

# Effect of Polyethylenimine on Hydrolysis and Dispersion Properties of Aqueous Si<sub>3</sub>N<sub>4</sub> Suspensions

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**The roles of polyethylenimine (PEI) in the hydrolysis and dispersion properties of aqueous Si<sub>3</sub>N<sub>4</sub> suspensions were studied in terms of the hydrolysis, adsorption, electrokinetic, and rheological measurements. It was found that the pH change of the suspensions in the acidic environment could be minimized in the presence of  $\geq 0.5$  dwb% PEI. The ammonia and oxygen measurements suggest that this phenomenon is primarily attributed to the buffer mechanism generated by the ionized PEI, instead of the protection mechanism. The constant pH enables the suspensions to retain a better stability with time at acidic pH. The adsorption of PEI on Si<sub>3</sub>N<sub>4</sub> is a high-affinity type at highly basic pH, but is a low-affinity type at acidic pH. As the PEI amount increases, the adsorption shifts the isoelectric point (IEP) of Si<sub>3</sub>N<sub>4</sub> from pH 5.9 to pH  $\sim 11$  until complete coverage is attained. The stability of Si<sub>3</sub>N<sub>4</sub> suspensions is found to depend strongly on the saturated adsorption of PEI, which is as a function of the pH and PEI amount. Once the saturated adsorption limit is reached, the excess free PEI molecules become more detrimental to the stability with increased solid loading. The stabilization mechanisms of Si<sub>3</sub>N<sub>4</sub> suspensions by PEI were discussed in detail.**

## I. Introduction

COLLOIDAL processing has received much interest in producing advanced Si<sub>3</sub>N<sub>4</sub> ceramics because of the potential capacities of minimizing strength-degrading defects, forming complex shapes, and tailoring microstructure, compared with the conventional dry-powder pressing method.<sup>1–3</sup> For example, the production of highly textured ceramics can be readily accomplished by orientating ceramic particles through tape casting of large seed particles-containing slurry<sup>4</sup> or through slurry consolidation in a strong magnetic field.<sup>5</sup> In colloidal processing, the dispersion and stability of the suspensions are of particular importance in controlling the quality of the final products. Owing to the safety, economic, and environment considerations, much attention has been focused on the aqueous Si<sub>3</sub>N<sub>4</sub> processing.<sup>6–11</sup>

The most common polyelectrolytes used for dispersing aqueous Si<sub>3</sub>N<sub>4</sub> suspensions are acrylic-based polymers, such as poly(acrylic acid) (PAA) or its ammonium salt (PAA-NH<sub>4</sub>), known as anionic polyelectrolytes.<sup>6–11</sup> These studies showed that better stabilization of Si<sub>3</sub>N<sub>4</sub> suspensions by PAA occurs in the alkaline region of pH > 9. As PAA is fully ionized and remains in the solution as free polymers with a stretched configuration at pH > 9, the stabilization is widely believed to be dominated by

the electrostatic interactions rather than electrosteric interactions.<sup>9–11</sup> In general, the effectiveness of polymer dispersants is related to the Lewis acid–base character of the powders. It is generally accepted that the isoelectric point (IEP) of Si<sub>3</sub>N<sub>4</sub> powders is determined by the relative site density of acidic silanol (Si–OH) and basic amine (Si<sub>2</sub>–NH) groups present mainly on the surface of Si<sub>3</sub>N<sub>4</sub> powders.<sup>12</sup> The presence of a large number of silanol groups shifts the IEP to lower pH values, whereas a large number of amine groups shifts the IEP to high values. The IEP of commercial Si<sub>3</sub>N<sub>4</sub> powders was reported to vary from pH  $\approx 3$  to 9, depending on the powder origin,<sup>6–9,12,13</sup> hydrolysis,<sup>12,13</sup> and oxidation.<sup>6,14</sup> A commercial Si<sub>3</sub>N<sub>4</sub> powder (UBE SN-E10), one of the most widely used Si<sub>3</sub>N<sub>4</sub> powders, was reported to be mildly acidic (IEP < 7).<sup>9,11–13</sup> This means that the cationic polymers may be more effective than the anionic ones in stabilizing the aqueous suspensions of this powder.

As a cationic polyelectrolyte, polyethylenimine (PEI) has been widely used to stabilize aqueous suspensions of various ceramic powders, such as SiO<sub>2</sub>,<sup>15,16</sup> ZrO<sub>2</sub>,<sup>17,18</sup> TiO<sub>2</sub>,<sup>19</sup> ZnO,<sup>20</sup> Y<sub>2</sub>O<sub>3</sub>,<sup>21</sup> SiC,<sup>15,22–26</sup> TiC,<sup>27</sup> and TiN,<sup>28</sup> similar to the anionic PAA. PEI is a highly branched macromolecule with a general chemical formula of [–CH<sub>2</sub>–CH<sub>2</sub>–NH–]<sub>n</sub>.<sup>29</sup> The unionized or partially ionized PEI is readily adsorbed to the negatively charged surface and thus provides an “electrosteric” or “steric” stabilization for ceramic suspensions. Zhang *et al.*<sup>30</sup> firstly made an attempt to use PEI as a dispersant to stabilize the aqueous Si<sub>3</sub>N<sub>4</sub> suspensions. They reported that in the presence of PEI, the optimum pH is not at the acidic and neutral pH regions, but at the basic region of > pH 9 and even near the pH  $\approx 10.8$ , where PEI is essentially uncharged. However, a full understanding of the role of PEI in the aqueous Si<sub>3</sub>N<sub>4</sub> dispersion is difficult to establish because of the limited experimental data.

In addition, Si<sub>3</sub>N<sub>4</sub> powder tends to hydrolyze in water, resulting in the time-dependent behavior of the suspensions.<sup>13,31,32</sup> Unfortunately, less attention has been paid to the protection of Si<sub>3</sub>N<sub>4</sub> powder against hydrolysis in aqueous media, not as the case of AlN powder.<sup>33–35</sup> This could be due to three major facts: (i) the hydrolysis of Si<sub>3</sub>N<sub>4</sub> is not as intense as that of AlN; (ii) the Si<sub>3</sub>N<sub>4</sub> powder is usually dispersed at the basic pH range, where the formation and dissolution of the oxide layer (SiO<sub>2</sub>) enhance the suspension stability because of the formation of a more negatively charged surface; and (iii) the polymer dispersants (e.g. PAA) probably play an important role in suppressing simultaneously the hydrolysis of Si<sub>3</sub>N<sub>4</sub>, to some extent, similar to the case of AlN.<sup>33–35</sup> Despite this, the control of hydrolysis is necessary for improving the stability of aqueous Si<sub>3</sub>N<sub>4</sub> suspensions. One effective method is to form a thicker layer of SiO<sub>2</sub> on the Si<sub>3</sub>N<sub>4</sub> particle by pre-oxidation treatment.<sup>6,14,36</sup> Moreno *et al.*<sup>8</sup> reported that tetramethylammonium hydroxide (TMAH) as a dispersant can provide a protective layer against hydrolysis for Si<sub>3</sub>N<sub>4</sub> powder by adsorption. Therefore, we guess that as a polymer dispersant, PEI may play a positive role in protecting Si<sub>3</sub>N<sub>4</sub> powder against hydrolysis in water.

