

NANOCOMPOSITE PARTICLES FOR THE PREPARATION OF ADVANCED NANOMATERIALS

P. SOMASUNDARAN, T. CHEN

Langmuir Center for Colloids and Interfaces, Henry Krumb School of Mines, Columbia University, New York, NY 10027

ABSTRACT

New composites based on nano-size particles provide a promising route to the fabrication of novel materials for advanced technology applications. To produce desired materials, it is important to control the composition and distribution of nanoclusters within the bulk or surface coating of nanostructured materials. Towards this purpose, we have developed a novel method of processing nanocomposite materials utilizing colloidal chemistry techniques to tailor their microstructure. Unique composite aggregates of nanoparticles with a core-shell structure were prepared using a special scheme of controlled polymer adsorption. Polymers which specifically adsorb on both nano- and micron- size particles are used as tethers to enable desired coating of the later particles with the former and to enhance the cluster integrity. Nanocomposite particles consisting of micron-size alumina or silicon nitride as cores and nano-size alumina, titania, or iron oxide as shell particles have been successfully prepared using this process.

The surface charge of the core particles is reversed after the adsorption of polyacrylic acid polymers. This promotes the interaction between the core and the shell particles and therefore nanoparticles added subsequently to the core particle suspension coat on core particles by electrostatic as well as possibly hydrogen bonding bridging mechanisms. Success of the process depends to a large extent on the absence of homoflocculation of nanoparticles and this is achieved by removing all the unadsorbed free polymers from the bulk solution before introducing them to coat on the polymer coated core particles. Coating itself is estimated by monitoring change in the zeta potential of core-shell structure. The coating scheme as well as the characterization of these nanocomposite particles are discussed in detail. This processing scheme provides a simple way for the preparation of both bulk and surface coatings with these engineered nanostructured particles as building blocks.

INTRODUCTION

Synthesis and processing of nanomaterials have drawn considerable attention in recent years [1,2]. The exceptional properties of these nanomaterials have made them potential materials for advanced applications in the 21st century. The speciality of these nanomaterials lies largely on their ultrafine grain size and microstructures. Decreased grain/particle size in these materials suggests also the high expanse of interfaces and surfaces inside them. Higher energy state and dynamic nature of these interfaces separate these nanomaterials from those of traditional microstructures.

Currently there is considerable effort devoted to the synthesis of nanoparticles and clusters. Processing of these ultrafines is however done mostly following current techniques that are problematic and remains challenging because of difficulties in dispersing and mixing of the nano-particles/clusters. Due to their small size, particles of nano- and sub-micrometer size tend to agglomerate. Wet processing methods utilizing colloidal techniques can be used to provide means for countering agglomeration problems and achieving improved green microstructures in the fabrication of ceramics [3]. In colloidal processing, particle-particle interactions are controlled by creating repulsive forces between particles using either electrostatic or steric interactions [4,5,6]. The resultant particle suspensions are stable and suitable for further processing. Using the principle of colloidal processing, it is therefore possible to overcome the aggregation problem of nanoparticles and develop suitable processing methods.

Stabilization of particles in solution is strongly dependent on the solid/liquid interfacial properties, which are closely related to the interactions among ions, adsorbed polymers and/or surfactant molecules

and surface functional groups in the interfacial region. Adsorption of polymers on the particle surface offers a most effective way to modify particle surface properties and thus particle-particle interactions [4-7].

The adsorption of polymers at solid/liquid interface with a wide range of applications [8,9] is the result of energy balance between the enthalpy gain of attached polymer segments and the entropy loss of the adsorbing polymer. Factors such as functional groups and molecular weight of the polymer, nature of the solvent, properties of the substrate, temperature, and the solids loading in the system all affect the polymer adsorption [9]. It is important to note that polymers can act as dispersants or flocculants of particles depending on parameters such as polymer molecular weight and surface coverage [10]. The mechanism of polymer induced flocculation is attributed to particle bridging and/or particle charge neutralization [10,11,12,13]. Adsorption of polyelectrolytes on oppositely charged particle surface can cause charge neutralization of the particles and induce flocculation. On the other hand, adsorption of high molecular weight polymers and polyelectrolytes can cause flocculation by bridging between the particles. Currently, there are two possible mechanisms known for polymer bridging [14]: particle/polymer-particle bridging; particle/polymer-polymer/particle bridging. The former is likely when the polymer is long enough and the polymer coverage on particles is low. Bridging by two polymers on different particles occurs mostly when the polymer is long and the surface coverage of particles by polymer is high, and in addition, when the affinity for polymer chains to each other is high enough to overcome the repulsion caused by the entropy reduction due to polymer conformation confinement.

As mentioned earlier, adsorption of polymers on particulate surface can be used to control particle interactions and to modify the particle surface properties [4-7]. Coating of particulate surface by other particles or inorganic layers, on the other hand, have been studied in the past to improve the composition and structural homogeneity of ceramic materials [15,16,17,18,19]. A widely studied example is that of coating of silicon nitride by oxide sols to enhance its sintering using methods such as solution precipitation [20,21,22] and colloidal coating [23,24]. The improvement in homogeneity results in enhanced sintering of the green compacts and permits use of less additives to sinter materials to high density.

Here, a novel method for designing and building nanocomposite particles utilizing colloidal chemistry techniques involving polymer adsorption followed by particle coating to tailor the microstructure of advanced nanomaterials is discussed. In this method, submicrometer size particles are used as core particles and are coated with nanoparticles layer by layer to yield multilayer core-shell composite particles. Polymers which specifically adsorb on both small and large particles are used as bridging aids to enable the coating process and also to enhance the cluster integrity. The composition and microstructure of the multilayer composite particles are tailored as desired by using the appropriate starting materials and coating sequence. Utilizing the same technique for preparing multilayer nanocomposite particles, it will also be possible to prepare multilayer nanocomposite thin films on flat substrates for special composite coating. Such multilayer nanocomposite particles and thin films with specially designed shell/layer structure will enable control of the local composition and environment of nanosized clusters for enhanced properties. To illustrate this processing method, a schematic diagram of the sequence of operations involving controlled polymer bridging is shown in Figure 1.

