Electrophoretic kinetics of nanomullite, nanoSiC and their composite suspensions

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In detail characterisation of suspensions including nanomullite, nanosilicon carbide and various percentages of their composites has been studied in this letter. Mechanism of particle ionisation, alternate pH and surface charge, particle size distribution, zeta potential, current density, electrophoresis movement and kinetics of time–weight curves has been studied, thoroughly. It was illustrated that triethanolamine cannot stabilise powders as well. However, poly-vinyl pyrrolidone could stabilise the particles as well but the particles could not move easily in the presence of applied electrical field due to the lack of enough surface charge. In this case, iodine (I) could be utilised as the preferred surfactant due to good stability and enough surface charge even though it could increase the concentration of free ions and conductivity of particles may be decreased. It was also found that in the case of utilising optimum surfactant, the amount of zeta potential for mullite suspension is more than composite powder and these two have a greater zeta potential than SiC suspension. Last but not least, it was found that the velocity of deposition reduces by increasing the time and its reduction depends on resistance and permittivity of suspension.

1. Introduction: The suspension is a mixture in which the solid particles do not dissolve but get suspended throughout the medium. It is when particles are left floating in a solvent. The solid phase is dispersed throughout the fluid phase using mechanical agitation, and in many cases with the use of certain surfactants. Unlike colloids, suspensions will eventually settle over time if left undisturbed. Suspensions also are different from solutions, in which the solid substance does not exist separately, and they are homogeneously mixed. Suspensions are unstable from the thermodynamic point of view; however, they can be kinetically stable over a large period of time. This time span and characterisation of stable suspension needs to be measured to ensure the best product quality to the final consumer [1–9].

There are a lot of experiments related to the kinetics of deposition process from suspensions. Hamaker [10] observed a linear dependence between deposited weight and the amount of suspension concentration. Sarkar et al. [11] demonstrated the kinetic aspects of electrophoretic deposition (EPD) for four possible deposition conditions: constant-current and constant-suspension concentrations, constant-current but decreasing suspension concentration, constant-voltage and constant-suspension concentrations and constant-voltage but decreasing suspension concentration. As they have reported, the decreasing suspension concentration reduces the final yield of deposition. Furthermore, decrease in particle rate during constant-voltage state is due to the fact that deposited mass acts as a shield of electrical resistance. Consequently, as the deposit grows with deposition time, the available electrical driving force or voltage per unit length of suspension decreases with time. Mathematically modelling of constant-voltage EPD from stable suspension was reported by Gonzalez-Cuenca et al. [12]. The influence of deposit formation on deposit growth is implemented, which is a refinement of the model described earlier by Biesheuvel and Verweij [13]. According to Zhang et al. [14], the kinetic equation for deposited weight can be expressed as an exponential function of time. Wang et al. [15] suggested that for uniform and dense packing layers, it is more convenient to use the deposited thickness instead of the weight but it added some uncertainty to the resulting equation.

2. Experimental procedure: Nanomullite with the stoichiometric composition of 3Al2O3·2SiO2 was synthesised using following procedure. Al(NO3)3·9H2O was dissolved in distilled water. The resulting solution was heated up to 60°C for 1 h on a magnetic stirrer. (C2H5O)4Si was dissolved in ethanol and added to the former solution drop by drop. The resulted solution was heated up to 60°C for 4 h on a magnetic stirrer for making gel. The resulted gel was dried in air for 3 days and calcinated at 1400°C for 2 h. X-ray diffraction, Unisantis XMD 300 was used for determination of phase analysis and crystalline size of the powder. Furthermore, in order to calculate zeta potential and particle size distribution, Dynamic Light Scattering (DLS), Nanotrac Wave, USA was utilised. Nanomullite and nanosilicon carbide (nanoSiC) powders with different weight percentages were grinding using planetary ball mill.

Various amounts (6–42 mg) of poly-vinyl pyrrolidone (PVP), iodine (I) and triethanolamine (TEA) were solved in 30 ml of ethanol and 0.3 g of nanomullite, nanoSiC or composite powder (1 wt% of solvent) was added to the resulting solution to be agitated for 1 h on magnetic agitator. Then the solution was placed in the ultrasonic bath for more stabilisation. The amount of pH was calculated using Metrohm827 pH meter, Switzerland. Suspension conductivity was measured using Metrohm712 conduction meter, Switzerland. Zeta potential of suspensions was measured using Nanotrac Wave, produced by Microtrak Co. zeta seizer.

