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# Analysis of the action mechanism of polymer dispersant on dense ethanol alumina suspension using colloidal probe AFM

Toshio Kakui[a,*], Takeshi Miyauchi[b], Hidehiro Kamiya[b]

[a] Chemicals Research Laboratories, Chemicals Division, Lion Corporation, 13-12, Hirai 7-chome, Edogawa-ku, Tokyo 132-0035, Japan
[b] Graduate School of Bio-Application and Systems Engineering, BASE, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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## Abstract

The action mechanism of a polymer dispersant on dense $Al_2O_3$ ethanol suspension was investigated using a colloidal probe AFM and branched and linear polyethyleneimines (PEIs). To obtain the minimum viscosity and Newtonian flow property of the dense ethanol suspension, the optimum molecular weights of the branched PEIs were determined over the range from 10,000 to 70,000. The linear PEI with Mw 1400 did not reduce the suspension viscosity compared to the branched PEI with the same molecular weight. The amount of adsorbed PEI did not significantly change regardless of the molecular structure and weight of the PEIs. However, the surface interaction between $\alpha$-$Al_2O_3$ solids depended on the molecular structure and weight of the PEIs. The branched chain of the PEI adsorbed on the $Al_2O_3$ surface facilitated the short-range steric repulsion between particles. Based on the results, the increase in steric repulsive force and the disappearance of the adhesion force by the adsorption of the polymer prompted the dispersion of aggregates in suspension and reduced the viscosity of ethanol dense suspension.

*Keywords:* Interface; Surfaces; Polyethyleneimine; Steric repulsion; Atomic force microscope; $Al_2O_3$; Suspensions

## 1. Introduction

Dense ceramic suspensions play a key role in controlling the properties and microstructure of the green body for the final sintered ceramics with high density and high performance. To obtain a dense homogeneous suspension with high fluidity, the viscosity and aggregation and dispersion behavior of particles have to be usually engineered using various polymer dispersants.

Non-aqueous suspensions are often required when the presence of water in the suspension causes deleterious effect or when complicated ceramic forming processes are used such as the tape casting process. Various mechanisms (electrostatic repulsion, steric or overlap force, and re-bridging, etc.) have been discussed on the non-aqueous suspension behavior. The behavior of a dense suspension is influenced by various conditions and different additives, for example, particle specie, size and shape of particle, solid concentration, organic solvent and additives (binder, dispersant and plasticizer). Some researchers have discussed the electrostatic repulsion force for the dispersion of $TiO_2$ and $Al_2O_3$ particles in suspensions with alkyl amines in various organic solvents.[1,2] However, many researchers have reported that the steric repulsion between particles promotes a dominant dispersability and stability in non-aqueous suspension. To select the optimum polymer dispersant, the combination between the surface characteristics of the powder material and organic solvent needs to be considered.

The particle surface has active sites for chemical or physical interaction, for example, hydroxyl group and acidic or basic groups, etc.[3] The acidic $SiO_2$ can be dispersed with a basic dispersant, and the basic $Al_2O_3$ with an acidic one.[4] Alkyl ethoxylate surfactant with a maleimide functional group adsorbed onto acidic SiC and basic $Y_2O_3$ and showed a good dispersibility in various solvents.[5] Moreover, the residual water in ceramic particles or the water content in organic media also played an important role in the dispersion mechanism.[6]

In many papers, three types of dispersants (surfactants, polymer dispersants, and coupling agents, which produced a chemical reaction on a powder surface) have been used for non-aqueous suspension. Many surfactants with low

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* Corresponding author. Tel.: +81-3-3616-3074; fax: +81-3-3616-5376.
*E-mail address:* kakusan@lion.co.jp (T. Kakui).

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molecular weight (about 1000) containing a functional group such as phosphate ester, amine, acid, maleimide and succinimide have been proposed for dense non-aqueous suspensions with high fluidity.[5] The effect of the protective layer of the particle for steric repulsion was discussed using $Si_3N_4$ particles with chemical and physical adsorption of long chain alcohol or $SiO_2$ grafted with long polydimethylsiloxane.[7,8] Some polymer dispersants for non-aqueous dense suspensions, such as fish oil, copolymer of methacryl ester and methacryl acid, and commercial polymer dispersants have also been reported.[9–11] In a non-aqueous solvent, the dispersant with effective dispersability consists of the functional groups for the adsorption on a particle and the steric repulsive chain, which is long enough to overcome van der Waals attractive forces. However, the molecular structure of a dispersant has not been completely clarified or systematically investigated.

As for the dispersion medium, the competitive adsorption of solvent and dispersant on a particle has been discussed using various organic solvents, and the physical and chemical properties of a solvent affected the steric chain for repulsive force.[12,13] That is why hydrocarbons and halogen solvents lacking an interaction with a particle were generally preferred as the organic solvents. The mixed solvent used for tape casting has also been examined.[14–16] However, the dispersibility of ceramic particles in a dense suspension has not been investigated using an alcohol, which has strong hydrogen bonding to the ceramic particle surface.