MATERIALS AND METHODS

Materials

Solids

Core particles: Two different materials, aluminum oxide and silicon nitride powders of different particle size, are studied as core particles for nanoparticle coating. They are selected because of their important applications in structural and electronic ceramics, and also because of their amphoteric nature in aqueous solutions that facilitates control of particle-particle and particle-polymer interactions.

AKP α -alumina powders (AKP-15 and AKP-50) of mean particle size of 0.7 μm and 0.2 μm and obtained from Sumitomo Chemical Co. are used as core particles in this study. The specific surface area of

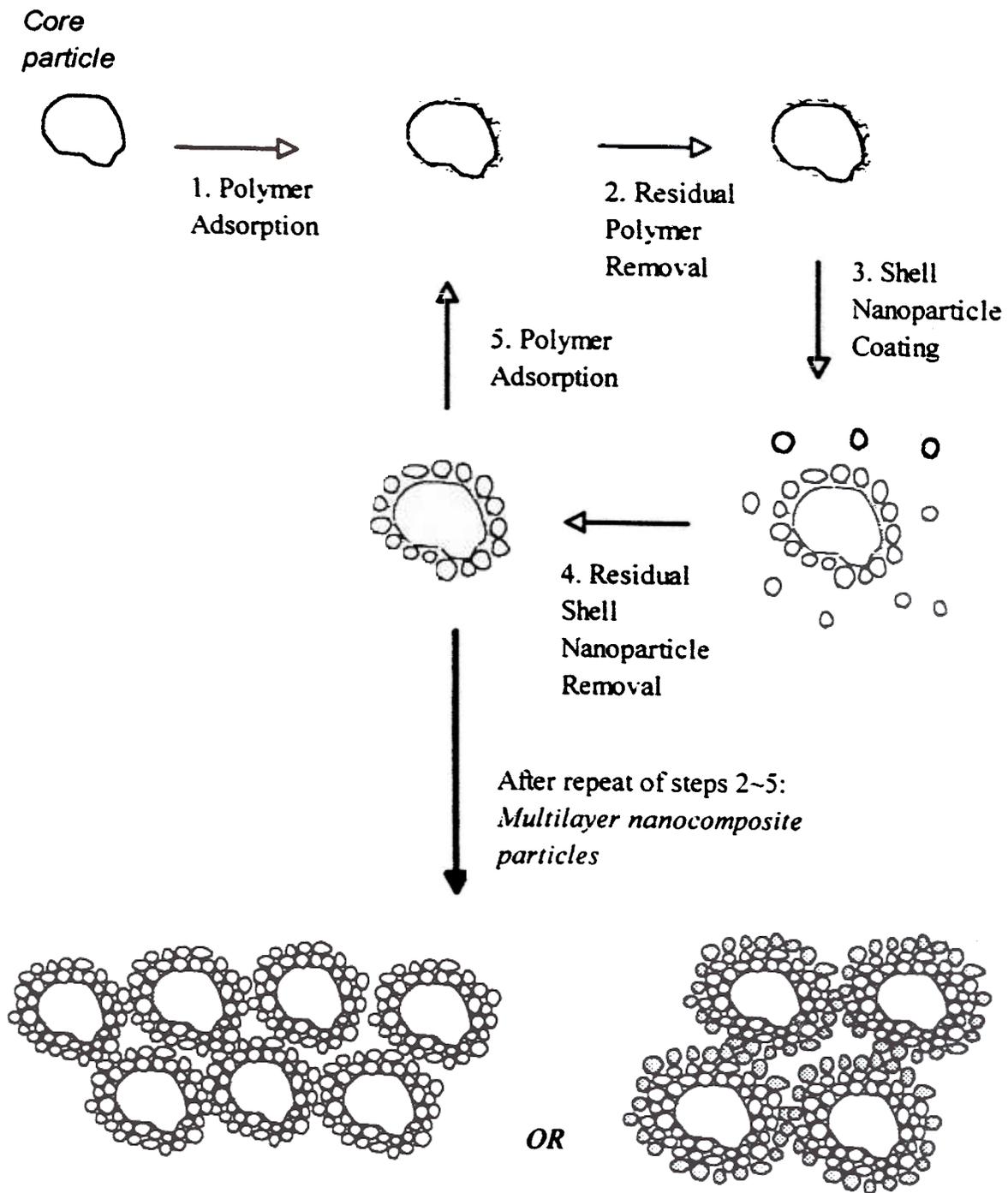


Figure 1. A schematic drawing of the procedure for preparation of engineered nanocomposite particles.

two powders are 3.6 m²/g and 10.9 m²/g respectively as measured by BET nitrogen adsorption. Silicon Nitride powder (UBE SNE-3) used as core particles was obtained from UBE Co. and had a mean particle size of 1.1 μm and a specific surface area of 3.1 m²/g.

Shell particles: Three different nanosize particles from Nanophase technologies co. (Nanotek aluminum oxide, titanium oxide and iron oxide powders) were used as shell layer particles in the coating procedure. The specific surface area of Nanotek aluminum oxide, titanium oxide, and iron oxide are 47, 45, and 51 m²/g respectively. Nanotek aluminum oxide consists mainly of γ-alumina. Nanotek titanium oxide is a mixture of 20% rutile and 80% anatase. Nanotek iron oxide is γ-hematite. Table I lists some properties of the powders used in this study.