C–C composite and graphite electrodes with 1.3 cm diameter were placed inside the suspensions with 1 cm parallel distance. Electrodes then were connected to power supply, ASTECH DC HY30001E 9225 China, applying a voltage of 60 V.

The deposition process was modelled by Simulink modelling toolbox of MATLAB software utilising equivalent circuit modelling due to the high correspondence between particle deposition curves and charging of a reservoir in an RC circuit.

3. Results and discussion

3.1. Nanomullite–nanoSiC composite powders: Different percentages of nanomullite and nanoSiC powders were grinded for 12 h in high energy ball mill.

Fig. 1 illustrates scanning electron microscopy of 50%mullite–50%SiC (wt%) composite powder after 12 h of grinding process. According to Fig. 1, it is obvious that the size of the powder is in the range of nano and the powder grains are approximately
spherical. In addition, agglomerated particles could be identified in Fig. 2. The existence of such structures may destroy mechanical behaviour of final coating by the creation of porosities and non-condensing layers. The mentioned problem will happen due to the integration of agglomerated particles on the substrate and development of porous layers. In the scale of nanopowders, agglomerated particles always will be created for reduction of surface energy of a single grain. Hence, the excessive size of agglomerated structures is a reason for the destruction of the final coating. For reduction of the size of agglomerated particles, the ball milled powders were grinded by hand. Albeit, large agglomerated particles could not be stabilised in suspension and they will be settled in the bed which is a reason for large agglomerates not to be moved toward the opposite electrode in the deposition process.

3.2. Effect of dispersant on stability of suspensions: Fig. 2 shows the effect of different types of dispersants on stabilisation of nanomullite, nanoSiC and their different compositions of composite powders. The weight percentage of powder which is settled in the bed of suspension after 24 h has been plotted against various amounts of dispersants.

As it is illustrated from Fig. 2a, the sedimentation of 50% mullite–50%SiC particles is reduced by increasing PVP in the suspension. The minimum amount of sedimentation occurs in the
presence of 24 mg PVP. More amount of PVP increases sedimentation and reduces the stability of the suspension. Furthermore, the optimum amount of iodine and TEA surfactants are at 48 and 6 mg, respectively. Table 1 illustrates the optimum amount of surfactants for production of each suspension as it is derived from results of Fig. 2.

PVP and iodine somewhat could stabilise all powders (Figs. 2a–e), while TEA could not stabilise the powders as well. As it is obvious, there are three different general kinds of surfactants according to the mechanism of stabilisation of particles in suspensions, i.e. electrostatic, steric and electro-steric [16].

In this research, three different surfactants have been utilised which the mechanism of stabilisation in everyone is different. TEA is an electro-steric surfactant, while iodine is an electrostatic one and PVP is steric [17]. As it is illustrated from Fig. 2, TEA as an electro-steric surfactant cannot stabilise suspensions as well. In this case, the electrostatic repulsiveness of iodine and steric separation of PVP could improve stabilisation process. Creation of large suspended agglomerates is the major reason for further sedimentation of powders in the presence of TEA. It is also expressible that steric surfactants can improve the amount of stability of suspensions. By the way, there is not enough electrical charge on the surface of suspended particles when they are stabilised using steric surfactants. In this case, low rate of the deposition process is the limitation of EPD [18]. PVP could stabilise the particles as well but the particles could not move easily in the presence of an applied electrical field. Therefore, iodine could be utilised as the preferred surfactant in the case of simultaneous stabilisation and EPD.

3.3. Study of surface charge: Fig. 3a illustrates pH versus iodine concentration for mullite, SiC and 50%mullite–50%SiC suspended powders in ethanol.

