New sorbents for electrochromatography based on polymer-inorganic dielectric composites

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Abstract. Oligomeric diisocyanate based coatings with different contents of barium titanate (BaTiO₃) submicron sized particles as a ferroelectric filler are synthesized on poly(dimethylsiloxane) (PDMS) supports. The study of thus obtained coatings using confocal scanning electron microscopy allowed the characterization of their morphology and features of BaTiO₃ particles distribution in the polymer binder, including the determination of threshold filler contents corresponding to the formation of an infinite cluster, matrix-island and chain-like structures as well as the percolation. Dielectric permittivity and dielectric losses of the composites are measured and studied depending on BaTiO₃ filler content and relating structural features.

1. Introduction

One of the most promising application areas of nanomaterials is analytical chemistry, including the development of chemical and biochemical sensors [1], study of bio-transformations [2], development of polymer sorbents comprising nanoparticles and nanocomposites [3], etc. In particular, composite sorbents based on stationary phases with distributed nanoparticles are advantageous compared with conventional sorbents in respect of enhanced stability in extended pH range, highly developed surface and simplicity of modification providing a wide range adjustment of the surface chemical composition. In electrochromatography, a stationary phase provides a selective separation of analytes and adjustment of electroosmotic flow rate. A promising class of materials for obtaining electrochromatographic sorbents are polymer based composites with inorganic fillers such as metal nanoparticles or metallized nanoparticles (MNP) with “ferroelectric core – metal-containing shell” structure possessing electromagnetic (ferromagnetic) properties. Presently, the application of MNPs in capillary electrophromatography involves the use of hollow [3, 4] and monolithic [4, 5] capillary columns for stationary phase surface modification or introduction into polymer binder. The increasing interest to sorbents involving dielectric nanostructures relates to the possibility for introducing the dielectric permittivity of the sorbent as a new essential factor in the separation process affecting the electromigration performances and separation of analytes. This approach provides the adjustment of such characteristics of the sorbents used in capillary columns as polarity, charge, ionization degree, adsorption activity, hydrophilic-hydrophobic properties, etc. However, the difficulty of obtaining sorbents with uniform MNPs distribution and lack of theoretical simulation describing the effect of nanoparticles on electrokinetic processes in the sorbent complicate a detailed consideration of physical properties proceeding in a column or microfluidic chip in the course of electrophoretic separation, e.g.
during the change of permittivity in the near-wall layer. In a series of recent theoretical studies the effect of MNPs upon mass transfer rate in hollow capillary columns stimulated by combined electroosmotic and electrophoretic flow was modelled [6], heat power and \( \zeta \)-potential values in MNP-containing capillary columns were estimated [7] and the effect of MNPs upon analyte peak parameters including the residence time and FWHM were assessed [8]. The present study is aimed at experimental verification of the obtained modelling data and analysis of the effect of ferroelectric filler content in the synthesized composites upon the performances of coatings prepared therefrom.

2. Experimental
Poly(dimethylsiloxane) (PDMS) Sylgard-184 (Dow Corning) plates with the size 10x10 mm and thickness 4 mm were used as supports. These supports were covered with layers of composites based on oligomeric diisocyanate Crosslinker CX-100 (Cytec,USA, molecular weight \( M_n\approx1500 \), content of isocyanate groups 5.6%) with preliminarily dispersed submicron (500±20 nm) BaTiO\(_3\) particles (US Research Nanomaterials, Inc. Houston, TX, USA) in the concentration 5-50 %vol. relating to diisocyanate in the reaction mixture. The composite layers were deposited through a jet followed by drying at 50°C for 60 min [9].

The morphology of thus obtained layers was characterized by laser confocal scanning electron microscopy using Leica TCS SP5 microscope (Leica Microsystems). The filler distribution density was calculated using a textural segmentation method (random field model) [10].

Upon drying, composite layers of 0.2-0.25 \( \mu \)m thickness were obtained, followed by the deposition of electrodes of silver based conducting glue onto their surface to measure the electric properties.

The capacity (C) and dielectric loss tangent (tg\( \delta \)) of the prepared samples were measured using immittance meter E7-20 (MNIPI, Minsk, Belarus) at the frequency 1 kHz. The dielectric permittivity was calculated as

\[
\varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot S}
\]

where \( C \) is the measured capacity, \( d \) and \( S \) are the composite layer thickness and surface area, respectively, \( \varepsilon_0=8.85 \times 10^{-12} \) F/m – dielectric constant. The relative errors of \( \varepsilon \) and tg\( \delta \) determination averaged for 3-5 electrodes at each sample was below 15 and 10%, respectively.

3. Results and discussion
Confocal microscopy images of the obtained composites with barium titanate content 5, 15, 25, 35 and 50 %vol. are shown in Figures 1a-e. The images for other studied samples are similar in respect of the trends described below.

