

# RHEOLOGY OF TITANIA BASED CERAMIC NANODISPERSIONS STABILIZED BY CATIONIC COMB COPOLYMERS

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## ABSTRACT:

Rheological studies of the ceramic based concentrated titania nanoparticle dispersions showed a clear correlation between molecular structure of the cationic polymers used as dispersants and the viscosity of the slurries. Dynamic viscosity of the electrostatically stabilized alkaline (pH 10.0) dispersions of the bare titania nanopowders with a solid loading of 15–25 wt.% was rather high (about 1 Pa·s) and the dispersions exhibited shear-thinning flow behavior. For electrostatic and steric stabilization of the concentrated ceramic nanodispersions of titania in alkaline conditions, the dispersions were treated with cationic comb copolymers differing in charge density and the length of PEO side chains. The dispersions treated by the cationic comb copolymers acted as the Newtonian fluids at low and medium shear rates ( $< 200 \text{ s}^{-1}$ ) and showed shear-thickening flow behavior at higher shear rates. Dynamic viscosity of the dispersions with a solid loading of 15–25 wt.% treated by the cationic comb copolymers was very low (2 to 30 mPa·s).

## KEY WORDS:

Titania, nanoparticle, dispersion, surfactant, stabilization, aqueous

## 1 INTRODUCTION

Titanium dioxide ( $\text{TiO}_2$ ) remains the most widely used white pigment because of its brightness and very high refractive index ( $n = 2.5 - 2.7$ ). It is effectively applied in powder form as a pigment providing whiteness and opacity to products such as paints [1], coatings, plastics, and inks [2]. Particles of titanium dioxide can be used for bioceramic applications [3] and for the synthesis of nanostructured ceramics [4] as UV absorbers, photocatalysts [5], and in antibacterial [6] and self-cleaning coatings [7]. In most of the above applications titania particles are used in the dispersed form. Titania nanoparticles due to a high surface area and a high Hamaker constant in water ( $A = 5.35 \times 10^{-20} \text{ J}$ ) [8] have a high tendency to agglomerate, thus, such dispersions are unstable and sediment rapidly. Special additives are known to substantially affect dispersion stability and rheology of the colloidal dispersions [9–14]. These additives adsorb on the surface of the particles and change inter-particle interactions. Effectiveness of the additives, depend on their molecular structure as the additives usually contain charged or bulky groups. Usually, stabilization of the colloidal dispersions is related to a control of elec-

trostatic and/or steric forces between the particles [14, 15]. Electrostatic stabilization is based on adsorption of ions or charged polymers on the surface of the particles which creates an electric double layer, whereas steric stabilization can be achieved by adsorption of the large molecules such as polymers forming steric barriers to prevent particles approaching too close.

For stabilization of the aqueous titania dispersions, low-molecular-weight additives such as maleic, fumaric [9], citric acids [16] have been investigated. However, high-molecular-weight additives such as poly(meth)acrylates [12, 17–20], poly(acrylamides) [21], and poly(ethylene imines) [15] show better stabilization effects due to stronger adsorption onto oppositely charged surfaces of the titania particles. Adsorption of a long-chain polymer usually involves the attraction of polymer segments to the surface, so that if the affinity of individual segments with the surface is weak as in the case of low-molecular-weight additives, the polymer chain as a whole can still be strongly attracted [15]. The best effect of stabilization was achieved using comb and brush-type polyelectrolytes [13, 14, 22–25], which have a dual stabilizing effect based on electrostatic interactions of the charged groups and steric