Polyacrylic Acid

Polyacrylic acid of two different molecular weights, 2000 and 150000, were selected for the current study because of its popularity as a dispersant and binder in ceramic industry. The weak polyelectrolyte nature of the polyacrylic acid also enables us to control its charge easily through solution pH change. The polyacrylic acid of molecular weight 2000 is purchased from Aldrich Chemical Co. and the 150000 from Polysciences.

TABLE I. Characteristics of the powders used.

Powder Name	Density (g/cm ³)	Materials & Crystal Phase	Specific Surface Area (m ² /g)	Particle Size* (μm)
AKP-50	3.97	α - alumina	10.9	0.1 - 0.3
AKP-15	3.97	α - alumina	3.6	0.6 - 0.8
SNE-3	3.44	α - silicon nitride	3.1	1.1
Nanotek alumina	3.6	γ - alumina	47	
Nanotek titania	3.95	20% rutile - 80% anatase	45	
Nanotek hematite	5.2	γ - hematite	51	0.023

Particle size given by manufacturers: AKPs & SNE-3 by sedimentation method. Nanoteks by BET surface area

Salt and other reagents

Sodium chloride and ammonium nitride were used for the ionic strength control. Both are ACS grade, purchased from Fisher Scientific co., and used as received. Standard solutions of hydrochloric acid and sodium hydroxide /or nitric acid and ammonium hydroxide, purchased from Fisher Scientific co., were used for pH adjustment. The water used was triply distilled and of 10⁻⁶ mhos conductivity.

Methods

Preparation of Dispersions

First, particulate dispersions were prepared using the following procedure prior to polymer adsorption. In the experiments involving dilute suspensions, where the overall solids loading in the system was 5 wt. %, samples of 10 weight percent of suspensions were prepared using 0.03M salt solutions adjusted to the desired pH and then ultrasonicated using a Labline Microtip Ultrasonicator at 40 watt power for 1 minutes and magnetically stirred for 3 hours to wet and equilibrate solid surface completely. The pH of suspensions was adjusted and measured before and after the polymer adsorption.

For experiments conducted at high solids loading (15 volume %), 100 ml of 30 volume percent suspensions were prepared using the same procedure as above. The ultrasonication was done in this case

for 5 minutes at an increased power of 50 watts.

Polymer Adsorption and Desorption Tests

Polymer adsorption density at the solid/liquid interface was determined by measuring the polymer depletion from solution upon contacting it with the particles. For this, sample suspensions prepared using the above procedures were mixed with the same volume of polymer solution for 15 hours. The supernatants were then separated by centrifugation and the polymer concentration analyzed using a Tekmar-Dohrmann DC-90 Total Organic Carbon analyzer. Polymer adsorption density is calculated from the difference between the initial and residual polymer concentrations.

Polymer desorption experiments were carried out following the adsorption experiment in a similar manner. The rule of mass conservation was used to calculate the dilution ratio and the residual polymer concentration after each dilution procedure. Polymer concentration after the desorption procedure was determined and compared with the concentration calculated from the dilution ratio to estimate the polymer desorption.

Nanoparticle coating

Coating of nanosize particles on the polymer coated core particles was conducted by adding desired amounts of nanoparticle suspension into core particle suspensions while stirring. The solid loadings of both suspensions were the same to maintain it constant during the coating procedure. The mixed suspension was further conditioned for 30 minutes. For the investigation on kinetics of coating, the conditioning time was varied from 5 minutes to 3 hours.

Coating results were monitored in several ways. In most cases, the change of zeta potential of the core particles was used to monitor surface modification of core particles. Since the zeta potential of a particle is determined mainly by its surface property, any change in the potential will serve as an indicator of the surface modification of the core particles by nanoparticle coating. Examination of the morphology of the coated particles under Scanning and Transmission Electron Microscopes was also done to check the coating results.

Coating density of nanoparticles on core particles was quantitatively determined by measuring its depletion upon mixing them with each other. Concentration of nanoparticle suspension was measured by monitoring its light transmission using a Shimadzu UV-1201 UV-VIS spectrometer. Differential sedimentation method was used to separate excess nanoparticles from the composite suspension. The optimum centrifugation conditions for separation of nanoparticles from core and composite particles were determined prior to coating density measurements.

Electrokinetics

Zeta potential was measured using a PenKem Laser Zee Meter Model 501. Sample suspensions for the electrokinetic measurements were prepared by diluting the original 5 weight percent or 15 volume percent particulate suspensions with their own supernatants to very dilute concentrations, typically around 50 ppm.

Green body preparation

Ceramic green bodies were prepared from the particulate suspensions using pressure filtration method. Sample suspension was poured into the filter chamber and pressed slightly in the beginning to help start the particle buildup and prevent the breakage of membrane filter. A constant load of higher pressure was then applied to complete the cake formation. The optimum pressure for the green body preparation was determined from the volume variation of the cakes. Ceramic cakes of circular disk shape with 1 inch diameter and approximately 1/4 inch height were prepared by this method for further processing.

Density measurement

The bulk density of a green body consisting of interconnected porosity that is open to the compact surface can be determined either from the measured mass and bulk dimensions of the compact [25] or by

hydrostatic weighting [26] (Archimedes method) with an immersion medium of deionized water. From the difference in mass between the dry sample and the one saturated with liquid, penetration of water into the open pores of the sample is estimated. The apparent density and open porosity of each sample were calculated based on the data from the hydrostatic weighting method.

RESULTS AND DISCUSSIONS

To achieve the proposed processing scheme, exploratory experiments probing the interactions of polymers and particles under various experimental conditions were first conducted. The results are presented in this section following the processing sequence.

