Methodology for selection of charging agents for electrophoretic deposition of ceramic particles

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The zeta potential of particles is a key factor in the electrophoretic deposition process. It plays a role in the stabilization of the suspension by determining the intensity of repulsive interactions as well as in determining the direction and velocity of particle migration.

The zeta potential can be controlled by addition of charging agents such as acids, bases, and specifically adsorbed ions or polyelectrolytes, to the suspension. Thus there exist a variety of additives that affect the charge magnitude and its polarity. These additives act by different mechanisms.

The main criteria for the selection of a charging agent are the preferred polarity and deposition rate of the particles. While the deposition rate is directly dependent on the zeta potential, which is determined by the charging additive, the influence of such an additive is exerted also by its effect on the ionic conductivity of the suspension. The latter determines the potential drop in the bulk of the suspension, which constitutes the driving force for the transfer of the particles to the electrodes.

The present work will describe the methodology developed at Cerel for the selection of a charging agent based on its effect on the zeta potential/pH curve, on the isoelectric point and on the ionic conductivity of the suspension.

1. Introduction

The importance of electrophoretic deposition (EPD) rose in the last decade, because it allows products with complex geometries, and films of variable thickness to be processed in a low cost and simple setup. This advantage has made EPD more economical than conventional methods such as CVD, sol-gel deposition and sputtering for producing both thick and thin ceramic deposits to be used for superconductors, laminar components, multichip modules, fuel cells and etc. [1].

The zeta potential of particles is a key factor in the electrophoretic deposition process. It plays role in stabilization of the suspension as well as in the deposition stage. The zeta potential can be controlled by addition of charging agents such as acids, bases and specifically adsorbed ions or polyelectrolytes, to the suspension [2]. Thus there exist a variety of additives that affect the charge magnitude and its polarity. These additives act by different mechanisms [3].

The objective of the present work is to develop a methodology for selection of a charging agent for a specific powder to be deposited by EPD. The methodology presented in this work is based on data obtained from zeta potential/pH curves and from conductivity measurements [4, 5]. It is demonstrated on a barium titanate suspension in aqueous medium based on a mixture of water and ethanol. Barium titanate is the key material in one of the promising applications of EPD: the deposition of dielectric materials for electronic purposes such as production of multilayer capacitors.

In aqueous media barium titanate may undergo leaching of Ba^{2+} ions from the particle surface at pH values lower than 9. This may change the ratio of Ba/Ti and affect the dielectric properties of the material. Treatment with oxalic acid results in passivation of the particle surface by formation of an insoluble barium oxalate layer. Subsequent washing of the powder removes the excess of Ba^{2+} ions and reduces the conductivity of the suspension [6].

2. Experimental

2.1. Materials and methods

The ceramic powder studied was barium titanate produced by Degussa with D_{50} of 0.97 µm. The powder was suspended in a mixture of absolute ethanol (“Riedel de Haen”) and water (HPLC grade “Merck”) at a ratio of 30:70 vol%. The charging agents studied are presented in Table I. In this work we concentrate on polyelectrolytes since they are expected to exert the strongest effect on the zeta potential. In addition they may create an electrosteric effect due to the organic component thus enhancing suspension stability.

2.2. Suspension preparation and zeta potential measurements

The suspension was prepared by dispersion of BaTiO_3 particles (solid phase concentration 500 g/l) in the ethanol water mixture (30:70 vol%). The powder was suspended by an ultrasound treatment of 5 min (“Fisher Scientific 550” dismembrator) while maintaining a
TABLE I Chemical name and supplier of tested additives

<table>
<thead>
<tr>
<th>Additive, supplier</th>
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<tbody>
<tr>
<td>Polydiallyl dimethyl ammonium chloride PDADMAC, 20 wt%. Solution in water, “Aldrich Chemical Company, Inc.”</td>
</tr>
<tr>
<td>Polyethylene imine (PEI), “Aldrich Chemical Company, Inc.”</td>
</tr>
<tr>
<td>Polyethyleneimine epichlorohydin modified (Co-polymer), 17 wt%. Solution in water, “Aldrich Chemical Company, Inc.”</td>
</tr>
<tr>
<td>Poly (bis(2-chloroethyl) ether-alt-1,3-bis (3-dimethylamino)propyl) urea), quaternized(Polyquaterium-2), 62 wt%. Solution in water, “Aldrich Chemical Company, Inc.”</td>
</tr>
<tr>
<td>Polyacrilic acid, PAA “Aldrich Chemical Company, Inc.”</td>
</tr>
<tr>
<td>OROTAN’s, “Rohm and Haas UK Limited OROTAN-681 (Na salt of Polyacrilic acid), 850E (NH4 salt) and 731 K (K salt)</td>
</tr>
<tr>
<td>Polyethylene glycol-400, PEG-400; “Aldrich Chemical Company, Inc.”</td>
</tr>
</tbody>
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constant temperature of the suspension using a water bath. The charging agents were added in most experiments at a concentration of 150 µl/100 ml. This concentration was chosen based on numerous previous experiments. In later experiments the concentration was varied in order to determine the optimal concentration.

The zeta potential of the particles at different pH values was measured using a zeta potential analyzer (ESA-8000, Matec Applied Sciences). The pH was adjusted using nitric acid and ammonium chloride for the acidic and the alkaline range, respectively. Conductivity measurements were made using a conductivity meter (WTW-LF 330).

3. Results and discussion

3.1. Standard zeta potential curves

Zeta potential curves in the absence of additives (standard zeta potential curves) were prepared for three suspensions: non-treated powder washed powder and passivated powder. The powder was washed repeatedly with an ethanol water mixture 30:70 vol%, until the conductivity of the suspension of powder in washing liquid is constant. Passivation of the powder was performed by dispersing it in a solution of 0.1 M oxalic acid (5 ml for 10 g powder) and maintaining the dispersion until its conductivity reaches 2 µS/cm. Fig. 1 shows the curves obtained.

The washing reduced the zeta potential of the powder in the positive range and the passivation with oxalic acid practically nullified the zeta in whole pH range. These phenomena can be explained as follows: In the non-washed powder a positive particle charge is obtained by adsorption of Ba\(^{2+}\) ions leached out of the BaTiO\(_3\) in the acidic pH range. The passivation process results in a thermodynamically stable surface layer of barium oxalate rendering the particle not charged in the entire pH range. In order to decide which surface treatment should be applied to the powder prior to the charging experiments, the effect of PEI on powder with and without treatment was studied. Fig. 2 shows that the effect is practically the same for the three tested powders and therefore further experiments were carried out on untreated powder, referred to further as “standard” powder.

3.2. Effect of cationic agents on standard zeta curve of BaTiO\(_3\)

The cationic polymers used in this work are divided in two groups: polyethylene imines and polyamines. Polyethylene imine (PEI) is a highly branched aliphatic polyamine characterized by the repeating chemical unit denoted as \(-\text{(CH}_2\text{CH}_2\text{NH})\text{--}\). The amine groups in PEI exist in primary, secondary and tertiary form in the approximate ratio 1:2:1. Primary amine groups, which are the chain terminating units, are the most basic and reactive. PEI’s function as weak Lewis bases in aqueous media. The high degree of branching is thought to be due to the chain transfer reaction of amine groups with the quaternary ammonium ion. As the molecular weight of PEI increases, the polymer structure assumes a characteristic spherical configuration. The viscosity of PEI is directly proportional to its concentration and molecular weight. PEI is soluble in most polar materials including water and alcohols. PEI...