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Journal of the European Ceramic Society 26 (2006) 1555–1560

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Effect of polyethylenimine on the dispersion and electrophoretic deposition of nano-sized titania aqueous suspensions

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Received 27 August 2004; received in revised form 26 February 2005; accepted 5 March 2005
Available online 13 April 2005

Abstract

The dispersion and electrophoretic deposition (EPD) behavior of an aqueous suspension of nano-sized titania particles stabilized with a dispersant of polyethylenimine (PEI) were systematically investigated. The adsorption behavior of PEI on the titania surfaces indicated a high affinity adsorption of PEI at a high pH value while a low affinity adsorption was observed at a low pH value, which is consistent with the viscosity behavior of the suspension. The influences of the suspension pH, the added amount of PEI and the salt addition on the electrophoretic deposition behavior of the suspensions were studied.

Keywords: Suspensions; TiO_2; Electrophoretic deposition

1. Introduction

The electrophoretic deposition technique has attracted increasing interest for the fabrication of ceramic films due to its advantages of simplicity, low cost equipment, easy control of the film thickness and feasible design of complex shapes.[1–3] Basically, EPD is a process based on the motion of charged particles in a suspension towards an electrode of opposite charge under an applied electric field. The electrophoretic forming process depends on the dispersibility of the powder used, the stability of the resulting suspension, the electrophoretic mobility of the individual particle and the particle interaction force. Consequently, the colloidal property of the particle suspension is of great importance for the EPD process. In general, well-dispersed suspensions containing particles of high electrical charges are preferable because they may lead to the higher average packing densities of green bodies during the EPD compared with that of a flocculated suspension, which is essential for the final sintering properties of ceramics.[4] The preparation of stable colloidal suspensions of ceramic powders for EPD require careful consideration of many factors including the selection of the solvent, the addition of the polyelectrolyte dispersant, pH value, ionic strength, etc.[5–7] A recently developed EPD process for the fabrication of bubble-free deposits in aqueous suspensions provides a promising and economical approach to prepare ceramic films.[8]

Titanium dioxide is an important functional oxide with a wide range of applications in electronic, photocatalytic and electrochemical systems and thus has attracted much interest.[9,10] Although nanoparticles of titania is one of the most important forms due to its large surface area and high activity, few studies have mentioned the rheological properties of nano-sized TiO_2 powders and their EPD behavior in aqueous suspensions.[2] Because the information regarding the EPD process of nano-sized TiO_2 is limited, the examination of the rheological properties of positively charged TiO_2 powders and their EPD behavior in aqueous suspension is important and interesting. We have been interested in the preparation of well-dispersed TiO_2 powders with highly positive surface charges, which can be then used for the electrophoretic deposition of TiO_2 on a cathode to form TiO_2 films in aqueous suspensions. In this study, a cationic polyelectrolyte of polyethylenimine was selected as a dispersant to modify the surface charge of the TiO_2 powders.[11–16]

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doi:10.1016/j.jeurceramsoc.2005.03.240

The concentrations of the PEI, pH value of the suspensions and conductivity of the suspensions were examined in detail to elucidate their influences on the EPD behavior of TiO_2 suspensions.

2. Experimental

2.1. Materials and reagents

Commercially available spherical TiO_2 powder with an average primary particle size of 30 nm and a BET surface area of 43 m^2/g (NanoTek, C.I. Kasei Co. Ltd., Tokyo, Japan) was used in this study. Polyethylenimine with an average molecular weight of 10,000 (Wako Pure Chemical Industry Ltd., Tokyo, Japan) was used as the dispersant. Its unit formula of $–[CH_2–CH_2–NH]_n–$ indicates the functional amine –NH group. Reagent grade HCl and ammonium solutions were used for the pH adjustment.

2.2. Colloidal suspension characterizations

Aqueous suspensions with a 10 vol.% solids content for the viscosity measurements were prepared at different pH values using a magnetic stirrer in distilled water. An ultrasonic horn (USP-600, Shimadzu Inc., Kyoto, Japan) with 160 kW power was operated for 10 min to disperse the suspensions,[17] then the suspensions were stirred for at least 12 h to ensure the saturated adsorption of the PEI on the particle surfaces. The viscosities of the suspensions were measured using a cone-plate type rotational viscometer (Model RC-500, Toki Sangyo Co. Ltd., Tokyo, Japan) with a shear rate ranging from 0 to 400 s^{-1}. The zeta potential (ζ) of the powders was acquired using a laser electrophoresis zeta-potential analyzer (LEZA-600, Otsuka Electronics Co. Ltd., Japan) in a 10^{-2} M NaCl solution with different amounts of PEI. The adsorption amount of PEI on the particles was evaluated as follows. Five weight percent TiO_2 suspensions with different amounts of PEI addition were prepared, and then the suspensions were centrifuged and the sediment powders were collected and dried in 120 °C for 1 day. The adsorbed quantities of PEI were calculated from the total carbon content of the sample, which was determined using a gas analyzer (CS-444LS, LECO Corp., USA), the instrument uses an IR detector to measure the content of CO_2 released by the sample during combustion with high-frequency heating in oxygen flow furnace. The background sources of carbon content without PEI adsorption was deducted from the sample.