When considering the dispersion properties of colloidal particles in aqueous solutions, the electrostatic force is an important factor that governs not only the particle-particle interactions but also the interactions of other organic and salt species with the solid surface. A positively charged particle surface will, for example, repel the adsorption of cationic polyelectrolytes on it unless the energy barrier is overcome by other attractive forces. It is therefore important to characterize the charge nature of particles in aqueous solution. This is normally achieved by measuring the zeta potential of particles, which is defined as the electrostatic potential at the shear plane of particles moving in aqueous medium, at the desired solution pH and salt concentration. Figure 2 shows the zeta potential of the sample powders in 0.03M salt solution. It can be seen that AKP and Nanotek powders are all highly positively charged at low pH. The isoelectric point (i.e.p.) of both AKP15 and AKP50 alumina powders is pH 9 while the i.e.p. of Nanotek alumina is slightly higher at pH 9.4. The i.e.p. of Nanotek hematite and titania are pH 7.8 and 5.4, respectively. The UBE SNE-3 silicon nitride powder has a reported i.e.p. of pH 5.5. The electrokinetic data indicates that these particulate suspensions can be well dispersed at low pH and dispersion and coating of these particles can hence be conducted with minimal aggregation problems.

To use a polymer as the bridging aid between core and shell particles, it is necessary to know the adsorption behavior of polymers under different solution conditions. Figure 3 shows the adsorption of polyacrylic acid on alumina to decrease with increase in pH. Since polyacrylic acid is a weak anionic polyelectrolyte, the pH has an effect on the ionization of its carboxyl groups and thus its interaction with

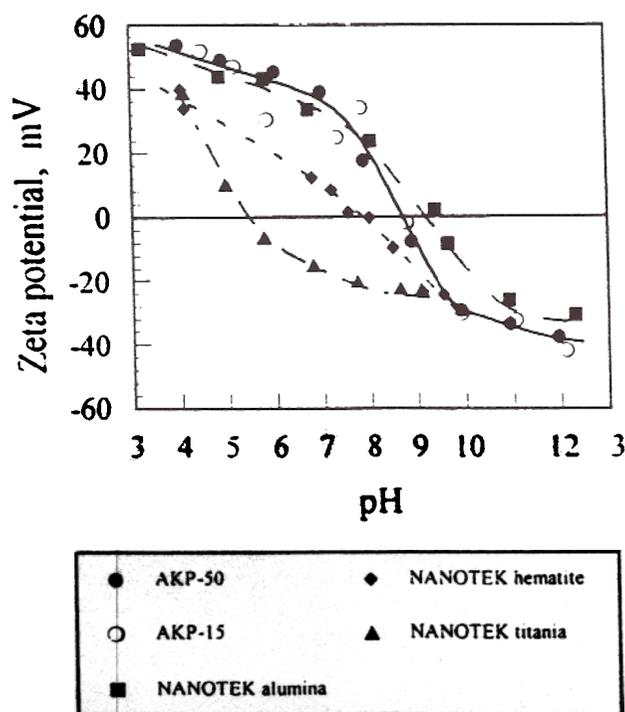


Figure 2. Zeta potential of AKP and Nanotek powders in 0.03M NaCl solution.

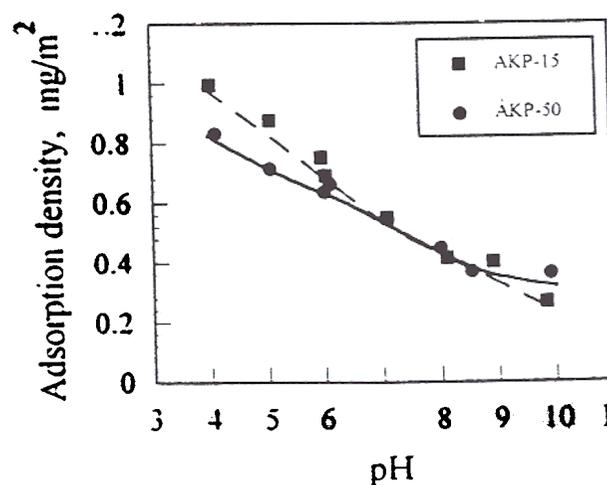


Figure 3. Effect of suspension pH on adsorption of polyacrylic acid on AKP alumina particles. PAA Mw 2000, I 0.03M, s/l = 5 wt.%.

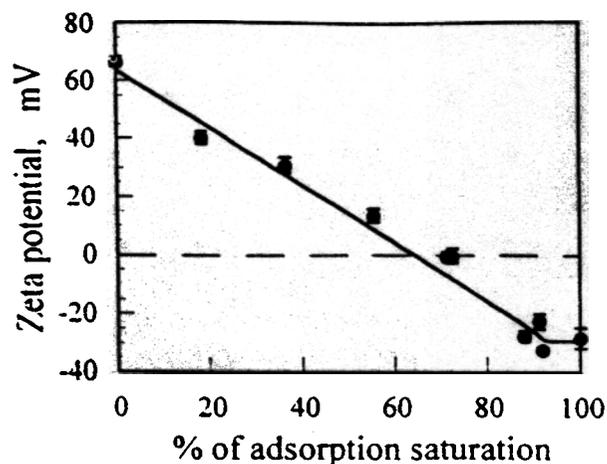


Figure 4. Effect of polyacrylic acid adsorption on the zeta potential of AKP15 alumina particles. PAA Mw 150,000, pH 4, I = 0.03M NaCl, s/l = 5 wt. %

charged surfaces. At high pH, where both polyelectrolyte and particle surface are negatively charged, the adsorption density drops to a minimum as expected.