The objective of this work is to carry out a systematic investigation of the aqueous dispersion of Si<sub>3</sub>N<sub>4</sub> powder with PEI dispersant. The contents involved in the present work include:

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(1) the effect of PEI on the hydrolysis of  $\text{Si}_3\text{N}_4$  in water was studied at the acidic and basic environments; (2) adsorption behavior of PEI on  $\text{Si}_3\text{N}_4$  was characterized to understand and establish the stabilization mechanisms; (3) electrokinetic behavior of  $\text{Si}_3\text{N}_4$  versus the pH and PEI amount was characterized by electroacoustic measurements on the concentrated suspensions; and (4) the stability of  $\text{Si}_3\text{N}_4$  suspensions was evaluated by rheological measurements as a function of the pH, PEI amount, solid loading, and stirring time (hydrolysis effect). Our goal is to provide a better understanding of the role of PEI in the aqueous  $\text{Si}_3\text{N}_4$  dispersion in this study.

## II. Experimental Procedure

### (1) Materials

A commercial  $\alpha$ - $\text{Si}_3\text{N}_4$  powder (SN E10, UBE Industries, Tokyo, Japan) was used in this study. As the manufacturer claimed, this powder had a specific surface area of  $11.1 \text{ m}^2/\text{g}$  and an oxygen content of 1.27 wt%, and major metallic impurities (like Al, Fe, Ca) with levels of <100 ppm. According to the electroacoustic measurements, which will be described later, the  $\text{Si}_3\text{N}_4$  powder had a minimum average particle size of  $0.51 \mu\text{m}$  in suspension. PEI, a highly branched macromolecule with an average molecular weight of 10000 (Wako Pure Chemical Industries Ltd., Tokyo, Japan), was chosen as a dispersant. The distilled water was used as the dispersing medium.

### (2) Suspension Preparation

The suspensions used for all measurements were prepared at powder volume percentage. The density of  $\alpha$ - $\text{Si}_3\text{N}_4$ ,  $3.19 \text{ g}/\text{cm}^3$  was used for this calculation. The procedure of suspension preparation was as follows: (i) the 5 wt% stock PEI solution was pre-mixed with the distilled water in a beaker by magnetic stirring; (ii) the dry powder was slowly added to the pre-mixed solutions by stirring; (iii) the suspensions were then ultrasonicated for 5 min to break up the agglomerates, using an ultrasonic horn (USP-600, Shimadzu Inc., Kyoto, Japan) at an output power of 160 W in an ice bath; and (iv) after ultrasonication, the suspensions were kept continuously stirred before analysis. The suspension pH was adjusted using reagent-grade hydrochloric acid (HCl) and potassium hydroxide (KOH). Without particular illustration, the pH adjustments were conducted from the initial (or native) pH points of the suspensions prepared by procedures (i), (ii), and (iii), using KOH solution to increase the pH and HCl solution to decrease the pH in the opposite directions. The added PEI amount was expressed as the dry weight percentage of the  $\text{Si}_3\text{N}_4$  powder basis (dwb%).

### (3) Hydrolysis Test

The hydrolysis tests were performed at two different starting pH values, pH 4 and 10, using the 5 and 10 vol% suspensions with various amounts of PEI, prepared by the procedure described above. Then, the beakers were sealed with parafilm<sup>®</sup> and the suspensions were kept continuously stirred at a mild speed. The pH values were monitored at the predetermined time intervals. Then, the suspensions were centrifuged at 5000 rpm for 30 min. After decanting the supernatant, the sediments were dried in an oven at  $50^\circ\text{C}$  for 24 h, and then at  $110^\circ\text{C}$  for 24 h. The oxygen content in the dried powder was determined by an oxygen/nitrogen analyzer (Model TC-436, LECO Co., St. Joseph, MI). Furthermore, the supernatants were filtered through a  $0.2 \mu\text{m}$  membrane. Then, the amount of ammonia leached into the solutions was measured using a pH-ion meter equipped with an ammonium ion selective electrode (Model 5002-10C, HORIBA Ltd., Kyoto, Japan). As the electrode is sensitive only to free ammonia, the pH of each sample was adjusted to pH > 12 using 10 N NaOH before measurement. This converts all  $\text{NH}_4^+$  into the free  $\text{NH}_3$  form. Three different concentrations of standard  $\text{NH}_4\text{Cl}$  solutions, 1, 10, and 100 mg/L, were used to calibrate the electrode.

### (4) Adsorption Measurements

The adsorption of PEI on  $\text{Si}_3\text{N}_4$  was determined by thermogravimetric analysis (Thermoplus TG 8120, Rigaku Co., Tokyo, Japan). The 5 vol%  $\text{Si}_3\text{N}_4$  suspensions with various amounts of PEI were prepared by the procedure described above. The suspension pH was adjusted to pH 4 and 10 using 1 N KOH and 1 N HCl, respectively. Then, the suspensions were kept continuously stirred for 4 h to reach equilibrium. Then, the suspensions were centrifuged at 5000 rpm for 30 min. As a reference, the sediments from the suspensions without PEI at pH 4 and 10 were also prepared using the same procedure. After decanting the supernatant, the sediments were dried in an oven at  $50^\circ\text{C}$  for 24 h, and then at  $110^\circ\text{C}$  for 24 h. Figure 1 gives the thermogravimetric analysis curves of pure PEI and a typical  $\text{Si}_3\text{N}_4$  powder adsorbed by PEI at a heating rate of  $10^\circ\text{C}$  in air. The decomposition of pure PEI occurs mainly between  $250^\circ$  and  $350^\circ\text{C}$ , similar to the report of Wang and Wei.<sup>22</sup> Accordingly, the powder adsorbed by PEI shows a clear weight loss between  $200^\circ$  and  $500^\circ\text{C}$ , which was used to determine the adsorbed amount of PEI.