According to Fig. 2, it was shown that iodine could stabilise all suspensions while the amount of surface charge in suspensions is almost suitable for EPD. When iodine is added to ethanol, H⁺ and I⁻ ions release inside the media as follows [19]:

$$\text{CH}_3\text{CH}_2\text{OH} + \text{I}_2 \rightarrow \text{ICH}_2\text{CH}_2\text{OH} + \text{H}^+ + \text{I}^-$$  (1)

In this case, some of the protons gather on the surface of nanoparticles and some will remain in the suspension. This phenomenon affects pH, conductivity, surface charge and consequently the stabilisation of suspension. Reduction of pH, while iodine surfactant increases in the suspensions, is one of the specified observation in all suspensions. This is because of more creation of H⁺ ions by increasing iodine surfactant [20]. According to (1), enhancement of iodine increases the concentration of I⁻, which is a preferred reason for the enhancement of conductivity of suspensions. Because of this reason, more concentration of iodine has not been added to suspensions. Table 2 shows the amounts of isoelectric point (IEP) of suspensions, pH of suspensions in presence of optimum amounts of iodine surfactant and the difference of these two parameters. Using the data in Table 2, zeta potential variations of suspensions could be predicted.

A greater difference between IEP and pH of suspension causes more surface charge following by zeta potential enhancement. According to the data in Table 2, it is predictable that the amount of zeta potential for mullite suspension is more than composite powder and these two have a greater zeta potential than SiC suspension. Fig. 3b depicts the zeta potential versus iodine concentration for mullite, SiC and their composite suspended powders.

### Table 1 Optimum amount of surfactants for stabilisation of different powders

<table>
<thead>
<tr>
<th></th>
<th>Iodine</th>
<th>PVP</th>
<th>TEA</th>
</tr>
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<tbody>
<tr>
<td>mullite</td>
<td>36</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>SiC</td>
<td>18</td>
<td>24</td>
<td>12</td>
</tr>
<tr>
<td>25%mullite–75%SiC</td>
<td>36</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>50%mullite–50%SiC</td>
<td>42</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>75%mullite–25%SiC</td>
<td>30</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
ic movement depends on zeta potential, permittivity and viscosity.

According to Table 3, electrophoretic movements: Table 3 illustrates the inherent characterisation of ethanol solvent. According to Hokel approximation the amount of deposited weight is inversely proportional to the size distribution of particles. Coated weight is higher for SiC and lowers for composite powder. As it was mentioned earlier, the size distribution of SiC is smaller than nanomullite and the size of powder, there are three kinds of suspensions including stable, flocculated and agglomerated suspensions. It is obvious that the greater size of the powder is more affected by gravity and particles will be precipitated faster. Precipitation of agglomerated particles is faster than flocculated suspension and it is easier than stable suspended particles. Accordingly, the zeta potential of small narrow distributed particles is as high as they could be stabilised more than large particles [22]. From the data of Fig. 3c, it is clear that the particle size distribution of SiC, mullite and 50%SiC–50%SiC is about 50–220, 70–260 and 180–420 nm, respectively. It is predictable that EPD of composite powder will do, harder than other powders.

Table 2 pH of IEP, pH of stable suspensions and their difference.

<table>
<thead>
<tr>
<th>Powder</th>
<th>pH of IEP</th>
<th>pH of stable suspension</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mullite</td>
<td>7</td>
<td>2.3</td>
<td>4.7</td>
</tr>
<tr>
<td>SiC</td>
<td>5</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>25%mullite–75%SiC</td>
<td>5.5</td>
<td>1.6</td>
<td>3.9</td>
</tr>
<tr>
<td>50%mullite–50%SiC</td>
<td>6</td>
<td>1.8</td>
<td>4.2</td>
</tr>
<tr>
<td>75%mullite–25%SiC</td>
<td>6.5</td>
<td>2</td>
<td>4.5</td>
</tr>
</tbody>
</table>

According to Fig. 3b, it is almost obvious that initial enhancement of iodine concentration leads to enhancement of zeta potential and it reaches a maximum for all suspensions. After a maximum point, more enhancement of iodine decreases zeta potential. In this case, more enhancement of iodine produces more free ions in solution. According to the interactions between the surface charge of particles and free ions, the amount of repulsion between particles is dropped and zeta potential will be decreased [21].

3.4. Particle size distribution: Fig. 3c shows the particle size distribution of mullite, SiC and 50%SiC–50%SiC powders in stabilised suspensions.

Depending on the size of powder, there are three kinds of suspensions including stable, flocculated and agglomerated suspensions. It is obvious that the greater size of the powder is more affected by gravity and particles will be precipitated faster. Precipitation of agglomerated particles is faster than flocculated suspension and it is easier than stable suspended particles. Accordingly, the zeta potential of small narrow distributed particles is as high as they could be stabilised more than large particles [22]. From the data of Fig. 3c, it is clear that the particle size distribution of SiC, mullite and 50%SiC–50%SiC is about 50–220, 70–260 and 180–420 nm, respectively. It is predictable that EPD of composite powder will do, harder than other powders.

