



## Surface properties of nanozirconia modified by ionic polyacrylamide – Impact of polymer functional groups type



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### ABSTRACT

The effects of the type of functional groups of ionic polyacrylamide (PAM) and solution pH on the adsorption, electrokinetic and stability properties of aqueous nanozirconia suspension were examined. The spectrophotometry, potentiometric titration, doppler laser electrophoresis and turbidimetry were applied for this purpose. It was demonstrated that adsorption of anionic PAM (containing carboxyl groups) decreases with the pH rise, whereas in the case of cationic PAM (with quaternary amine groups) it increases. The greatest impact of ZrO<sub>2</sub> suspension stability is found for cationic PAM at pH 6, at which electrosteric stabilization mechanism is dominant.

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### 1. Introduction

Zirconium dioxide (ZrO<sub>2</sub>, zirconium(IV) oxide, zirconia) occurs naturally in the monoclinic form as a baddeleyite mineral. This ceramic material is polymorphic and at very high temperatures ZrO<sub>2</sub> exists in tetragonal (above 1170 °C) and regular – cubic (above 2370 °C) forms. The hydrothermal technique is widely applied for the synthesis of this solid [1]. Zirconia is characterized by many excellent properties, such as high resistance to chemicals and corrosion, high strength, excellent resistance to breakage, high density, high hardness and wear resistance, lack of magnetism, low thermal conductivity, electrical insulation, thermal expansion coefficient similar to iron and elasticity modulus comparable to steel. Additionally, the most important from the medical point of view is excellent biocompatibility of ZrO<sub>2</sub> with human tissue. For this reason zirconia ceramics is a medical material widely applied in prosthetic dentistry and implantology [2,3]. Zirconia is commercially available as a nano-sized solid. It is worth noting that nanotechnology provides numerous opportunities in diagnostics and treatment of various diseases in medicine.

On the other hand, macromolecular compounds are of great interest as regards solid surface properties modification. For example, polymer (especially natural) adsorption on the metal oxide surface plays an essential role in the implantation process – it prejudices about implant acceptance or rejection [4]. Advanced drug delivery systems also benefit from the excellent properties of polymers which allow the controlled drug release [5].

Taking the above into consideration, the main aim of the presented studies was determination of structure of ionic polyacrylamide (PAM) adsorption layer on the nanozirconia surface and its influence on the aqueous solid suspension stability. The applied zirconia was characterized by a nanoscale size (particle size below 100 nm). The obtained results can be helpful for the development of modern implant coatings for tissue regeneration and innovative drug delivery systems.

Polyacrylamide hydrogels (with dispersed water phase) are used in the compresses for the treatment of burns [6] and as a soft-tissue filler in the reconstruction processes in human body [7]. The hydroxyapatite-polyacrylamide nanocomposites was prepared and examined for possible application in bone implantology [8]. To stabilize the activity of cellulase and hemicellulase enzymes they were covered with polyacrylamide layers [9]. The antimicrobial activity of nanocomposites of silver/starch/polyacrylamide

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[10], as well as hybrid materials of polyacrylamide with gold [11] and silver [12] was proved.

## 2. Material and methods

Zirconium(IV) oxide (*Sigma-Aldrich*), used in the experiments as an adsorbent, has the average particle size smaller than 100 nm (Mastersizer 2000, *Malvern Instruments*). The zirconia specific surface area is 21.7 m<sup>2</sup>/g and the average size of pores is equal to 31 nm (BET method, ASAP 2405 analyzer, *Micromeritics*).

Ionic polyacrylamide – PAM samples (*Korona*) – its anionic and cationic forms, were applied as an adsorbate. The content of ionizable groups in the polymeric chains was equal to 50%. The anionic PAM (AN PAM) was characterized by the weight average molecular weight 15 500 kDa and pK<sub>a</sub> value 3.6, whereas cationic PAM (CT PAM) – by the molecular weight 7 000 kDa and pK<sub>b</sub> value 9.9 [13,14].

All measurements were made at 25 °C in the NaCl solution (1·10<sup>-2</sup> mol/dm<sup>3</sup>) which was used as the supporting electrolyte. The polymer concentration was 100 ppm.

The adsorbed amount of polymer was determined using the spectrophotometry method (UV–VIS spectrophotometer Carry 1000; *Varian*) from the difference between the PAM concentration in the solution before and after the adsorption process. For this purpose, the reaction of CT PAM with a saturated solution of bromine, sodium formate and starch (in the acetate buffer) was used (the solution was coloured blue, absorbance was measured at 610 nm) [15]. In the case of anionic polyacrylamide the reaction with hyamine was applied (solution turbidity was measured after 15 min at 500 nm) [16].

The potentiometric titrations of nanozirconia in the absence and presence of PAM were performed for the solid surface charge density and pH<sub>pzc</sub> (pzc-point of zero charge) values determination. The special program Titr\_v3 (author W. Janusz) was used for this purpose.

Zeta potentials of the zirconia particles in the presence and absence of polyacrylamide, enabling determination of pH<sub>iep</sub> (iep-isoelectric point), were measured using doppler laser electrophoresis and the Zetasizer Nano ZS with a universal dip cell and MPT-2 titrator (*Malvern Instruments*).