### (5) $\zeta$ -Potential Measurements

The  $\zeta$ -potential measurements were performed for the 5 vol%  $\text{Si}_3\text{N}_4$  suspensions without and with the desired amounts of PEI, which were prepared by the procedure described above, using an acoustic & electroacoustic spectrometer (Model DT-1200, Dispersion Technology Inc., Bedford Hills, NY). No background electrolyte solution was used, e.g. KCl, NaCl, etc. The  $\zeta$  potentials were measured as a function of pH by the titration of a single suspension because of the advantages of the least amount of time and material required.<sup>37</sup> Note that all 5 vol%  $\text{Si}_3\text{N}_4$  suspensions with and without PEI showed initial pH values > 8. As the PEI amount increases to 1.5 dwb%, the pH increases from 8.3 to 10.3. Thus, the titration was automatically performed with a built-in autotitrator from the initially basic pH to 12 by 1 N KOH, and then, a back titration was performed from pH 12 to 3 by 1 N HCl. It is worth mentioning that this titration method has no effect on the IEP of  $\text{Si}_3\text{N}_4$ , but the  $\zeta$ -potential value from descending pH by back titration of 1 N HCl is slightly lower than that from initially ascending pH by 1 N KOH from the initial pH to 12. This is due to the fact that the increased concentration of salt ions ( $\text{K}^+$  and  $\text{Cl}^-$ ) causes the compression of the electrical double layer (EDL), thereby decreasing the  $\zeta$ -potential values. The  $\zeta$ -potential-pH curves presented in this study were obtained from the measured data by the back titration from pH 12 to 3. The details of the theory and applications of this measuring technique have been described in some review papers.<sup>38</sup>

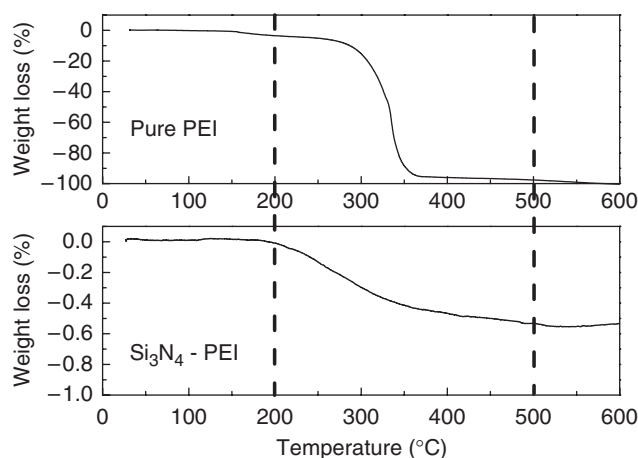


Fig. 1. Thermogravimetric (TG) curves of pure PEI and a typical  $\text{Si}_3\text{N}_4$  powder adsorbed by polyethylenimine (PEI) ( $\text{Si}_3\text{N}_4$ -PEI) at a heating rate of  $10^\circ\text{C}/\text{min}$  in air.

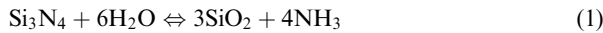
(6) Rheological Measurements

The rheological measurements of the suspensions were conducted with a cone-type viscometer (RC-500, Toki Sangyo Co. Ltd., Tokyo, Japan) at a constant temperature of 25°C. Considering the fact that in the presence of PEI, the initial suspensions with solid loadings of 10 and 30 vol% have highly basic pH values of >9.5, and this value moves to more highly basic pH range (~11) with increasing PEI amounts, all viscosity measurements as a function of pH were conducted only by descending pH via acid titration (HCl). All the initial suspensions were prepared by means of the procedure described above. Each suspension with a conditioned pH point was obtained by stirring for 20 min. All measurements were performed immediately when the suspensions were conditionally prepared.

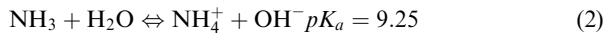
III. Results and Discussion

(1) Hydrolysis Behavior

It is recognized that the hydrolysis of Si<sub>3</sub>N<sub>4</sub> powder in water occurs through the following reaction:



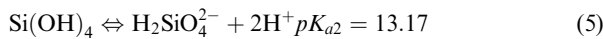
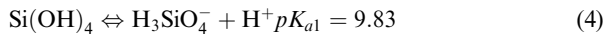
The release and dissolution of NH<sub>3</sub> lead to an increase in suspension pH as follows:



Moreover, the oxidized surface layer dissolves in the following way:



Again, the Si(OH)<sub>4</sub> dissociates in the following way:



According to reactions (4) and (5), reaction (3) is catalyzed by hydroxyl ion (OH<sup>-</sup>). The previous leaching experiments revealed that the surface dissolution behavior of Si<sub>3</sub>N<sub>4</sub> powder in water is similar to that of amorphous SiO<sub>2</sub> in water.<sup>12,13,31,32</sup> The dissolution rate of surface oxidized layer is low in the pH range of pH <9, but is high in the pH range of pH >9.<sup>39</sup>

Figure 2 gives the pH change with stirring time for the 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with various amounts of PEI at the initial pH 4 and 10. In the absence of PEI or the presence of PEI of lower than 0.5 dwb%, the pH shows a rapid increase from the initial pH 4 to above 9 (~9.2) after stirring for 48 h. This could be attributed to the release of NH<sub>3</sub> species because of the hydrolysis of Si<sub>3</sub>N<sub>4</sub>, according to reactions (1) and (2). However, when the amount of PEI reaches 0.5 dwb%, the pH shows a very slow increase, only close to pH 5. In the case of initial pH 10, the suspension pH change with stirring also depends on the amount of PEI, although this dependence is not as strong as the case of the initial pH 4. Without and with 0.05 dwb% PEI, both the suspensions show a steep decrease from pH 10 to ~9.7 within the initial 4 h. With further increased time, the rate of the decrease in pH slows down. After 48 h, the pH reaches ~9.5. This is attributed to the dissociation of the soluble SiO<sub>2</sub> (Si(OH)<sub>4</sub>) through reaction (4), as is observed by Zhang *et al.*<sup>30</sup> However, when the PEI amount reaches 0.5 dwb%, the suspensions do not show a steep decrease in pH within the initial 4 h, which is different from the cases of without and with 0.05 dwb%. Even with the further stirring, the suspension shows no significant change in pH. This means that in the basic pH, PEI also allows the Si<sub>3</sub>N<sub>4</sub> suspensions to retain a more stable pH. Moreover, it is shown that when no PEI is added, the suspension pH eventually approaches near pH 9.3 with time whether at an initial pH 4 or at an initial pH 10. This is attributed to the buffer effect pro-

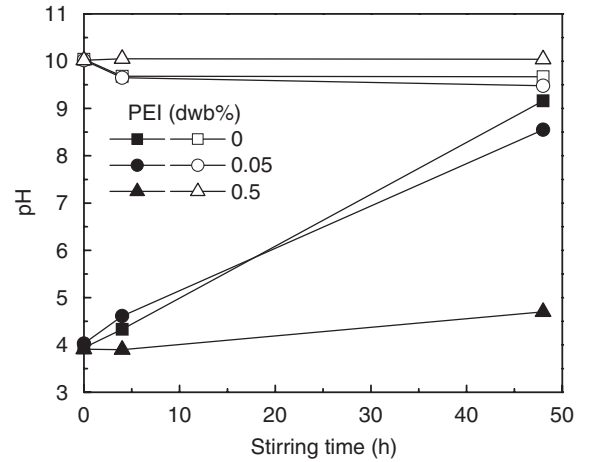
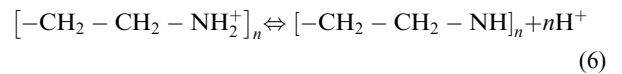


Fig. 2. pH versus stirring time for 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with various amounts of polyethylenimine (PEI) at the initial pH 4 and 10, representing the acidic and basic environments, respectively.

vided by reactions (2) and (4), which makes the final pH remain in the range of pH = 9–10.