3.5. Electrophoretic movements: Table 3 illustrates the inherent characterisation of ethanol solvent. According to Table 3, permittivity constant of ethanol is almost suitable for dispersion phenomenon due to polarity and inter molecular forces [23].

A thorough study of particle movements helps the EPD process. Electrophoretic movement is the rate of charged particles under the unit electric field. According to Henry equation [24], electrophoretic movement depends on zeta potential, permittivity and viscosity of solution

\[ U_E = \frac{2\pi\zeta F(ka)}{3\eta} \]  

(2)

where \( \varepsilon \) is the electrical permittivity of solution, \( \zeta \) is the amount of zeta potential of particles, \( F(ka) \) is the Henry function and \( \eta \) is the viscosity of suspension. Furthermore, \( a \) and \( k \) are particle’s radius and Debye length, respectively. For small particles in organic solutions and according to Hokel approximation the amount of Henry function is almost 1. Accordingly, corrected form of (2) is as follows:

\[ U_E = \frac{2\pi\zeta}{3\eta} \]  

(3)

Table 3 Inherent characterisation of ethanol solvent

| electrical conductivity, \( \mu \)S/cm | 4.25 |
| pH | 7 |
| pH in the presence of iodine | 3.91 |
| viscosity (\( 10^{-5} \) Nm\(^{-1}\)m\(^{-1}\)) | 1.09 |
| vapour pressure, kPa | 5.8 |
| Permittivity, F/m | 24.3 |

According to (3), enhancement of zeta potential of particles and permittivity of the solution and also reduction of viscosity of suspension increase the electrophoretic movement. Actually, the high zeta potential of particles not only increases the stability of particles but also increases their movements. It seems that a solution with high permittivity and low viscosity is suitable for the EPD process. On the other hand, the high permittivity of solution causes enhancement of free ions in solution and accordingly reduction of surface charge and zeta potential of suspension [24].

The main factor affecting conduction of suspension is the concentration of free ions [25]. If the concentration of free ions in the suspension is high, they will mainly move in an electric field and the movements of particles will be limited. Iodine increases the concentration of free ions of suspension. In this regard, the optimum amount of iodine could increase the surface charge while the concentration of free ions is minimised. In this state, the role of particles in conductivity is maximised and coating procedure will be done, easily.

3.6. Current density of suspensions: Fig. 3d shows the current density changes of suspensions containing nanomullite, nanoSiC and 50%SiC–50%SiC powders in the presence of an optimum amount of iodine dispersant in ethanol solution. As it is illustrated, initiation of current density curve of mullite is higher than other suspensions. Since applied electric field and cross section of electrodes are the same for all suspensions, initial changes of current density illustrate the electrical conductivity of suspensions. It confirms the results of pH calculation which was presented previously in Section 3.2. In general, the current density curve of mullite is higher than other suspensions. This shows the rate of particle movements in mullite suspension is higher than other suspensions.

A reason for the severe drop in current density in all curves could be a reduction of conductivity due to the formation of a ceramic layer on the electrode. However, this drop is smaller for mullite suspension in comparing with other ones. This could be attributed to higher electrophoretic movements and zeta potential of mullite particles in compare with other particles. The mentioned drop could be also attributed to the enhancement of charged particles near cathode (graphite) and creation of concentration potential which acts against the electrical field and reduces the deposition rate [26].

3.7. Weight–time curves: Fig. 4a illustrates the weight–time curves of nanomullite, nanoSiC and 50%SiC–50%SiC powders moved at the voltage of 60 V.

As it is illustrated, the rate of deposition is almost linear. It will decrease gradually and after a while, the rate of deposition will reach to zero, approximately. A suitable reason for these changes could be attributed to the thickening of coated layer and its resistance. It is also recognisable that the amount of deposited weight is conversely proportional to the size distribution of particles. Coated weight is higher for SiC and lowers for composite powder. As it was mentioned earlier, the size distribution of SiC is smaller than mullite and these two are smaller than composite powders.

3.8. Kinetics modelling: Fig. 4b shows the weight–time curves of mullite suspension in different coated voltages of 40, 60 and 80 V.