Moreover, the optimum molecular structure of the polymer dispersant and its additive conditions to obtain a high dispersion were determined based on macroscopic empirical data, for example, suspension viscosity and aggregate size distribution. The characterization of the adsorbed structure and action mechanism of polymer dispersants could not be analyzed based on the microscopic direct information about the interaction among particles with a polymer dispersant.

In our previous investigations, the microscopic interaction between ceramic surfaces by an atomic force microscope (AFM) and the macroscopic behavior of the suspension (viscosity, zeta potential, green body structure, etc.) were investigated using polymer dispersants with different molecular structure. The optimum molecular structure of anionic polymer dispersants with different hydrophilic and hydrophobic ratio was determined in dense aqueous suspensions with various ceramic powders. The increase in electrosteric repulsion force decreased the viscosity of dense suspensions.[17–19] However, few papers have examined the microscopic interfacial behavior between ceramic particles in a non-aqueous system using AFM.

Our previous work investigated the affect of a polymer dispersant molecular structure on the ethanol suspensions with SiC using polymer dispersants with multi-amino functional groups, branched and linear polyethyleneimines (PEIs).[20] As shown in Table 1, the amount of adsorption of the linear PEIs with Mw of 600 and 1800 was almost equal to that of the branched PEIs. However, the 20 vol.% SiC ethanol suspensions with linear PEIs did not display a low viscosity.

Table 1
The amount of polymer adsorption on the SiC particles, and the viscosity of 20 vol.% suspensions with branched and linear PEIs

| | Mw of PEI | Amount adsorbed ($mg/m^2$) | Apparent viscosity (mPa s) |
|---|---|---|---|
| Branched PEI | 300 | 0.41 | 5600 |
| | 600 | 0.50 | 750 |
| | 1800 | 0.59 | 15 |
| Linear PEI | 600 | 0.47 | 4500 |
| | 1800 | 0.57 | 4100 |

The present paper focuses on the analysis of the action mechanism of a polymer dispersant on dense ethanol suspension using AFM with a colloidal probe method. $Al_2O_3$ ethanol suspensions with branched PEIs and linear PEI are prepared in this work. The suspension viscosity, the amount of adsorbed polymer on a particle and the surface interaction force between $Al_2O_3$ particles are examined to investigate the aggregation and dispersion behavior and interaction between $Al_2O_3$ surfaces. The affect of the polymer dispersant molecular structure on the dense $Al_2O_3$ ethanol suspension behavior is discussed based on the relationships between the macroscopic suspension viscosity and the microscopic surface interaction.

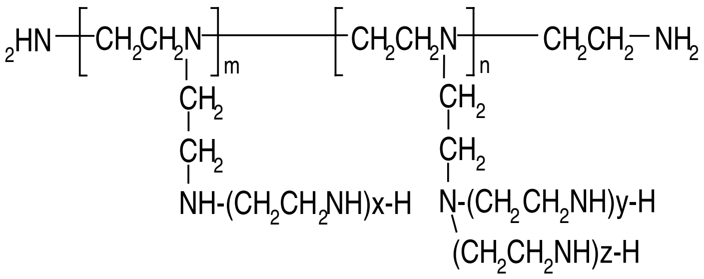
## 2. Experimental procedure

### 2.1. Polymer dispersant with molecular structure and $Al_2O_3$ powder

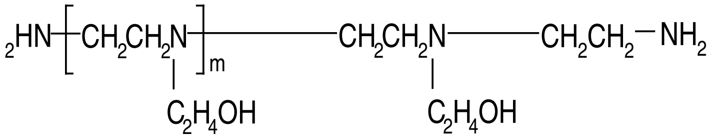
Branched and linear polyethyleneimines (Nippon Syokubai Co., Ltd., Japan) were used in this study as polymer dispersants with multi-amine functional groups. Fig. 1 shows representative molecular structures of each type of PEI. The branched PEI polymerized from ethyleneimine generally has a branched structure. The linear PEIs were polymerized using *N*-hydroxyl ethyleneimine. Six kinds of branched PEIs with a molecular weight ranging from 300 to 70,000 and the linear PEI with molecular weight of 1400 were used. A commercial $\alpha$-$Al_2O_3$ (AL-160SG4, Showa Denko K.K., Japan) was used for fine ceramic powder. The average particle size measured by the image analysis of FE-SEM was 370 nm, and the specific surface area calculated from BET was 6.15 $m^2/g$. Ethanol (purity 99.5 vol.%, Wako Pure Chemical Industries, Co., Ltd., Japan) was used without removing all traces of water or further purification.