Computer processing of the considered images allowed us to reveal the following features and trends of BaTiO\(_3\) particles distribution in the studied composites:
- BaTiO\(_3\) incorporation in the content of 5-10 %vol. does not provide the formation of an infinite cluster, only resulting in the increase of the filler local density (Figure 1a);
- the increase of BaTiO\(_3\) content to 15 %vol. results in the formation of a single infinity cluster with prominent chain-like elements of local percolation (Figure 1b), while at further increase to 25 %vol. BaTiO\(_3\) a matrix-chain structure with the first fragments of “island-like” structure is observed (Figure 1c);
- at BaTiO\(_3\) content about 35 %vol. the local density of the filler distribution grows to form “island” or “island-chain” near-percolation structures (Figure 1d);
- the increase of BaTiO\(_3\) content to 50 %vol. and higher leads to the filler particles aggregation resulting in the formation of large associates and drastic deterioration of the composite uniformity (Figure 1e).
BaTiO$_3$ distribution density analysis by textural fragmentation with splitting of each studied image by 62.5x62.5 µm square fragments and counting the corresponding numbers of the filler particles revealed that the number of particles in these fragments for the samples with BaTiO$_3$ content 15, 25 and 35 %vol. is $35 \pm 2$, $77 \pm 5$ and $128 \pm 7$, respectively with the confidence level 0.95.

The results of electric properties characterization summarized in Table 1 and Figure 2 indicate that permittivity and dielectric loss tangent changes with BaTiO$_3$ content in the filler change feature with mutually opposite oscillating trends in the entire range of the filler contents with a prominent minimum of $k$ and maximum of $\tan \delta$ at BaTiO$_3$ content 30 %vol.

**Table 1.** Dielectric properties of the composites with different BaTiO$_3$ content

| BaTiO$_3$ content, %vol. | $k$   | $\tan \delta$ |
|--------------------------|-------|---------------|
| 20                       | 1.75  | 0.006         |
| 25                       | 1.74  | 0.011         |
| 30                       | 0.93  | 0.019         |
| 35                       | 1.38  | 0.009         |
| 40                       | 1.4   | 0.007         |
| 45                       | 1.35  | 0.01          |
| 50                       | 1.16  | 0.012         |
The observed extreme performances for the composite with 30 \% vol. BaTiO$_3$ content can be determined by the aforementioned disordering of chain-like structure due to the filler particles aggregation into small associates resulting in a significant decrease of local percolation. It should be mentioned that percolation is a necessary condition for the increase of $k$ and reduction of $\text{tg}\delta$ values for such composites since their structure id similar to capacitors comprising consecutively connected layers of different materials featuring with an inverse correlation of the overall capacity and permittivity with the corresponding values of the components. Similar non-linear dependencies of dielectric performances upon barium titanate modification conditions responsible for the possibility of percolation were earlier observed in the composites based on other polymer binders with the same filler [11-13]. In this case, BaTiO$_3$ concentration 35 \% vol. is a threshold level corresponding to the formation of the matrix and chain-like structure in the infinite cluster with the transition to the total percolation in the system responsible for the observed permittivity growth. The further increase of BaTiO$_3$ content to 45-50 \% vol. leads to the opposite trend due to the aggregation of the filler particles into large associates.

4. Conclusion
The performed studies allowed us to suggest the compositions and preparation conditions for obtaining polymer based composite coatings with BaTiO$_3$ filler possessing physicochemical and structural performances required for the formation of model stationary phases. The concentrations of BaTiO$_3$ filler in poly(disocyanate) binder corresponding to reproducible formation of the composites with uniformly distributed filler providing a single infinite cluster (15 \%vol.), transition to chain-like structure and percolated matrix-chain structure (35 \%vol.), as well as massive aggregation of the filler particles (about 50 \%vol.) are determined. The observed trends in the change of the studied composites structure are in agreement with the revealed nonlinear behavior of their dielectric performances, featuring with a prominent minimum of permittivity and maximum of dielectric loss at BaTiO$_3$ content 30 \%vol. corresponding to the filler aggregation with the formation of “island-like” structure, followed by a marked growth of permittivity and reduction of dielectric loss at BaTiO$_3$ concentration increase to 35 \%vol. corresponding to the onset of percolation. The variation of barium titanate content in oligomeric disocyanate binder affords the adjustment of permittivity for these composites in the range of about 1...2 and decrease of the dielectric loss tangent to the level below 0.01. In couple with the data of earlier performed modelling of stationary phases comprising polymer layers with MNPs, the presented results provide a solid basis for the development of advanced coatings for analytical purposes.
allow us to conclude that the addition of structured MNPs to sorbents affords the adjustment of their dielectric permittivity, that in turn can provide a tool to control the electromigration parameters of analytes.

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