The adsorption isotherms of polyacrylic acid on AKP alumina were measured at pH 4. The high affinity type adsorption obtained suggests that controlling of desorption of adsorbed polyacrylic acid by dilution is feasible, as also indicated by the fact that at near saturation adsorption region the polymers adsorbed on surface are already at equilibrium with supernatants with nearly no residual polymer. The effect of polyacrylic acid adsorption on the zeta potential of AKP15 alumina particles was measured as a function of polymer adsorption density and the results obtained are given in Figure 4. Adsorption of polyacrylic acid on alumina surface makes the surface reverse its charge from highly positive to negatively charged. The change in the zeta potential of particle is linearly proportional to the adsorption density of polyacrylic acid on surface and it becomes constant near the saturation regime. From this result it was concluded that, to maximize the effect of polymers as bridging aid between particles and to maintain a stable dispersion of polyacrylic acid covered alumina suspension for further processing, it is desirable to obtain at least an 85 percent surface coverage of polyacrylic acid. This is an important criterion that needs to be met during the subsequent processing stages. From the results from electrokinetics and polymer adsorption experiments, it can be concluded that pH 4 is optimum for processing since particles are well dispersed and particle/polymer interaction is strong.

It is to be noted that the key factor for the success of this processing scheme is the successful coating of dispersed nanoparticles on the polymer covered core particle surface. To achieve this, removal of residual polymers in the supernatant is necessary to avoid their interference on the coating process due to adsorption onto nanoparticles and resultant self-flocculation among them. This was done by a dilution procedure to remove the excess free polymer in the supernatant but without removing any polymers adsorbed on the core particles. Experiments conducted to test the washing process showed that, under constant pH conditions, the residual polymer concentration can be lowered to below 1 ppm within three washings. Kinetic studies on the desorption of polyacrylic acid from the core AKP alumina particle surface at constant pH showed that after dilution the adsorbed polymers remained attached even after 42 hours of stirring. Polymer molecular weight did not affect the desorption kinetics. It is thus possible to completely remove the residual polymer without detaching the adsorbed ones. On the other hand, when the suspension pH was changed, some of the attached polymer was found to desorb with the extent of desorption depending on the polymer molecular weight and adsorption density. Normally desorption of polymers from solid surfaces requires the detachment of all its adsorption anchors at more or less the same time. The low resistance of low molecular weight polymers to pH change thus can be understood since they possess less adsorption anchors on the solid surface. Polymers at near saturation adsorption regime are likely to adsorb with more loops and tails and fewer attached train segments and therefore are also vulnerable to the change

in pH. These results suggest that moderate molecular weight polymers are particularly suitable for this processing scheme.

Coating of nanoparticles on the polymer covered AKP alumina was monitored from the zeta potential change of the composite particles. Results of the zeta potential measurements are shown in Figure 5(a) & 5(b). In Figure 5(a), coating of Nanotek alumina on polyacrylic acid covered AKP-50 alumina was monitored via zeta potential change as a function of added Nanotek alumina amount, polymer molecular weight, and adsorption density. Figure 5(b) shows zeta potential change of AKP15 alumina upon coating with Nanotek titania and hematite nanoparticles and that of SNE-3 silicon nitride upon coating with Nanotek alumina. A two stage increase in the zeta potential was found in all these cases and the transition points are found to be close to the 100% surface area ratio of nanoparticle to core particle. This two stage increase in zeta potential of composite particles could be viewed as a combined effect of the shear plane shift caused by nanoparticle attachment and the charge neutralization of the negatively charged polymer coated surface with the positive nanoparticles. The sharp rise in the first stage is proposed to result from the dominating effect of the shear plane shift induced by nanoparticle deposition on core surface. The

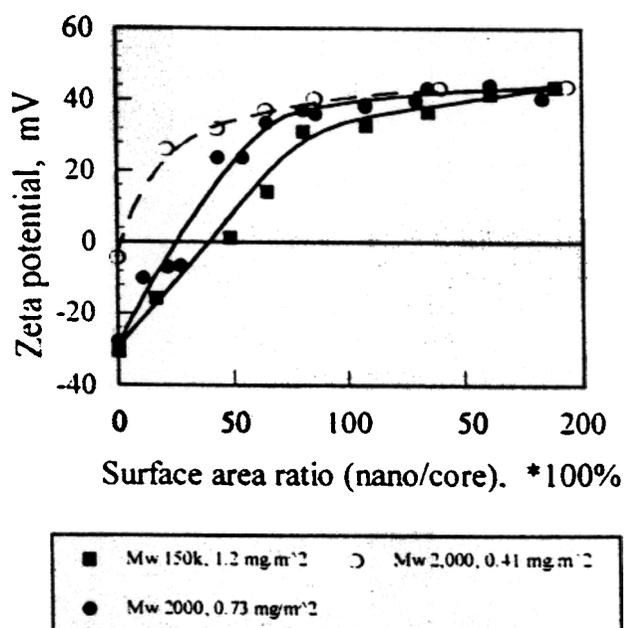


Figure 5(a). Coating of Nanotek alumina on polyacrylic acid covered AKP50 alumina. Effects of polymer molecular weight and adsorption density are also shown in the figure. PH 4, I = 0.03M NaCl, s/l = 5 wt. %