Figure 3 further gives the effect of stirring time on the pH of the 10 vol% Si<sub>3</sub>N<sub>4</sub> suspensions at the initial pH 4. It is very clear that when the PEI amount reaches 0.5 dwb% and above, the suspensions show a very small increase in pH, less than one pH unit within the stirring time of 75 h. The present result reveals that the presence of PEI does result in the stabilization of the pH of aqueous Si<sub>3</sub>N<sub>4</sub> suspensions to a larger extent whether at the acidic region or at the alkaline region, particularly in the acidic region. One possible mechanism for this phenomenon is the protection mechanism, in which the adsorption of PEI molecules prevents the hydrolysis reaction (1) of Si<sub>3</sub>N<sub>4</sub> by forming a surface-protective layer, similar to the protection of AlN powder against hydrolysis by anionic polymers, such as PAA.<sup>34,35</sup> Laarz and Bergström also reported that the WC-Co suspensions with PEI show no change in the pH with time, suggesting a suppressed dissolution of WC.<sup>40</sup> The other possible mechanism is the buffer effect generated by ionized PEI molecules. At the acidic pH 4, PEI molecule is highly ionized. Thus, the OH<sup>-</sup> generated by reactions (1) and (2) can react with the H<sup>+</sup> released from the ionized PEI by the reaction:



Then, the pH of the system does not change so much. Table I gives the effect of stirring time on the amount of ammonia

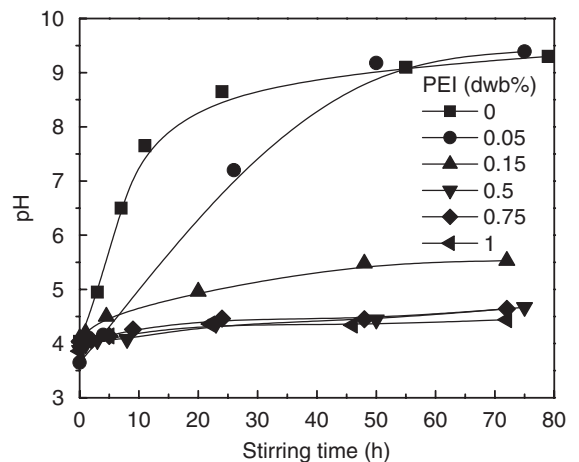


Fig. 3. pH versus stirring time for 10 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with various amounts of polyethylenimine (PEI) at the initial pH 4.



**Table I.** Amount of Ammonia (NH<sub>3</sub>) Released into the 5 vol% Si<sub>3</sub>N<sub>4</sub> Suspensions without and with 0.5 dwb% PEI as a Function of Stirring Time at the Initial pH 4

PEI amount (dwb%)	Stirring time (h)	pH <sup>†</sup>	NH <sub>3</sub> amount (μmol/m <sup>2</sup> ) <sup>‡</sup>
0	4	4.3	2.11
	48	9.2	2.21
0.5	4	4	1.36
	48	4.7	2.13

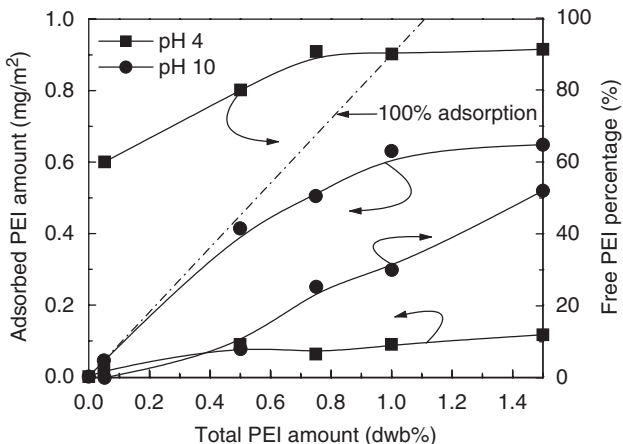
<sup>†</sup>pH = monitored pH value of suspension after stirring for different time.

<sup>‡</sup>Amount normalized to the specific surface area of Si<sub>3</sub>N<sub>4</sub> powder. PEI, polyethylenimine.

released into the 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions without and with 0.5 dwb% PEI at the initial pH 4. It can be found that in both cases, the amount of NH<sub>3</sub> released shows an increase with increased stirring time. Nevertheless, the amount of NH<sub>3</sub> shows a substantially larger increase with time in the presence of 0.5 dwb% PEI than in the absence of PEI. This could be associated with the higher evaporation loss of free NH<sub>3</sub> in the latter during stirring because the increased pH converts more NH<sub>4</sub><sup>+</sup> ions into free NH<sub>3</sub>. The result indicates that in the presence of 0.5 dwb% PEI, reaction (1) also proceeds with stirring, compared with the absence of PEI. Moreover, Table II shows that there is almost no difference in the oxygen content between the hydrolyzed Si<sub>3</sub>N<sub>4</sub> powders without and with 1 dwb% PEI. As a result, it can be concluded that the minimized change in the pH of the suspensions, particularly at the acidic pH, is primarily due to the buffer mechanism provided by PEI, instead of the protection mechanism. This buffer mechanism is achieved when the amount of PEI reaches up to 0.5 dwb%.

## (2) Adsorption of PEI

Figure 4 gives the adsorption behavior of PEI on the surface of Si<sub>3</sub>N<sub>4</sub> particles at pH 4 and 10. In the figure, the dotted line represents complete adsorption of PEI molecules on the solid surface, and free PEI percentage represents the percentage of the nonadsorbed PEI present in solution based on the total amount of PEI added. It is clear that there is a significant difference in the adsorption behavior between pH 4 and 10. At pH 10, as the PEI amount increases, most of the PEI molecules are adsorbed onto the solid surface before a saturated adsorption is attained; particularly, almost 100% PEI are adsorbed to the solid surface at a low PEI amount (<0.5 dwb%), suggesting a high-affinity adsorption type. Once the adsorption exceeds the saturation limit, the nonadsorbed PEI amount significantly increases. However, at pH 4, most of PEI molecules are not adsorbed to the solid surface, but remain as free polymer in the solution, suggesting a low-affinity adsorption type. At pH 4, the saturated adsorption amount is approximately 0.09 mg/m<sup>2</sup>, corresponding to the added PEI amount of about 0.5 dwb%. But the saturated adsorption amount is approximately 0.65 mg/m<sup>2</sup> at pH 10, corresponding to the added PEI amount of 1.5 dwb%. This means that the saturated adsorption decreases as the pH decreases. This is similar to the adsorption of PEI on SiO<sub>2</sub>,<sup>25,29</sup> SiC,<sup>23,24,26</sup> ZrO<sub>2</sub>,<sup>17,18</sup> and TiO<sub>2</sub>.<sup>19</sup> This adsorption behavior is related to the segment charge density of PEI molecule and its conformational

**Fig. 4.** Adsorption isotherms and free PEI percentage of PEI on Si<sub>3</sub>N<sub>4</sub> versus amount of PEI for 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions at pH 4 and 10.

transition with pH, and the charging character of the powder surface.