The stability measurements of the nanozirconia-PAM systems were made using Turbiscan Lab<sup>Expert</sup> with the cooling module TLab Cooler. The changes in the suspension stability were detected registering intensities of light passing through and backscattered by the examined suspension. Based on the backscattering data, the stability coefficients TSI (Turbiscan Stability Index) were calculated [17].

## 3. Results and discussion

As can be seen in Fig. 1 the adsorbed amounts of ionic PAM on the nanozirconia surface are strongly influenced by the solution pH. The greatest adsorption level is obtained under the conditions of electrostatic attraction between the PAM chains and solid surface and for the more coiled conformation of adsorbed macromolecules – i.e. at pH 3 for AN PAM and at pH 9 for CT PAM. Such coiled conformation is a result of the smallest dissociation of anionic PAM at pH 3 (dissociation degree  $\alpha = 20.1\%$ ) and cationic PAM at pH 9 ( $\alpha = 88.8\%$ ). At pH 6 and 9 dissociation of both ionic polymers exceeds 99%. Moreover, pH<sub>pzc</sub> and pH<sub>iep</sub> of zirconia particles without PAM are equal to 5.9 and 6.2, respectively (Fig. 2). Thus, the adsorption of anionic polyacrylamide is electrostatically favourable at pH values lower than 6 (at which the solid surface is positively charged). In turn, for cationic PAM such conditions occurs at pH values higher than 6 (negatively charged ZrO<sub>2</sub> surface).

Under unfavourable electrostatic conditions ionic polyacrylamide adsorption reaches the lowest level and undergoes only through hydrogen bridges formation.

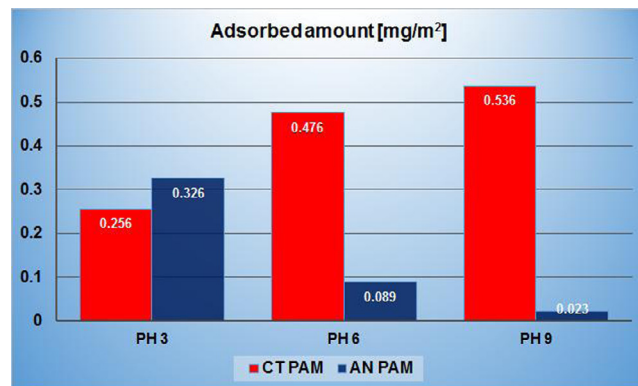


Fig. 1. Adsorbed amount of ionic polyacrylamide on the zirconia surface at pH values: 3, 6 and 9.

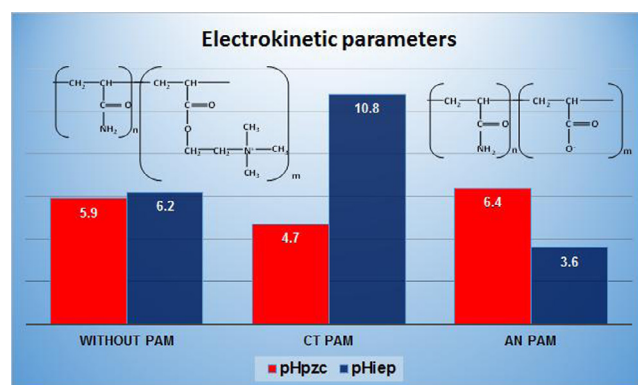


Fig. 2. Electrokinetic parameters characterized ZrO<sub>2</sub> suspensions without and in the presence of ionic PAM.

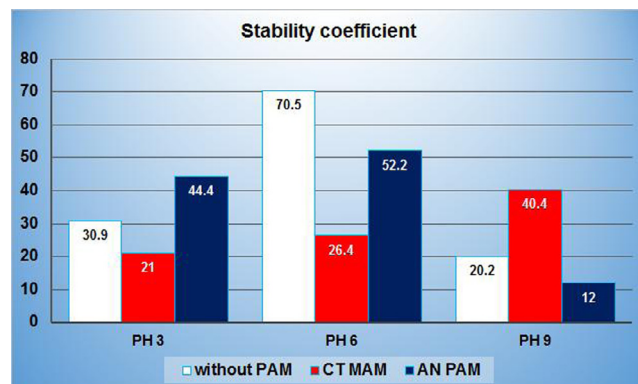


Fig. 3. Stability coefficients for ZrO<sub>2</sub> suspensions without and in the presence of ionic PAM; TSI = 0 for extremely stable systems and TSI = 100 for drastically unstable suspensions.

Comparing the adsorption of anionic and cationic polymers on the neutral surface of ZrO<sub>2</sub> at pH 6, in which both forms of PAM are practically totally dissociated, one can notice that the adsorbed amount of cationic polyacrylamide is fivefold higher than that of the anionic polymer (Fig. 1). This is evidence of the preferential binding of cationic PAM functional groups with the zirconia hydroxyl groups in comparison to the carboxyl groups of anionic PAM. The quaternary amine moieties in the CT PAM chains are significantly longer compared to those of the anionic groups (Fig. 2). Thus the steric reasons facilitate their interactions with active sites on the adsorbent surface (even partly covered with the polymer).

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