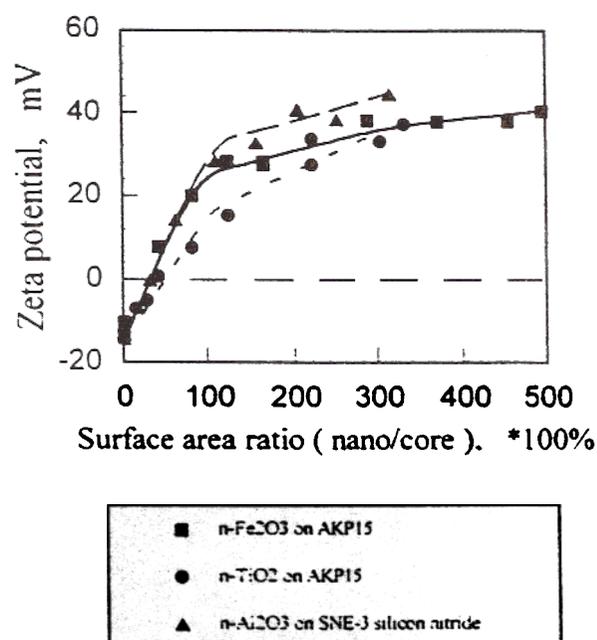


Figure 5(b). Coating of Nanotek particles on polyacrylic acid covered AKP15 and SNE-3 powders. PAA Mw 150,000, pH 4, I = 0.03M NH_4NO_3 , s/l = 5 wt. %

transition point near 100% surface area ratio thus suggests the completion of shear plane shift whereas the subsequent smooth rise in zeta potential is mostly the result of charge neutralization. This distinct two-stage feature of the zeta potential change differentiates the nanoparticle coating from those of planary surface modifications induced by surface oxidation or organic adsorption.

To further characterize the coating of nanoparticles on core particles quantitatively, differential centrifugation method was employed to separate the excess free nanoparticles in the supernatant from the composite particles. Since the settling rate of a particle in solution depends on its density and size, particles of different size can be separated by choosing appropriate centrifugation conditions. After differential centrifugation, the concentration of residual nanoparticles in the supernatant was determined and the calculated coating isotherm of Nanotek alumina on polyacrylic acid covered AKP-15 is shown in Figure 6. The maximum coating density is determined as 62 mg/m^2 . The coating isotherm of Nanotek alumina resembles a high affinity type adsorption isotherm which is often observed for adsorption of polyelectrolytes to oppositely charged surfaces. The coating isotherm was also found to fit Langmuir

adsorption model, as shown in Figure 7, and the theoretical maximum adsorption density is calculated to be 67 mg/m^2 . The similarity between nanoparticle coating and polyelectrolyte adsorption indicates that strong electrostatic attraction between nanoparticles and the polyacrylic acid polymers on core particles is the major driving force for this coating. Another indication of the strong attraction is seen from the kinetics of the coating process. It can be seen from Figure 8 that the coating is complete typically in less than five minutes. The high affinity coating isotherm also suggests that the core particle surface can be coated to

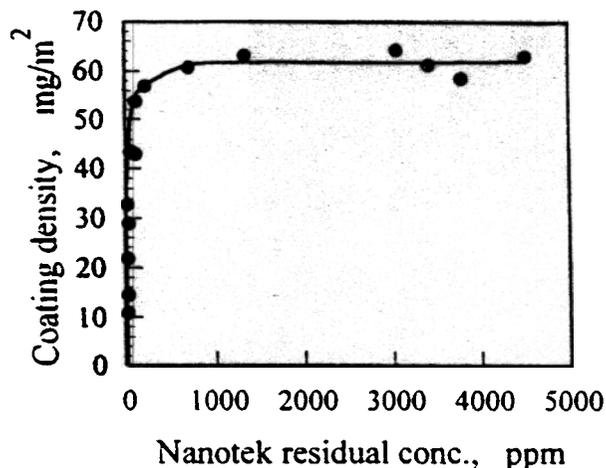


Figure 6. Coating isotherm of Nanotek alumina on polyacrylic acid covered AKP15 alumina. PAA Mw 150,000, pH 4, I = 0.03M NaCl, s/l = 5 wt. %

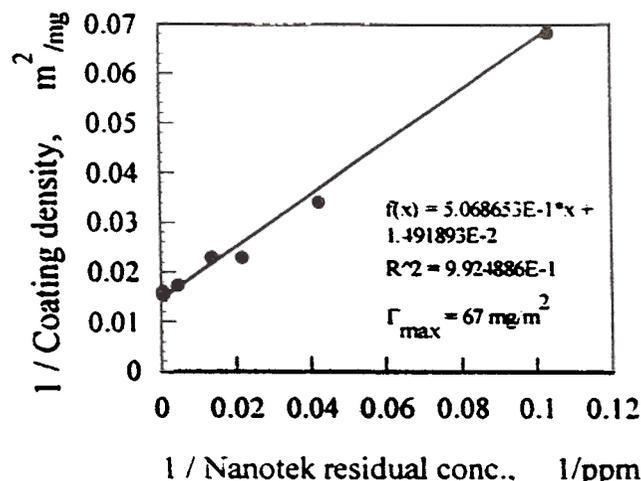


Figure 7. Fitting of the Nanotek alumina coating isotherm with Langmuir model. Core: AKP15, PAA Mw: 150,000, pH 4, I = 0.03M NaCl, s/l = 5 wt. %

near saturation with only very little excess nanoparticles in the supernatant. Therefore by carefully choosing the initial nanoparticle concentration to near-maximum coating, one can minimize the dilution steps needed for removal of excess nanoparticles and continue the coating process to obtain subsequent layers.

Figure 9 shows the results obtained for similar coating process but conducted in concentrated suspensions. Solids loading of the suspensions was increased from 5 weight percent to 15 volume percent. As in the case of dilute system, a two stage increase in zeta potential of composite particles was observed. Kinetics studies of the coating process for full coverage in such concentrated systems also showed a fast process with coating complete in less than five minutes. The successful coating obtained in concentrated systems indicates the feasibility of applying this method for preparing bulk composites as well as surface coatings on various substrates.