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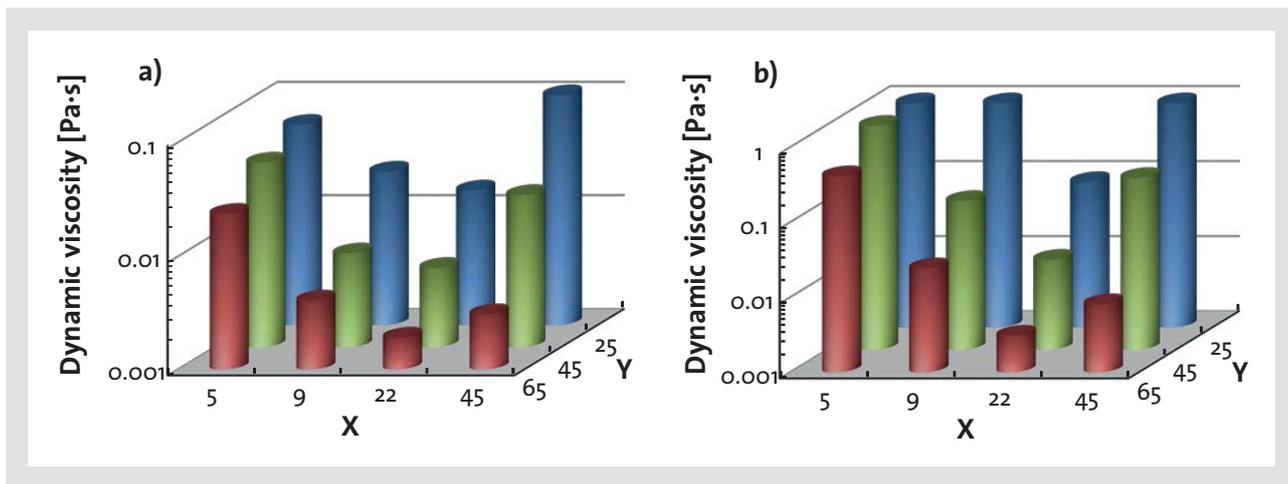


Figure 7: Rheological behavior of 15 wt.% (a) and 25 wt.% (b) titania nano-sized dispersions treated with the cationic comb copolymers  $p(\text{PEO}_x\text{MEMA:METAC})\text{-Y}$  differing in charge density (Y, mol% of METAC units) and the length of PEO side chains (x, number of the repeating units of ethylene oxide) at the constant shear rate of  $105 \text{ s}^{-1}$ . Concentration of the polymers is  $2 \text{ mg/m}^2$ .

bilization of the concentrated titania nanoparticle dispersions at alkaline (pH 10) conditions? High charge density is a prerequisite for strong adsorption of the copolymers on oppositely charged surface of titania and formation of stable adsorbed layers [27]. High charge density (65 mol% of the charged units) means that only one third of the repeating units of the copolymers contains PEO side chains. Possibly, such density of PEO chains is sufficient for creation of steric barriers preventing the nanoparticles approaching too close and agglomeration. In this approach, the comb copolymers with longer PEO side chains (45 repeating units of EO) should not behave worse and even increase steric barriers around the nanoparticles. An increase in viscosity of the dispersions treated by the cationic comb copolymers with the longest side chains could be explained by interpenetration of the chains forming barrier layers around the nanoparticles under applied shear stress. Relatively high viscosity of the concentrated titania dispersions treated by the cationic comb copolymers with short side chains ( $x = 5, 9$ ) is likely related to rather small steric barrier around the nanoparticles insufficient for achieving full steric stabilization.

#### 4 CONCLUSIONS

Dynamic viscosity of the ceramic based alkaline (pH 10.0) concentrated dispersions of the bare titania with the solid loading 15–25 wt. % was rather high, about  $1 \text{ Pa}\cdot\text{s}$ , and the dispersions exhibited shear-thinning flow behavior. For electrostatic and steric stabilization of the concentrated titania nanoparticle dispersions at alkaline conditions, the nanodispersions were treated with the cationic comb copolymers differing in charge density and the length of PEO side chains. The ceramic based alkaline (pH 10.0) concentrated titania nanoparticle dispersions treated by the cationic comb copolymers acted as Newtonian fluids at low and medium shear rates ( $< 200 \text{ s}^{-1}$ ), and showed shear-thickening

flow behavior at higher shear rates. Dynamic viscosity of the dispersions with the solid loading 15–25 wt.% treated by the cationic comb copolymers was very low at 2 to  $30 \text{ mPa}\cdot\text{s}$ . The minimal viscosity (2–3  $\text{mPa}\cdot\text{s}$ ) was characteristic for the dispersions treated by the cationic comb copolymers with high density of the charged groups (65 mol%) and medium length of PEO side chains (22 repeating units of ethylene oxide). Concentration of this cationic comb copolymer indispensable for the reduction of dynamic viscosity of the concentrated titania dispersions to the minimal values was about  $1 \text{ mg/m}^2$  ( $1.5 \mu\text{mol/m}^2$  of the charged groups on the surface). The length of PEO side chains with 22 repeating units is optimal because of sufficient steric barriers preventing the nanoparticles approaching too close and low interpenetration of the chains under applied shear stress.

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