With increasing of applied voltage, coating weight increases, intensively. Equivalent circuit modelling is a method of modelling in which there is a component in a circuit that its response is similar to the behaviour a scientist observes in another field of study. In this case, the mentioned circuit is the equivalent circuit of the observed process in another field. Therefore, all equations used for that circuit could be used also for the observed process. According to an equivalent circuit modelling, there should be an electric circuit in which one of the components (\( V–\beta \) plot) is similar to Fig. 4a. The charging of a reservoir in an RC circuit has gotten the same plot.
The charging of a reservoir versus time has been determined as a reservoir in an RC circuit. The charging of a reservoir versus time will be discussed more at the following. It is also noticeable of EPD process, composition of suspension and so on. Kinetic constants in suspension and accordingly, corresponding equation for curves in Fig. 4a is

\[ w = w_M (1 - e^{-kt}) \]  
(4)

where \( w \) is the coated weight at time \( t \), \( w_M \) is the amount of powder in suspension and \( k \) is a kinetic constant that depends on the voltage of EPD process, composition of suspension and so on. Kinetic constant will be discussed more at the following. It is also noticeable that fitness of (4) could lead to the same equation.

As mentioned, Fig. 4a and (4) are the same to those for charging of a reservoir in an RC circuit. The charging of a reservoir versus time has been determined as

\[ v = v_L (1 - e^{-t/RC}) \]  
(5)

There is one-by-one correspondence between the parameters in (4) and (5). Consequently, \( k \) corresponds to \( 1/RC \). \( R \) and \( C \) are defined by

\[ R = \frac{pL}{A} \]  
(6)

where \( \rho \) is the specific resistivity, \( L \) is the distance between electrodes, \( A \) is the cross-section of anode and \( \varepsilon \) is the dielectric constant of suspension.

If the behaviour of EPD is considered as an RC circuit, the electrophoretic cell could have twofold characterisation of resistor and reservoir together. As a result, constant value of \( k \) corresponding to \( 1/RC \) could be calculated as

\[ k = 1/RC = 1/\rho e \]  
(8)

Both \( \rho \) and \( \varepsilon \) are the inherent parameters of suspension [25]. Furthermore, \( \rho \) and \( \varepsilon \) will be varied in different temperatures and voltages. Hence, \( k \) constant depends on the composition and temperature of suspension as same as the voltage of EPD process.

The kinetic model which is introduced in (4) is the same with the model reported by Zhang et al. previously. There are two differences between these two models. Initially, equivalent circuit modelling was a more routine method for extraction of the model which is used in this Letter. Finally, the introduced equation for kinetic constant \( (k) \) is so simple and easy to calculate in comparing with Zhang’s kinetic constant. Fig. 4c shows the model for each three deposited samples depicted by DC current in Simulink.

There is a good correspondence between curves of Figs. 4b and c, with \( R^2 \) which are reported in Table 4.

### 4. Conclusion:
Suspension behaviour and electrophoresis movements of stable particles of nanomullite, nanoSiC and their composite have been thoroughly investigated in this Letter. It was illustrated that TEA cannot stabilise powders as well. However, PVP could stabilise the particles as well but the particles could not move easily in the presence of applied electrical field due to the lack of enough surface charge. In this case, iodine could be utilised as the preferred surfactant due to good stability and enough surface charge even though it could increase the concentration of free ions and conductivity of particles may be decreased. It was also found that in the case of utilising optimum surfactant, the amount of zeta potential for mullite suspension is more than composite powder and these two have a greater zeta potential than SiC suspension. Finally, an exponential equation was presented for the kinetics of electrophoresis movements which depends on the composition and temperature of suspension, electrical properties of substrates as same as the voltage of EPD process.

### 5. References


### Table 4 \( R^2 \) of Figs. 4b and c curves

<table>
<thead>
<tr>
<th>Sample coated at, V</th>
<th>( R^2 ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>97</td>
</tr>
<tr>
<td>60</td>
<td>96</td>
</tr>
<tr>
<td>80</td>
<td>94</td>
</tr>
</tbody>
</table>

Fig. 4 Weight-time curves of

a Nanomullite, nanoSiC and 50%mullite–50%SiC powders moved at the voltage of 60 V

b Mullite suspension in coated voltages of 40, 60 and 80 V

c Output of model for each three deposited samples depicted by DC current in Simulink