It can be seen that, with flexible polymers attached between core and nanoparticles, the nanocomposite particles will have some structural flexibility and can deform under pressure without any permanent change to the structure. The structural flexibility is thus an distinct intrinsic advantage of these composite particles. Figure 10 shows the effect of compression pressure on the green density of compacts prepared from the Nanotek/AKP15 alumina nanocomposite powders. Sample cakes were prepared using a pressure filtration setup following procedures described earlier. Compression pressures ranging from 20 MPa to 100 MPa were applied to sample suspensions to prepare green compacts. The densities of the composite compacts were found to be linearly proportional to the compression pressure, lying between the densities of compacts from AKP15 alone and those from AKP15 and Nanotek alumina mixtures. The correlation between the green density of nanocomposite compacts and the compression pressure indicates the flexible nature of the composite microstructure. The compression pressure can therefore be used to control the microstructure and density of the nanocomposite compacts.

The sintering profile of Nanotek/AKP15 alumina nanocomposites was also investigated. Green compacts made from pressure filtration setup with a compression pressure of 80 MPa were used for the sintering studies. Figure 11 shows the change of compact density and open porosity as a function of

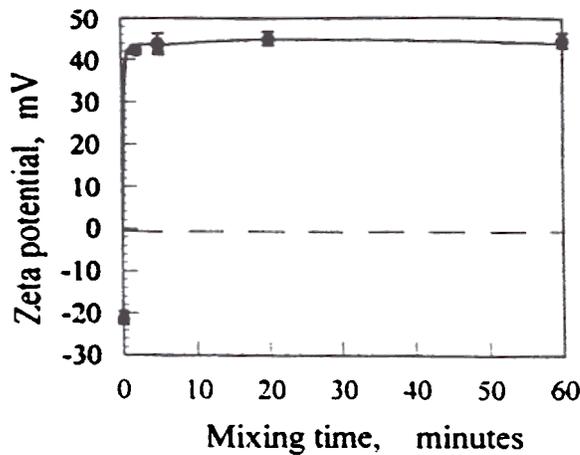


Figure 8. Kinetics of coating Nanotek alumina on polyacrylic acid covered AKP15 alumina particles. PAA Mw 150,000, pH 4, I = 0.03M NaCl, s/l = 5 wt. %

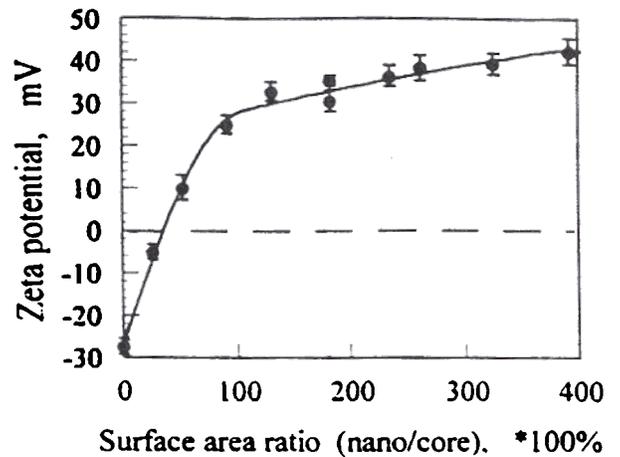


Figure 9. Coating of Nanotek alumina on polyacrylic acid covered AKP15 alumina at 15 volume percent solids loading. PAA Mw 150,000, pH 4, I = 0.03M NH_4NO_3 , s/l = 15 vol. %

sintering temperature. Without further soaking, the alumina nanocomposites can be sintered at 1500 °C in air to 98% theoretical density of α -alumina. Further investigation on the density profile showed that although the bulk density increased steadily with increasing temperature, the apparent density of the composites reached theoretical density at a temperature as low as 1000 °C. Open porosity of the composite compacts remained near 32% at 1000 °C and decreased with increase in sintering temperature. From the results obtained for the density change, it is proposed that the sintering mechanism starts with the surface diffusion and rearrangement of nanoparticles between coarse particles, followed by the rearrangement of coarse particles in the microstructure until full sintering is reached. It is clear that opportunity exists also to obtain superior compacts by optimizing the parameters in the compacting and sintering stages.

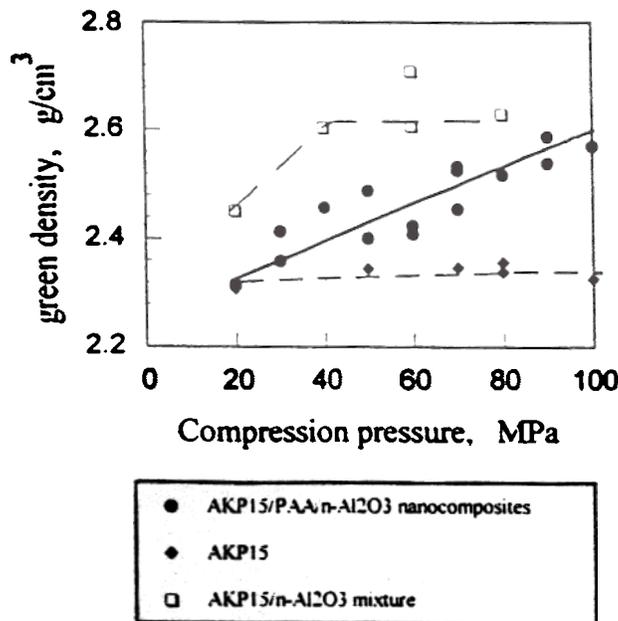


Figure 10. Effect of compression pressure on composite green density. PAA Mw 150,000, pH 4, I = 0.03M NH_4NO_3 .