At pH ~11, PEI is essentially uncharged ( $\alpha = 0$ ) and exists in a compact coiled conformation because of hydrophobic interactions. The strong nonelectrostatic affinity enables almost all neutral PEI molecules to adsorb onto the highly negatively charged particle surface until saturated adsorption is achieved. This results in the maximum saturated adsorption amount. As the pH decreases, the ionization ( $\alpha$ ) of amine groups ( $-\text{NH}-$ ) of PEI starts to occur by the reaction:



At pH 10 ( $\alpha \approx 0.1$ ), PEI molecule is slightly charged and still retains the coiled form. At the same time, the Si<sub>3</sub>N<sub>4</sub> surface is still highly negatively charged. Owing to the surface-segment electrostatic attraction, the adsorption is still high. As the pH further decreases, the increased charge density of PEI segments makes the segment-segments repel each other, eventually resulting in a conformational transition from the coiled ( $\alpha < 0.4$  and pH > 8) to the stretched state ( $\alpha > 0.4$  and pH < 8).<sup>25,29</sup> When the pH decreases to 4 ( $\alpha \approx 0.8$ ), the adsorption significantly decreases because of the strong repulsion between the highly positively charged PEI segments and positively charged powder surface. Once PEI is fully ionized ( $\alpha = 1$ ) at pH = ~2,<sup>25</sup> the adsorption becomes negligible. In addition, the hydrogen bonding probably occurs between the  $-\text{NH}-$  groups of PEI and Si-OH groups of Si<sub>3</sub>N<sub>4</sub> in the whole pH range examined.<sup>23</sup> In the high pH range of pH  $\geq 10$ , hydrogen bonding occurs between the dissociated surface silanol (Si-O<sup>-</sup>) and the  $-\text{NH}-$  groups, but in the pH range of pH < 10, hydrogen bonding also occurs between the undissociated silanol (Si-OH) and the ionized  $-\text{NH}_2^+$  groups. This is probably different from the adsorption of PAA on Si<sub>3</sub>N<sub>4</sub>.<sup>9,11</sup>

## (3) Electrokinetic Behavior

Figure 5 shows the  $\zeta$ -potential-pH curves of 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with various amounts of PEI. In the absence of PEI, the native IEP of Si<sub>3</sub>N<sub>4</sub> is ~5.9, which is very similar to that of the Si<sub>3</sub>N<sub>4</sub> powder reported by Laarz and Bergström (5.8).<sup>11</sup> This value is also close to other reported values (6.2 ± 0.2) for this powder by other authors.<sup>9,12,13</sup> The adsorption of PEI shifts the IEP from pH = 5.9 to higher pH values. At 5.9 < pH < 11, the sign of  $\zeta$  potential is reversed due to the specific adsorption of PEI on the surface of Si<sub>3</sub>N<sub>4</sub>. At 3 < pH < 5.9, the adsorption of PEI also contributes to the positive  $\zeta$  potential. But, below pH 3, there is no significant difference in the positive  $\zeta$  potential with various amounts of PEI. This is consistent with the negligible adsorption of PEI, owing to the enhanced repulsion between the highly positively charged Si<sub>3</sub>N<sub>4</sub> surface and highly ionized PEI

**Table II.** Oxygen Content of Si<sub>3</sub>N<sub>4</sub> Powder Treated Under Different Hydrolyzed Conditions

Powder	Oxygen (wt%)
As received	1.24
Hydrolyzed without PEI <sup>†</sup>	1.46
Hydrolyzed with 1 dwb% PEI <sup>†</sup>	1.49

<sup>†</sup>By stirring 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions for 48 h at the initial pH 4. PEI, polyethylenimine.

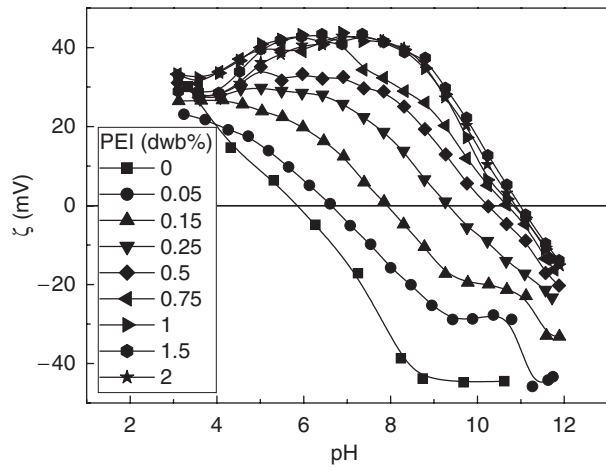


Fig. 5.  $\zeta$ -potential versus pH for 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with various amounts of polyethylenimine (PEI).

segments. This is similar to the case of PAA on Si<sub>3</sub>N<sub>4</sub> in the basic pH range of pH > 9.<sup>9,11</sup>

In order to understand the dependence of the PEI amount, the IEP of Si<sub>3</sub>N<sub>4</sub> as a function of the PEI amount was re-plotted in Fig. 6. It is clear that the IEP increases rapidly from pH 5.9 to 10.3 as the PEI amount increases to 0.5 dwb%. When the PEI amount further increases, the IEP increases very slowly and finally approaches pH ~ 11 at 1.5 dwb% PEI. If the PEI amount exceeds 1.5 dwb%, the IEP value no longer shows any change. Several studies revealed that similar to the charged colloidal particles, the charged PEI also shows an interesting electrophoretic behavior in water.<sup>29,41</sup> They reported that the point of zero charge (PZC) of PEI is near pH 11. Moreover, Hostetler<sup>41</sup> found that PEI shows a very slight native electrophoretic mobility in the range of pH > 11, although PEI contains no functional group that could give it an anionic charge. The author attributed the possible reason to the intramolecular segmental association and the presence of unhydrated negative ions in common solvent cavities. The electrophoretic mobility of polyelectrolytes in solution has been described qualitatively based on the porous sphere model (in the case of a coiled polyion) and the line charge model (in the case of a chain-like polyion).<sup>42</sup>

Assuming  $\text{pH}_{\text{IEP}} = \text{pH}_{\text{ZPC}}$  for the Si<sub>3</sub>N<sub>4</sub>-PEI systems, thus, the fraction of surface covered by PEI molecules,  $f$ , can be estimated by the following equation<sup>43,44</sup>:

$$f = \frac{\text{pH}_{\text{IEP}} - (\text{pH}_{\text{IEP}})_{\text{SN}}}{(\text{pH}_{\text{IEP}})_{\text{PEI}} - (\text{pH}_{\text{IEP}})_{\text{SN}}} \quad (8)$$

