ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1594–1595. © Pleiades Publishing, Ltd., 2013.
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# FROM MATERIALS OF ALL-RUSSIAN CONFERENCE “CHEMISTRY OF SURFACE AND NANOTECHNOLOGY”

# Modification of Submicron Barium Titanate Particles via Sol-Gel Synthesis of Interface Layers of $SiO_2$ for Fabrication of Polymer-Inorganic Composites with Improved Dielectric Properties

**T. V. Khamova[a], E. S. Kolovangina[b], S. V. Myakin[b], M. M. Sychov[b], and O. A. Shilova[a]**

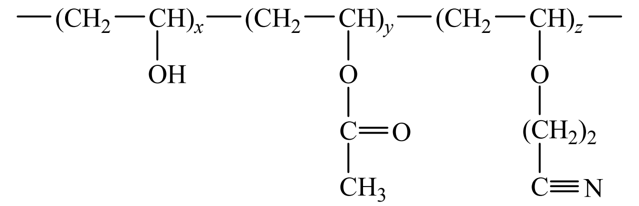
[a] *I.V. Grebenschikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia*
[b] *St. Petersburg State Technological Institute (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia*
*e-mail: sergey_mjakin@mail.ru*

Received November 22, 2012

**Abstract**—Modification of the surface of submicron $BaTiO_3$ particles by $SiO_2$ layer using sol-gel method has led to significant (>50%) increase in the dielectric permittivity and decrease in the dielectric losses of the composites prepared via introduction of $BaTiO_3$ into a matrix of poly(vinyl alcohol) cyanoethyl ester. The effect has been due to the formation of basic hydroxy groups (Brønsted centers) at the filler surface; these groups can interact with weakly acidic hydroxyl groups of poly(vinyl alcohol) cyanoethyl ester, thus improving the compatibility of the polymer matrix and the filler.

**DOI:** 10.1134/S1070363213080203

Development of dielectric polymer-inorganic composites with desired properties and homogeneous composition is an important technology task for fabrication of protective layers with improved characteristics used in the construction of capacitors, displays, electroluminescent light sources, and other modern electronic devices. In our previous works [1, 2]. we reported preparation and studies of composites based on poly(vinyl alcohol) cyanoethyl ester [having one of the highest dielectric permittivity (ε) values among polymer materials] and barium titanate. The composites composition was optimized; it was shown that the increase in ε was observed when the content of neutral and basic hydroxyl groups (p$K_a$ ~7–13) on the filler ($BaTiO_3$) surface increased; those groups improved the filler–polymer compatibility due to interactions with weakly acidic hydroxyl groups of poly(vinyl alcohol) cyanoethyl ester. Additionally, the composite dielectric permittivity was increased with the decrease in the content of the acidic hydroxy groups (p$K_a$ 2–5) at the filler surface, as they enhanced the interparticle interaction. Below the structure of poly(vinyl alcohol) cyanoethyl ester is shown.



$$-(CH_2-\underset{OH}{CH})_x-(CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH})_y-(CH_2-\underset{\substack{|\\O\\|\\(CH_2)_2\\|\\C\equiv N}}{CH})_z-$$

This work is an extension of the above-cited studies. Here, we modified $BaTiO_3$ (HPBT-1B, Fuji Titanium, Japan, particle size 300–400 nm, permittivity ε ≈ 4400) surface via the following procedures:

(1) hydration (immersion in water for 1 day at room temperature); or

(2) sol-gel process ($BaTiO_3$ treatment in silica sol).

For the latter procedure, $SiO_2$ sol was prepared via tetraethoxysilane hydrolysis in the acidic water-alcohol mixture:$Si(OEt)_4:EtOH:H_2O:HNO_3$ = 1:1.6:45:0.001

Properties of the studied fillers and composites

| Filler ($BaTiO_3$) | $S_{sp}$, $m^2 g^{-1}$ | Content of different centers at $BaTiO_3$, surface μmol $g^{-1}$ | | Dielectric properties of composites | |
|---|---|---|---|---|---|
| | | acidic OH gropus (p$K_a$ 2–4.5) | neutral and basic OH groups (p$K_a$ 7.3 and 12.8) | ε | tan δ |
| Original (non-modified) | 2.1 | 5.2 | 7.2 | 125.8 | 0.36 |
| Hydrated | 1.7 | 8.9 | 2.5 | 68.4 | 0.93 |
| Modified with $SiO_2$ layer | 188.0 | 5.0 | 9.4 | 242.3 | 0.22 |

(molar). The barium titanate particles were added to the silica sol (1:1) and stirred with magnetic stirrer at room temperature so that a homogeneous mixture was obtained. Thus, homogeneous gel was obtained within 30 min; it was dried at 100°C during 5 h.

Thus prepared modified powders were annealed at 700°C during 1 h to remove the unreacted components.

Functional composition of the prepared samples surface was studied by means of acid-base indicators adsorption, described in details in [3]. The specific surface of the original and modified $BaTiO_3$ samples was determined by thermal nitrogen desorption, using the SORBI®N.4.1 instrument, and calculated according the BET equation.

As described in detail in [2], the modified $BaTiO_3$ samples were dispersed in the solution of poly(vinyl alcohol) cyanoethyl ester (ε ≈ 19, AO Plastpolimer, St. Petersburg) (30 wt %). Then, the obtained composites (40 wt % of the filler) were deposited onto conductive supports as 60–100 μm layers, and their capacity (used to subsequently calculate ε values) and the loss factor tan δ were measured at the frequency of 1 kHz.

The results summarized in the table show that hydration of $BaTiO_3$ surface led to significant deterioration of the composites properties (approximately two-fold decrease in ε and 2.5-fold increase in tan δ), due to loss of neutral and basic hydroxy groups and growth in the content of acidic hydroxy groups on the filler surface as well as due to decreased specific surface. Seemingly, upon hydration the loose surface layer of barium carbonate was leached, and the weakly acidic ≡Ti–OH groups were formed. On the contrary, filler surface modification with $SiO_2$ layer led to approxi-mately 2-fold increase in the permittivity and 1.5-fold decrease in the loss factor. The achieved enhancement of dielectric properties was determined by the increase in the content of neutral and basic hydroxyl groups on the filler surface in combination with a drastic increase the filler specific surface the formation of the interface layer with a highly developed surface and the desired functional composition providing the improvement of the polymer–filler compatibility.

To conclude, we demonstrated an approach to obtaining polymer-inorganic composites with significantly improved dielectric characteristics via modification of composition and structure of the ferroelectric filler surface.

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