2.3. Electrophoretic deposition procedure

The EPD was performed in a cell with two electrodes vertically immersed in a 5 vol.% suspension of 50 ml. A stainless steel sheet was used as the anode, and a palladium sheet with a deposition area of 8 cm^2 was used as the cathode. They faced each other at a distance of 2 cm. The applied current was kept constant at 0.375 mA/cm^2 using a dc power source (Potentiostat/Galvanostat HA-3001A, Hokuto Denko, Japan). The relation between the deposit weight and time was investigated at different suspension pHs. The obtained deposits were dried in air at room temperature and weighed together with the cathodic substrates to determine the deposited weight. The conductivity of the suspensions was measured using a conductivity meter (ES-12, Horiba, Japan). Green densities of the TiO_2 deposits were measured by Archimedes' method in kerosene.

3. Results and discussion

3.1. Effect of PEI on suspension properties

Fig. 1 shows the adsorption isotherms of PEI on TiO_2 surfaces as a function of the amount of PEI introduced, plotted as mg/m^2 for PEI adsorbed on the surface area of TiO_2 versus the initial amount of added PEI (on a dry weight of TiO_2 basis, dwb). The dotted line indicates the ideal 100% adsorption of PEI on the particle surfaces. In general, the adsorbed amount of PEI tended to increase with the increasing added PEI concentration until a plateau region was reached. On the other hand, the adsorbed amount of PEI was also highly dependent on the pH value of the suspension. The adsorption of PEI at pH 4.2 can be classified as a low-affinity type, suggesting most of the polymer remains free in the solution with a low saturated adsorption. In contrast, the isotherms at pH 10.2 were quite consistent with the ideal 100% adsorbed line, suggesting a high-affinity type adsorption and characterized by a strong adsorption and apparent surface saturation. The transitional pH values yielded isotherms that exhibited an intermediate behavior between these two extremes. A saturated adsorption was achieved with 0.5 dwb% PEI addition at pH 4.2, 1 dwb% at pH 6.2, and 2 dwb% PEI at pH 8.2, respectively, while even 3 dwb% PEI addition could not provide a saturated adsorption state at pH 10.2. It should be of interest to discuss the conformational state of the polymer under various pH regions to elucidate the adsorption behavior of the PEI. For the PEI at pH $\geq$ 10.8, the

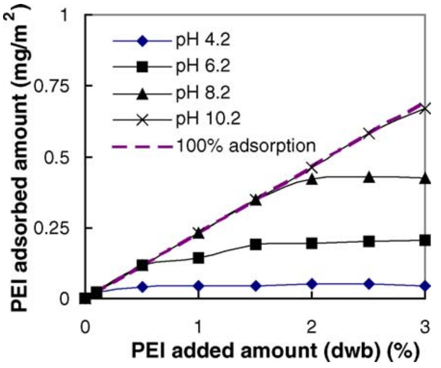

Fig. 1. Adsorption isotherms for PEI on TiO_2 surfaces as a function of the amount of PEI introduced on a dry weight of TiO_2 basis (dwb).

molecules actually carry no charge with the polymer chains approaching insolubility and form relatively compressed coils or clumps.[18] Thus, the surface area per adsorbed chains is relatively low and more PEI is required to establish a saturated monolayer. As the pH decreased, the number of positively charged sites is continually increased until the PEI is effectively positive at pH ≤ 3. Under this condition, the positively charged sites of the polymer chains tend to repel each other, and the molecules are in the form of relatively large and expanded stretched chains. Consequently, the polyelectrolyte can efficiently be adsorbed on the particle surface in a flat conformation. A similar pH dependence behavior was reported for the adsorption of PEI on SiO_2 surfaces.[18]