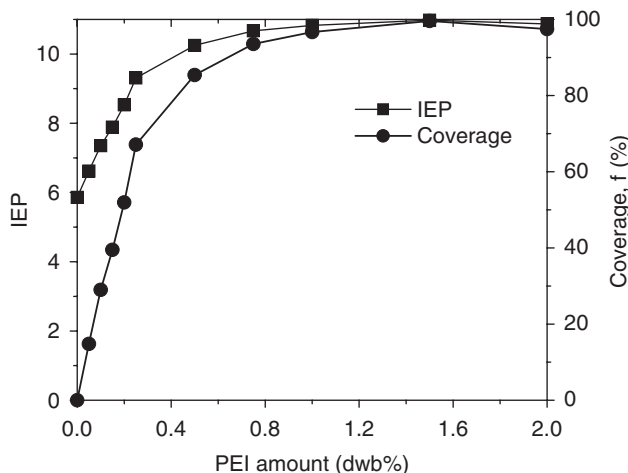


Fig. 6. Effect of polyethylenimine (PEI) amount on the isoelectric point (IEP) of Si<sub>3</sub>N<sub>4</sub> and its surface coverage ( $f$ ) by PEI.

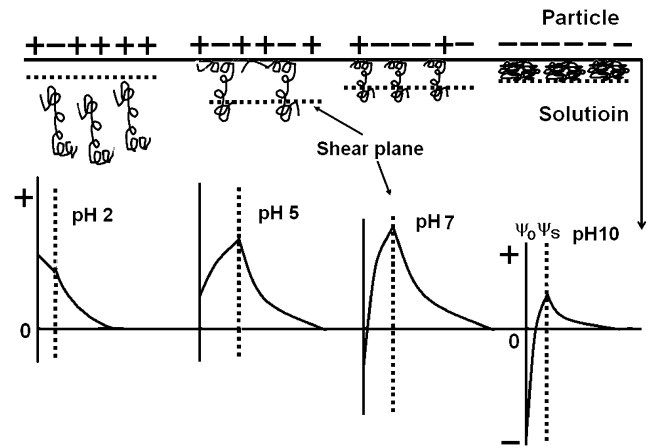


Fig. 7. Schematic of polyethylenimine (PEI) interactions at the solid-liquid interface as a function of pH (in the case of 1.5 dwb% PEI), showing possible PEI configuration change at the interface, and potential-distance diagrams indicating surface potential ( $\psi_0$ ) and shear-plane potential ( $\psi_s$ ).

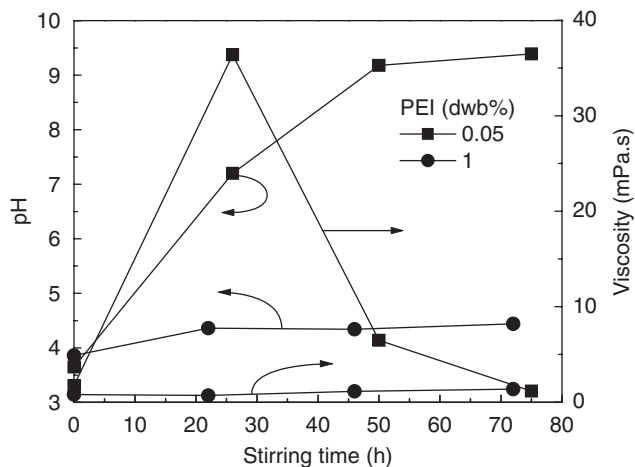
where  $(\text{pH}_{\text{IEP}})_{\text{SN}}$  and  $(\text{pH}_{\text{IEP}})_{\text{PEI}}$  are the native IEP values of Si<sub>3</sub>N<sub>4</sub> and PEI, corresponding to 5.9 and 11,<sup>29,41</sup> respectively, and  $\text{pH}_{\text{IEP}}$  is the IEP values of Si<sub>3</sub>N<sub>4</sub> in the presence of PEI. As a result, the coverage,  $f$ , can be calculated from the measured  $\text{pH}_{\text{IEP}}$ . The coverage as a function of total PEI amount is also plotted in Fig. 6. This clearly reveals that the IEP is essentially associated with the coverage of PEI molecules on the Si<sub>3</sub>N<sub>4</sub> surface. When the PEI amount increases to 1.5 dwb%, the Si<sub>3</sub>N<sub>4</sub> surface achieves a complete coverage. Then, the IEP attains a native IEP value of PEI, pH ~ 11, where PEI molecules are essentially neutral ( $\alpha = 0$ ). The calculated result is in agreement with the adsorption experiment as discussed above. Previous studies have shown that the adsorption of PEI shifts the IEP values of various ceramic powders to near pH 11, regardless of the acid-base character of the powder itself.<sup>15,18-24,26-28,30</sup> A similar behavior was also reported in the cases of anionic polyelectrolytes, like PAA.<sup>9</sup> These studies suggest that in the presence of the polymer molecules, the IEP of ceramic powders is controlled by the coverage of polymers on the powder surface.

Furthermore, the possible model of PEI interactions at the solid-liquid interface as a function of pH is schematically drawn in Fig. 7, according to the observed adsorption and electrokinetic results. This is the case of 1.5 dwb% PEI. The adsorption of PEI may make the hydrodynamic plane of shear move outwards from the particle surface. With the decreased pH, the conformational transition of PEI may shift the plane of shear further outwards.

#### (4) Rheological Behavior

(A) *Effect of Hydrolysis:* Figure 8 shows the pH and viscosity versus stirring time for 10 vol% Si<sub>3</sub>N<sub>4</sub> suspensions with 0.05 and 1 dwb% PEI at initial pH ~ 3.6. Evidently, at 0.05 dwb% PEI, as the stirring proceeds, the suspension undergoes a transition process: stabilization (well-dispersed) → destabilization (serious aggregation) → restabilization (re-dispersed), accompanied by a progressive increase in pH from the initial pH ~ 3.6–9.3. However, at 1 dwb% PEI, the suspension shows no significant change in both pH and viscosity with stirring, suggesting a better stability within the stirring time (3 days) examined.

