure 6**.



a) b)

Figure 6. SEM images of unmodified hydrogel (a) and hydrogel containing titanium (b).

Based on **Figure 6 a)** it can be noticed that material without any additives is characterized by inhomogeneous and corrugated surface. Addition of titanium into material's interior clearly smoothes the surface of the tested binder. Probably an introduced titanium suspension fills the unevenness on the surface of the tested sample. **Figure 6 b)** shows the large amount of tabs on the surface of examined sample that may result from the presence of titanium in the resulting chitosan binder.

Study of hardness of prepared binders using Shore Durometer A

The study was carried out in order to better understand the mechanical properties of the obtained chitosan binders. The sample of the tested material was pressed against the base with a hardness meter. The intender in the form of a needle was pushed out by a spring and stabbed into the examined binder. Once the balance between the binder and the pressure was established, a suitable hardness value was read from the Shore scale. For each sample, the measurement was repeated 10 times and then the arithmetic mean was calculated from the obtained results. The study was performed on the following apparatus: INSIZE Shore A. The results are presented in **Table 3**.

Table 3. Results of analysis performed using Shore durometer.

Amount of additive	Measurement										Average value
	1	2	3	4	5	6	7	8	9	10	
0 ml	51	31	33	51	54	60	57	29	38	35	**43.9**
TiO_2											
0.2 ml	61	68	60	35	76	48	67	49	48	53	**56.5**
0.6 ml	62	48	46	44	29	51	41	30	38	43	**43.2**
1.0 ml	75	63	71	45	61	56	61	55	46	49	**58.2**
1.4 ml	66	53	73	51	58	71	67	60	59	53	**61.1**
Ti											
0.2 ml	65	69	71	74	72	54	71	49	54	63	**64.2**
0.6 ml	81	80	82	81	80	80	65	82	81	82	**79.4**
1.0 ml	64	68	68	41	54	64	67	68	63	64	**62.1**
1.4 ml	70	72	65	69	71	66	64	71	64	63	**67.5**

The smallest hardness was determined for the material without any additives. This sample was very soft. Introduction of titanium and titanium dioxide affects the hardness of the tested binders – improvement of the mechanical properties of the material. It is worth mentioning that hardness does not grow along with the growing amount of the additive. In case of binders containing titanium dioxide the highest hardness was observed for the material modified with 1.4 ml of this inorganic compound. Regarding the binders with titanium, the amount of this additive resulting in the best mechanical properties is 0.6 ml. That sample was characterized by the highest swelling ability as demonstrated in previous studies. Probably the introduction of titanium in an amount of more than 0.6 ml causes the imbalance in the system, and hence this such modified material is characterized by worse mechanical properties. Various amounts of titanium dioxide and titanium can be introduced into the chitosan based binders in order to obtain the material having specific mechanical properties. This is important in many areas with special emphasis on foundry, because the binder will be subjected to the concentrated forces. Adjusting the optimum content of additives will increase the material's resistance to deformation.

SUMMARY

Chitosan based binders modified with various amount of additives such as titanium and titanium dioxide were formed as a result of the photopolymerization process. The obtained hydrogels obtained were characterized by good buffering properties in simulated body fluids. Introduction of additives into the polymer matrix affects the sorption capacity of the obtained chitosan binders. With the increasing amount of the additive and passing time of immersion in selected solutions, the tested material retains its swelling ability. However, too much additive results in an imbalance in the system as well as deterioration in sorption capacity of the tested binders. By choosing the adequate amount of the additives, the desired sorption properties of the material can be obtained, depending on the intended use. Research has shown that titanium binders are characterized by a higher swelling ratio therefore they will work best as molding components in foundry. As a binder in bone engineering it is possible to use a binder that is characterized by a lower content of additive, because in this case the high sorption capacity of the fluid is not a significant aspect. In the mentioned area the mechanical properties of the material are more important. Based on Shore hardness tests it can be concluded that the additives have a positive effect on the mechanical properties of the binder. In this case, the addition of 0.6 ml of titanium dioxide suspension in molding and in bone engineering is the most favorable – the material exhibits the best mechanical properties. Introduction of the greater amount of this additive will cause a system imbalance and subsequently a decrease of material hardness. Based on the results of the wettability tests, it was found that the additives influence the increase of the hydrophobicity of the material. Considering the specifics of foundry and medicine, the best addition to the polymer matrix on the basis of the chitosan is titanium. The binders containing this additive are durable, do not degrade in simulated body fluids. Furthermore, these material are characterized by better sorption capacity and are better polymerized (leaving less unreacted – non-crosslinked components) compared to the binders modified with titanium dioxide.

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