Fig. 2 presents the zeta potentials of the as-received nano-sized TiO_2 and PEI-modified TiO_2 powders. The isoelectric point (IEP) was determined at pH = 6.7 for the TiO_2 powder. A highly positive surface charge was only achieved below pH 4. The IEP of TiO_2 shifted to pH 7.7 with 1 dwb% PEI addition, while noticeable IEP shifts to pH 10.8 were observed for the 3 dwb% PEI addition, suggesting that the appropriate PEI is required to promote the IEP to a higher pH value. The significant IEP shift is attributable to the adsorption of the positively charged PEI on the surface of the TiO_2 particles. The addition of PEI not only promoted a shift in the IEP to a higher pH value, but also resulted in a good dispersion of the suspension with a positive charge. Similar tendencies have been observed in other suspensions of ceramic oxides.[18] The protonation of the amine groups in PEI molecules and subsequent expansion of the polyions due to mutual charge repulsion are assignable to the modification of the TiO_2 surface charge. It is also noteworthy that a highly positive zeta potential was achieved over a wider pH region with the increasing PEI addition. For example, a positive zeta potential with a value of over 30 mV was obtained in the range of pH < 6 for 1 dwb% PEI addition while the range expanded to pH < 8 for the 3 dwb% PEI addition (Fig. 2).

Viscosity measurements were conducted to evaluate the rheological properties of the suspensions. The viscosities of the 10 vol.% suspensions drastically increased in a narrow pH range at a certain PEI content, suggesting the transformation from a well-dispersed state to flocculated state (Fig. 3). On the other hand, the relatively well-dispersed suspension expanded over a wider range with the increasing PEI content, indicating that the PEI addition can improve the dispersion property of the suspension. The stabilized suspensions were obtained below pH 5.4, 5.8, 7.1 and 7.4 for the 1, 1.6, 2 and 3 dwb% PEI addition, respectively, this is in agreement with the adsorption data and ζ-potential of TiO_2, which suggesting that saturated adsorption of PEI and high ζ-potential are the requisite conditions for good dispersion of the TiO_2 suspensions.

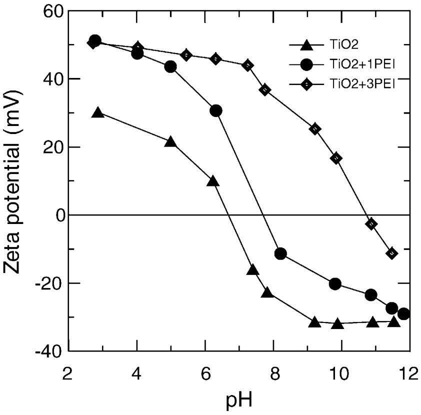

Fig. 2. Zeta potentials of TiO_2 and PEI-modified TiO_2 (with 1 and 2 dwb% PEI) in aqueous suspension.

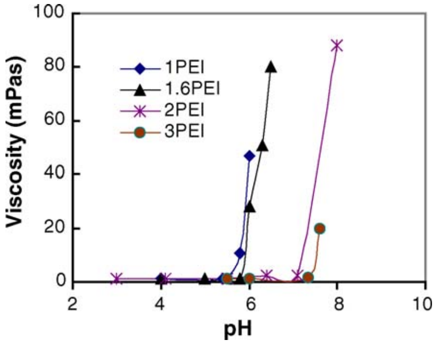

Fig. 3. Effect of PEI amount (1, 1.6, 2 and 3 dwb% PEI) on the viscosities of 10 vol.% TiO_2 suspensions vs. pH at a shear rate of 400 s^{-1}.

3.2. *Influence of suspension pH, PEI and salt addition on the electrophoretic deposition behavior of TiO_2 suspensions*

In order to well-understand the EPD behavior of the TiO_2 suspensions, the deposit weight, suspension conductivity and the effect of the ionic strength on the EPD process were examined via varying suspension pH, the amount of PEI addition and salt addition.

The deposit weight of the 5 vol.% TiO_2 suspensions as a function of the deposition time during the EPD shown in Fig. 4 indicated that the deposition rate is dependent on the parameters including the deposition time and suspension pH value. In most cases, the deposit weight increases nearly

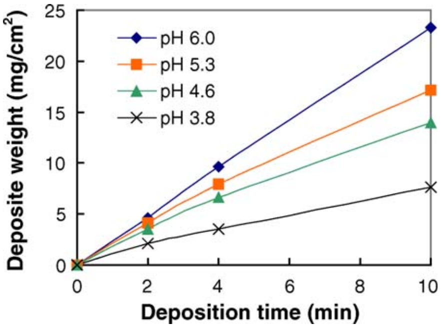

Fig. 4. Effect of suspension pH on the deposition rate of 5 vol.% TiO_2 suspensions with 2 dwb% PEI addition.