In order to understand the effect of hydrolysis on the suspension stability,  $\zeta$ -potential measurements as a function of stirring time for 5 vol% Si<sub>3</sub>N<sub>4</sub> suspensions without and with 1 dwb% PEI at initial pH ~ 3.6 were conducted, as shown in Fig. 9. In the absence of PEI, as the stirring proceeds, the pH shifts gradually to higher pH values, whereas the positive  $\zeta$  potential decreases. When the pH reaches ~ 7, the  $\zeta$ -potential value

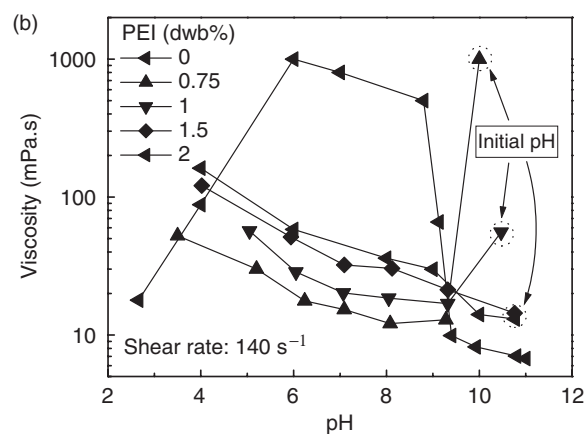
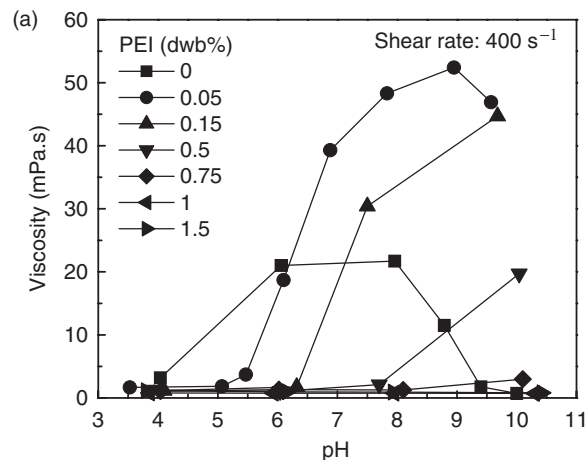


**Fig. 8.** pH and viscosity versus stirring time for 10 vol%  $\text{Si}_3\text{N}_4$  suspensions with 0.05 and 1 dwb% polyethylenimine (PEI) at the initial pH  $\sim 3.6$  (shear rate:  $400 \text{ s}^{-1}$ ).

becomes zero. As the pH increases further, the  $\zeta$ -potential value becomes negative. This changed trend in the  $\zeta$  potential against pH is in good agreement with the changed trend in the viscosity against pH with stirring. In contrast, in the presence of 1 dwb% PEI, there is almost no change in both the pH and  $\zeta$  potential with stirring. This illustrates that the constant pH is crucial for retaining the stabilization of the aqueous  $\text{Si}_3\text{N}_4$  suspensions. The increased pH changes the surface chemistry of  $\text{Si}_3\text{N}_4$  and thus destabilizes the suspension at acidic pH. The present result strongly suggests that the use of PEI is effective for stabilizing the aqueous  $\text{Si}_3\text{N}_4$  suspensions particularly in the acidic pH range by providing a buffer effect to maintain a stable pH.

**(B) Effects of pH, PEI Amount, and Solid Loading:** Figure 10 shows the viscosity versus pH for 10 and 30 vol%  $\text{Si}_3\text{N}_4$  suspensions with various amounts of PEI. In the absence of PEI, the pH dependence of the stability of  $\text{Si}_3\text{N}_4$  suspension is independent of solid loading, and the suspension reaches a better stability in the pH range of  $>9$ , but drastically aggregated in the pH range of 4–9, near the IEP. This is in good agreement with the  $\zeta$ -potential curve (see Fig. 5). Although the stabilization can also be achieved at highly acidic pH  $<4$ , this stabilization is transitional due to the hydrolysis, that is, this stabilization is less valuable in practice.

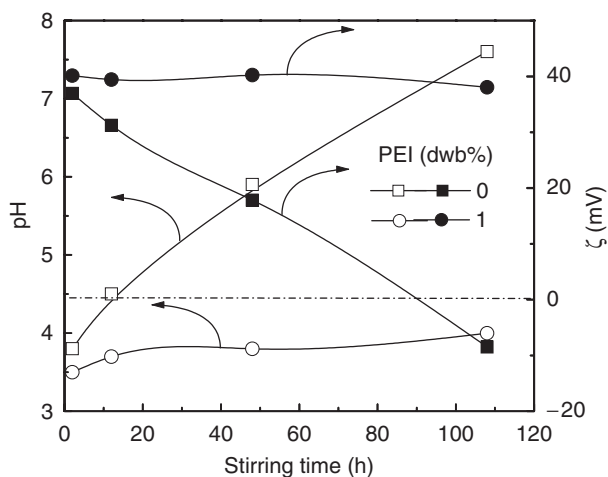
In the presence of PEI, PEI can either stabilize or flocculate the suspensions, depending on the PEI amount and pH, essen-



**Fig. 10.** Viscosity versus pH for (a) 10 and (b) 30 vol%  $\text{Si}_3\text{N}_4$  suspensions with various amounts of polyethylenimine (PEI).

tially the adsorption of PEI. As shown in Fig. 10, one of the most distinct features is that in the initial states, the addition of a small amount of PEI causes drastic flocculation for both the 10 and 30 vol%  $\text{Si}_3\text{N}_4$  suspensions. The adsorbed polymers induce the flocculation possibly by the bridging mechanism or surface charge neutralization.<sup>45</sup> It is widely believed that the bridging flocculation requires very long polymer chains. As PEI shows a compact coiled conformation before ionization and even at a low degree of ionization ( $\alpha < 0.4$  and  $\text{pH} > 8$ ),<sup>25</sup> the initial flocculation could be mainly attributed to the surface charge neutralization instead of the bridging mechanism. However, the PEI amount increases to 1 and 1.5 dwb%; the 10 and 30 vol% suspensions reach the minimum viscosity, respectively, despite being close to the IEP ( $\sim 10.8$ ). This is attributed to the steric stabilization induced by polymers. The following two major factors are responsible for the effectiveness of the steric stabilization: (i) the high affinity allows the high adsorption of PEI on the  $\text{Si}_3\text{N}_4$  surface to occur near pH 10.8, and (ii) the PEI adsorbs at the solid–liquid interface in a compact coiled configuration and thus forms a dense adsorbed layer, as schematically shown in Fig. 7. This is consistent with the adsorption behavior. As for the 10 vol%  $\text{Si}_3\text{N}_4$  suspension, the PEI amount for achieving the minimum viscosity, 1 dwb%, is slightly lower than the adsorption measured data ( $\sim 1.5$  dwb%). This is not surprising because the low solid loading is not as sensitive to the complete coverage as the high solid loading for achieving the stabilization.<sup>46–48</sup> The steric stabilization of PEI near the IEP of pH  $\sim 10.8$  has also been reported on  $\text{SiC}$ ,<sup>24</sup>  $\text{TiC}$ ,<sup>27</sup> and  $\text{Si}_3\text{N}_4$ .<sup>30</sup>

As shown in Fig. 10, another distinct feature is that the effect of PEI on the changed trend in the viscosity with pH depends on the solid loading. At a low solid loading of 10 vol% (see Fig. 10(a)), as the pH decreases, the viscosity shows an overall decrease. As the PEI amount increases, the pH range for