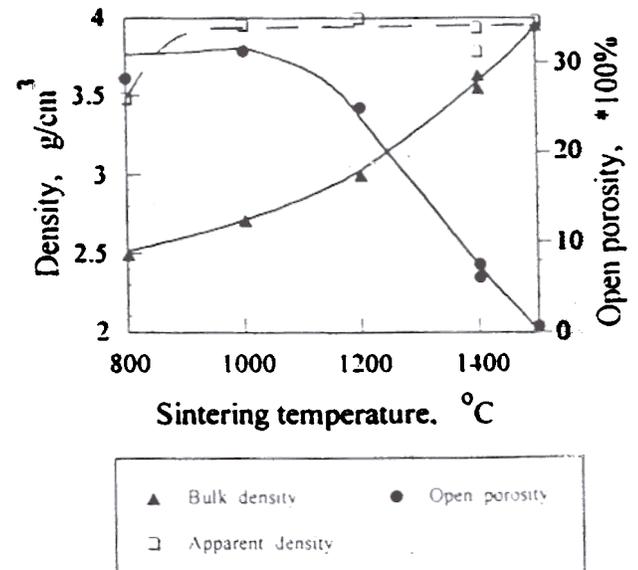


Figure 11. Sintering profile of alumina nanocomposites. System: AKP15/PAA/n-alumina, firing in air, heating rate: 100°C/hr, cooling rate: 125°C/hr, no soaking.

CONCLUSIONS

In summary, the new method proposed for the preparation of nanocomposite particles is shown to be feasible using controlled polymer adsorption and dilution so that coarse particles are modified by polymer adsorption yet the residual polymer in the supernatant is removed to avoid self-flocculation of nanoparticles. Coating of nanoparticles on coarse particles was successfully conducted in both dilute and concentrated suspensions. Green compacts made from the composite particles suggests structural flexibility reflecting the elastic nature of the composite particles. It can be seen that using this processing method, it is possible to prepare nanocomposite particles of controlled core-shell structure and composition as building blocks for the fabrication of nanocomposites and composite coatings.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Engineering Research Center (ERC) for Particle Science and Technology at the University of Florida, the National Science Foundation (NSF) grant #EEC-94-02989, and the Industrial Partners of the ERC.

REFERENCES

- 1 R.W. Siegel, in Physics of New Materials, edited by F.E. Fujita. (Springer-Verlag, Berlin, 1994), p. 65.
- 2 D. Chakravorty and A.K. Giri, in Chemistry of Advanced Materials, edited by C.N.R. Rao. (Blackwell Scientific, London, 1993), pp. 217-235.
- 3 I.A. Aksay, in Forming of Ceramics, Advances in Ceramics Vol.9, edited by J.A. Mangels and G.L. Messing. (The American Ceramic Society, Columbus, OH, 1984), pp. 94-104.
- 4 Th. F. Tadros, Colloids & Surfaces, **18**, 137 - 173 (1986).
- 5 C. Simon, in Coagulation and Flocculation: Theory and Applications, edited by B. Dobias, (Marcel Dekker, New York, 1993), pp. 495 - 537.
- 6 J. Cesarano III, A. Aksay and A. Bleier, J. Am. Ceram. Soc. **71** [4], 250 - 255 (1988).
P. Somasundaran and X. Yu, Adv. in Coll. and Inter. Sci., **53**, 31 - 49 (1994)
- 8 G.J. Fler, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, and B. Vincent, Polymers at Interfaces, (Chapman & Hall, London, 1993), p. 1.
- 9 T. Sato and R. Ruch, Stabilization of Colloidal Dispersion by Polymer Adsorption, Surfactant Science Series Vol. 9, (Marcel Dekker: New York, 1980), p. 1.
- 10 G.J. Fler and J.M.H.M. Scheutjens, in Coagulation and Flocculation: Theory and Applications, Edited by B. Dobias. (Marcel Dekker, New York, 1993), pp. 209 - 263.
V.K. La Mer and R.H. Jr. Smellie, J. Colloid Inter. Sci., **11**, 704 - 709 (1956).
- 12 X. Yu and P. Somasundaran, J. Colloid Inter. Sci., **177**, 283 - 287 (1996).
- 3 E.G.M. Pelssers, M.A. Cohen Stuart and G.J. Fler, Colloids & Surfaces, **38**, 15 - 25 (1989).

- 4 M.J. Rosen, Surfactants and Interfacial Phenomena, (John Wiley and Sons: New York, 1978). p 40.
- 5 P.G. Desai and Z. Xu. *J. Am. Ceram. Soc.*, **78** [11], 2881 - 2888 (1995).
- 16 C. Marquez-Alvarez, J.L. Fierro, A. Guerrero-Ruiz, and I. Rodriguez-Ramos, *J. Colloid Int. Sci.*, **159**, 454 - 459 (1993).
- 17 M. Ohmori and E. Matijevic, *J. Colloid Int. Sci.*, **160**, 288 - 292 (1993).
- 8 H.M. Jang, J.H. Moon, and C.W. Jang, *J. Am. Ceram. Soc.*, **75** [12], 3369 - 3376 (1992).
- 19 C. Hu and M.N. Rahaman, *J. Am. Ceram. Soc.*, **75** [8], 2066 - 2070 (1992).
- 20 E. Luther, F.E. Lange, and D.S. Pearson, *J. Am. Ceram. Soc.*, **78** [8], 2009 - 2014 (1995).
- 21 C.M. Wang, *J. Mat. Sci.*, **31**, 4709 - 4718 (1996).
- 22 T.M. Shaw and B.A. Pethica, *J. Am. Ceram. Soc.*, **69** [2], 88 - 93 (1986).
- 23 S.G. Malghan, P.S. Wang, A. Sivakumar, and P. Somasundaran. *Composite Interfaces*, **1** [3], 193 - 210 (1993).
- 24 E. Liden, M. Persson, E. Carlstrom, and R. Carlsson, *J. Am. Ceram. Soc.*, **74** [6], 1335 - 1339 (1991).
- 25 J.E. Shields, in Ceramics and Glasses, *Engineering Materials Handbook Vol. 4*, (ASM International, Materials Park, OH, 1991), pp. 580 - 584.
- 26 N.A. Pratten, *J. Mater. Sci.*, **16**, 1737 - 747 (1981).