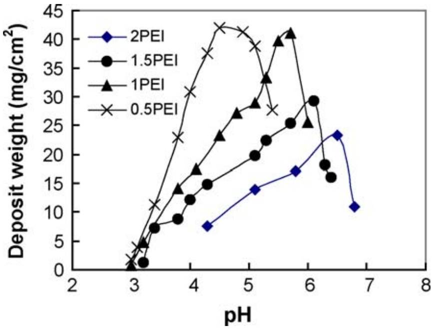

Fig. 5. Effect of suspension pH and PEI amount (0.5, 1, 1.5 and 2 dwb% PEI) on the deposition rate of 5 vol.% TiO_2 slurries deposited for 10 min at a current of 3 mA.

linearly with the deposition time at a constant current. Similar dependencies were obtained for other oxide systems.[11,19–22] The deposition rate tended to increase with the increasing suspension pH from an acidic condition to a nearly neutral medium, showing that adjusting pH value could rational control the EPD process. This can be associated with the above discussed surface charge changes in the TiO_2 particles for different pH values.

The deposit weight versus pH with different PEI contents shown in Fig. 5 indicated that the deposition rate of the TiO_2 suspension first increased and then gradually decreased with the increasing pH. The pH value for the highest deposition rate was 4.5, 5.7, 6.1 and 6.5 for the 0.5, 1, 1.5, and 2 dwb% PEI addition, respectively. This indicates that the pH value of the top-deposition-rate (TDR) shifts to a higher value with the increasing PEI amount, while the amount of TDR decreased for each suspension. The fact that the TDR shifted to a higher pH value and decreased with more PEI addition is noteworthy. Considering the above mentioned colloidal results for the suspensions, the readily flocculated suspensions with less PEI addition showed higher viscosities at a lower pH value than those having high PEI additions, as shown in Fig. 3, and thus will result in a higher deposition rate due to the mobility of the larger flocculated particles. The deposits obtained under such conditions were agglomerated and non-uniform.

The conductivity of the suspensions versus pH with the various PEI contents is shown in Fig. 6. The conductivities of the suspensions with 0.5 dwb% PEI addition first decreased and then increased with the increasing suspension pH at the transitional pH of 4.5. This is because the original suspension pH with 0.5 dwb% PEI was pH 4.5, either introducing an acid or base will increase the conductivity of the suspensions. The deposition rate decreased upon adjusting the pH value to the acidic range, which is assignable to the more dispersed suspension with higher conductivities (Fig. 5). Meanwhile, the suspension became flocculated upon adding more base to increase the suspension pH, corresponding to the increase in the suspension conductivity and the low deposition rate. For the 0.5 dwb% PEI addition, the lower conductivity of the suspensions resulted in a higher deposition rate. However, the conductivities decreased with the increasing suspension pH value for the suspensions containing more than 1 dwb% PEI addition, while the deposition weight first increased and then decreased (Fig. 5). This suggests that not all the suspensions with a low conductivity have a high deposition rate due to the influence of the suspension viscosity (Fig. 3). When the suspension pH was lower than 4.5, 5.7, 6.1 and 6.5 for the PEI content of 0.5, 1, 1.5, and 2 dwb%, respectively, the conductivity decreased and the viscosity increased with the increase in the suspension pH. The contribution of the relatively low ionic strength in the suspension and partial flocculation of the suspension may result in the change in the deposition rate.[19] However, the suspension became too viscous to significantly move the flocculated particles toward the oppositely charged electrode when the conductivity continually decreased with the further increasing suspension pH. Even though the ionic strength decreased, the dominating flocculation over the ionic strength resulted in the decreased deposition rate. The relative density of the TiO_2 green deposits with 1 dwb% PEI addition at various pH were shown in Fig. 7. The relative green densities decreased with a increase in pH, from 58.5% at pH 3.5 to 55.1% at pH 5.7, indicating that the well dispersed TiO_2 suspensions with higher ζ-potential produce the denser deposits. The density was low at pH 5.7 because of the flocculation of the suspension even though the deposition rate was high. This result suggests that through properly adjusting the suspension pH and the amount of PEI addition could control the property

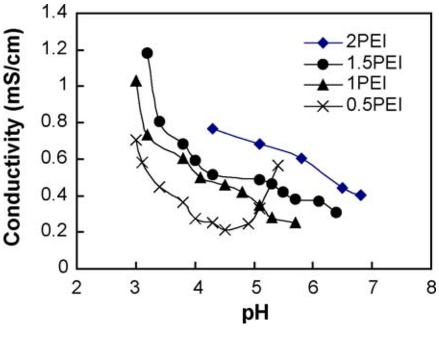

Fig. 6. Conductivity changes of 5 vol.% TiO_2 slurries with suspension pH for various amount of PEI additions (0.5, 1, 1.5 and 2 dwb% PEI).