**Fig. 9.** pH and  $\zeta$ -potential versus stirring time for 5 vol%  $\text{Si}_3\text{N}_4$  suspensions without and with 1 dwb% polyethylenimine (PEI) at the initial pH  $\sim 3.6$ .



achieving the minimum viscosity moves to higher pH values. This dependence of the PEI amount against pH has also been reported for  $\text{SiO}_2$ ,<sup>29</sup>  $\text{TiO}_2$ ,<sup>19</sup>  $\text{SiC}$ ,<sup>26</sup> and  $\text{ZrO}_2$ <sup>18</sup> in the literature. The reason for this is due to the following two major facts: (i) the decreases in the pH lead to a decrease in the PEI amount required for achieving the saturated adsorption; (ii) as the pH decreases, the increased positive charge density of PEI segments increases and thus provides a higher positive  $\zeta$  potential for particles below the IEP. It could be concluded that the electrosteric mechanism may be responsible for stabilizing the suspensions with the decreased pH. Moreover, when the PEI amount increases to 1 dwb% and above, the saturated adsorption provides a steric stabilization for the suspensions near the IEP. As the pH decreases, the suspensions still retain better stabilization even within the whole pH range studied, but the stabilization mechanism undergoes a transition from the steric to the electrosteric interactions. At the same time, this also indicates that the excess nonadsorbed PEI has less effect on the stabilization of the 10 vol% suspensions.

However, at a high solid loading of 30 vol% (see Fig. 10(b)), when the PEI amount is 0.75 and 1 dwb%, the minimum viscosity reaches pH 8.1 and 9.3, respectively, where the saturated adsorption may be achieved and thus results in electrosteric stabilization. Note that the viscosity measurements as a function of pH were not conducted for the cases of a low amount of PEI of 0.75 dwb%, because the 30 vol%  $\text{Si}_3\text{N}_4$  suspensions could not be obtained because of the considerable flocculation. As the pH decreases further, the viscosity increases, indicating a destabilization. When the PEI amount is 1.5 and 2 dwb%, the minimum viscosity occurs at pH  $\sim 10.8$  due to steric stabilization. But as the pH decreases, the viscosity increases, despite the increased positive  $\zeta$  potential (see Fig. 5). This is different from the case of the low solid loading of 10 vol%. The results indicate that the stabilization of the concentrated  $\text{Si}_3\text{N}_4$  suspensions strongly depends on the optimum pH and the saturated adsorption of PEI. The reason for this could be due to the flocculation induced by the excess nonadsorbed PEI molecules,<sup>46–48</sup> which accumulates with the decreased pH because of the desorption from the solid-liquid interface (see Fig. 7). Also, it is clear that at pH  $< 9.3$ , the viscosity generally increases with the increased PEI amount at a given pH, which is in good agreement with the increased free PEI concentration. The flocculation induced by the excess free PEI may be dominated by the depletion mechanism, which is primarily as a result of an osmotic pressure increase because of the exclusion of nonadsorbed polymers from the interstices between particles.<sup>47,49</sup> This effect increases with an increase in the particle volume fraction.

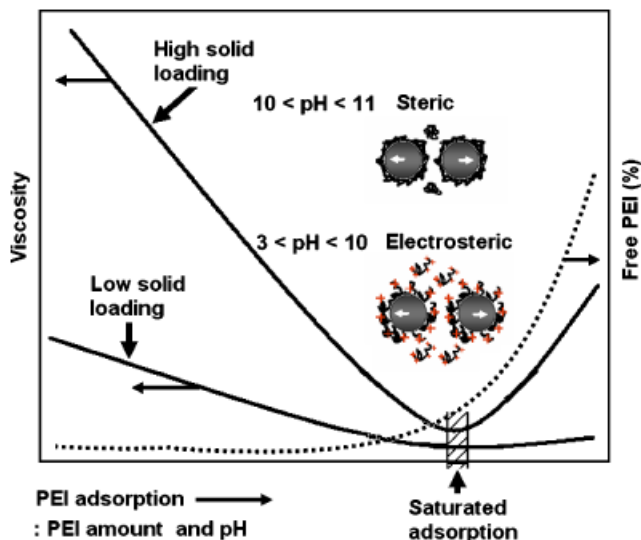


Fig. 11. Stabilization mechanisms of the aqueous  $\text{Si}_3\text{N}_4$  suspensions with polyethylenimine (PEI).

Based on the present study, a stability diagram for aqueous  $\text{Si}_3\text{N}_4$  suspensions with PEI has been proposed, as shown in Fig. 11. This figure shows that once the saturated adsorption is reached, the excess free PEI becomes more detrimental to the stability with increased solid loading. At a high pH range, the stabilization is dominated by the steric effect, but at pH of  $< 10$ , the stabilization may be dominated by the electrosteric effect. In addition, it is worth mentioning that the stabilization of the concentrated  $\text{Si}_3\text{N}_4$  suspensions with PEI is limited to a narrow pH range, but the stabilization of dilute  $\text{Si}_3\text{N}_4$  suspensions can be achieved even within the whole pH range (3–11) when the saturated adsorption is achieved at the starting pH values (no pH adjustor was used and PEI remains uncharged). The stabilization is also guaranteed by the stabilization in the pH of the suspensions, particularly in neutral and acidic pH ranges. This will offer more chance for the wide use of dilute  $\text{Si}_3\text{N}_4$  suspensions in some cases, such as aqueous electrophoretic deposition, in which palladium is preferably used as the cathode substrate to avoid bubble formation.<sup>50</sup>

#### IV. Conclusions

- (1) The pH change of aqueous  $\text{Si}_3\text{N}_4$  suspensions in an acidic environment could be minimized by the presence of  $\geq 0.5$  dwb% PEI. This is primarily attributed to the buffer mechanism generated by the ionized PEI, instead of the protection mechanism. The constant pH allows the suspension to maintain better stability with time at the acidic pH.
- (2) The adsorption of PEI on  $\text{Si}_3\text{N}_4$  is a high-affinity type at highly basic pH, but is a low-affinity type at highly acidic pH. The adsorption decreases with decreased pH. As the PEI amount increases, the adsorption leads to a shift in the IEP of  $\text{Si}_3\text{N}_4$  from pH 5.9 to pH  $\sim 11$  until complete coverage is attained.
- (3) The dispersion properties of aqueous  $\text{Si}_3\text{N}_4$  suspensions in the presence of PEI are controlled by the PEI amount, pH, and solid loading. Once the saturated adsorption limit is reached, the excess free PEI molecules become more detrimental to the stability of the suspensions with the increased solid loading.
- (4) At the high pH range near IEP (pH  $\sim 11$ ), the stabilization of the suspensions with PEI is dominated by the steric effect developed from the neutral PEI, whereas at the pH range of  $< 10$ , the stabilization may be dominated by the electrosteric effect developed from the ionized PEI.

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