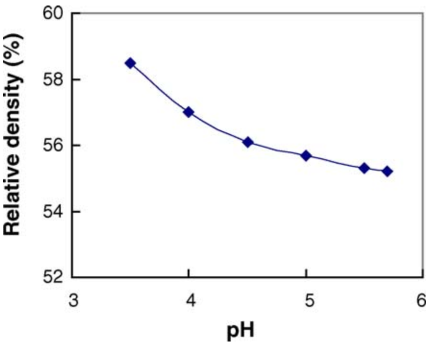

Fig. 7. Relative density of the TiO_2 green compacts vs. pH values when PEI addition is 1 dwb%.

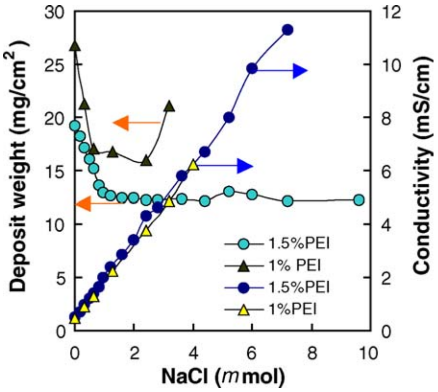

Fig. 8. Deposit weight and conductivity of TiO_2 suspensions with 1 and 1.5 dwb% PEI addition at pH 5.2 changes with the amount of NaCl addition.

of the deposit by balancing the deposition rate and deposit density.

In order to more clearly elucidate the influence of the conductivity on the EPD behavior, the effects of the addition of HCl and NaCl were also studied. Fig. 8 shows the conductivity and deposition rate of the suspensions changes as a function of the NaCl addition. The conductivity of the suspension for 1.5 dwb% and 1.0 dwb% PEI additions increased with more NaCl addition, while the value for the former one was slightly higher than the latter. On the other hand, more NaCl addition led to a decreased deposition rate, whereas the deposition rate of the suspension with 1 dwb% PEI addition was more sensitive to the addition of NaCl. This indicates that a high ionic strength in the suspension is not favorable for a dense deposit with a high deposition rate.

Fig. 9 presents the deposition rate and conductivity of the suspensions versus the amount of HCl addition. The suspension conductivities monotonously increased with the addition of HCl while the deposition rate showed a maximum and then decreased. As we know, the addition of HCl not only increases the ionic strength but also changes the suspension pH, which further influences the viscosity of the suspensions, as shown in Fig. 3. The synergetic effect of the ionic strength and the viscosity of the suspensions contribute to the EPD behavior of the TiO_2 particle. Because the deposition was conducted in a fixed electric current, a large number of ions in the suspension will inhibit the movement of the ceramic particles. On the other hand, the high viscosity of the suspension is usually associated with agglomeration of the particles. As discussed above, partly aggregated particles lead to a change in the deposition speed, while serious agglomeration may deteriorate the movement the particles to the electrode of the opposite charge. Consequently, the synergetic effect of the viscosity and conductivity of the suspension as well as the surface electric charge of the particles will determine the deposition behavior of the particles.

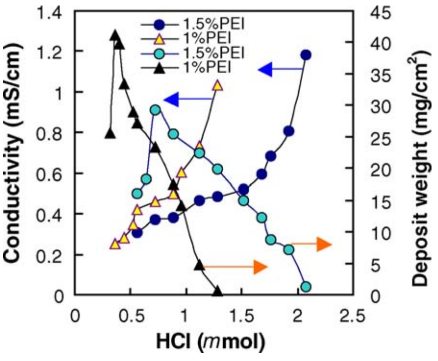

Fig. 9. Deposit weight and conductivity of TiO_2 suspensions with 1 and 1.5 dwb% PEI addition as a function of the HCl addition.

4. Conclusions

PEI is an effective surfactant to disperse the nano-TiO_2 suspensions and to modify the particles to become positively charged. Well-dispersed suspensions were obtained by rational modification of the surface charges of the TiO_2 particles. The electrophoretic deposition behavior of the TiO_2 suspension was dramatically influenced by the suspension pH, the amount of PEI addition, the viscosity and the conductivity of the suspensions. Good deposits could be obtained by carefully considering the synergetic effects of all these factors.

Acknowledgements

This research was supported in part by The Budget for Nuclear Research, and the Grant-in-Aid for Scientific Research (No. 15560593 and No. 16350117) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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