### 2.2. Preparation and characterization of dense $Al_2O_3$ suspension

The solid volume fraction of $Al_2O_3$ in the ethanol suspensions was set at 23 vol.%. The $Al_2O_3$ powder was mixed in



(a) Branched polyethyleneimine (PEI)



(b) Linear polyethyleneimine (PEI)

Fig. 1. The molecular structure of branched and linear polyethyleneimines.

ethanol containing 1.63 mg/m$^2$ of a PEI and then ball-milled for 24 h. The viscosity of the dense suspensions was determined by a concentric cylinder viscometer at a shear rate ranging from 1 to 100 s$^{-1}$, because the apparent viscosity can easily yield a macroscopic evaluation on the aggregation and dispersion behavior of particles in dense suspensions.

The amount of polymer dispersant adsorbed on the $Al_2O_3$ particle for each ethanol suspension was calculated from the difference between the original concentration of the polymer and that of the free polymer in the supernatants. The supernatants of suspensions containing the free polymer were obtained from each suspension using centrifugal sedimentation at 5000 rpm for 20 min. The amount of free polymer was determined by removing ethanol from the supernatant through distillation and then drying it (at 70 °C, for 1 day). The eluted amount of organic compounds from ceramic materials and the adsorption amount of polymer on the ball mill were measured corrected as a blank value.

### 2.3. *Measurement of electrosteric interaction using colloidal probe AFM*

To analyze the interaction between $Al_2O_3$ particles adsorbed on a polymer dispersant, the changes in the electrosteric repulsive force and adhesion force on the polished surface of sintered $Al_2O_3$ in ethanol with a polymer dispersant were examined by AFM (Model Nanoscope E, Digital Instruments, Inc., Tonawando, NY, USA) with a colloidal probe method. The interaction between a colloidal probe of $Al_2O_3$ and a polished surface of a sintered $Al_2O_3$ piece was measured. The colloidal probe was prepared by adhering a spherical single $Al_2O_3$ particle with about 10-μm diameter on the top of a commercial tip for AFM using micro-manipulation system for bio-technology. A spherical $Al_2O_3$ particle (Admafine AO-509, Admatechs Co., Ltd., Japan) for a colloidal probe was used as a raw material. Since the phase of the original particle was γ-$Al_2O_3$, this particle was washed in an ultrasonic washer for 3 min and given heat treatment at 1300 °C for 1 h to obtain the α-phase. The α-phase of $Al_2O_3$ particle was identified by the XRD patterns of particles before and after heat treatment. The sintered $Al_2O_3$ pieces were prepared from a fine α-$Al_2O_3$ powder (AKP-10, Sumitomo Chemical Co., Ltd., Japan). The $Al_2O_3$ powder compacts were consolidated by cold isostatic pressing at 200 MPa for 1 h and then sintered at 1300 °C for 2 h.

To adsorb the polymer dispersant on a polished surface of the sintered $Al_2O_3$ piece (under the same conditions of $Al_2O_3$ powder in suspension), the $Al_2O_3$ piece was mixed into a dense $Al_2O_3$ ethanol suspension. After ball milling of the $Al_2O_3$ slurry with the $Al_2O_3$ piece for 24 h, the piece was picked up from the suspension. Next, the suspension was separated into a dense powder layer and a clear ethanol layer by the centrifugal sedimentation method. The $Al_2O_3$ piece was washed by the clear ethanol layer with a polymer dispersant and then transferred into the AFM fluid cell filled with ethanol. The electrosteric repulsion force and adhesion force were determined, as the distance between a colloidal probe and an $Al_2O_3$ piece approached zero and departed from the contact condition, respectively. The surface interaction force distribution was calculated based on the measurement values of the different positions on the substrate.

## 3. Results

### 3.1. *Effect of molecular structure and weight of PEIs on suspension viscosity*

The effect of the molecular structure and weight of the polymer dispersant PEIs on the viscosity of the dense ethanol

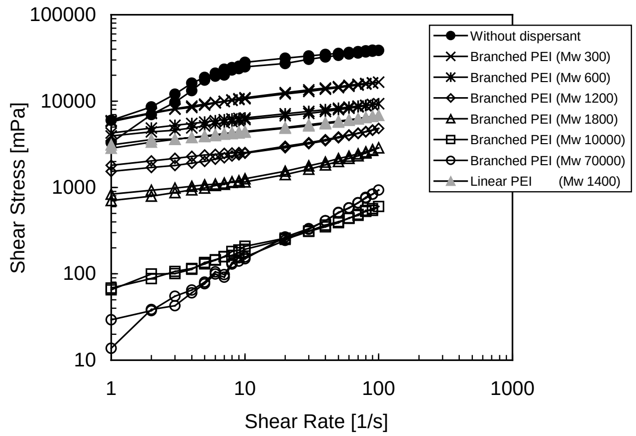


Fig. 2. The relationship between the shear stress and shear rate of the 23 vol.% $Al_2O_3$ ethanol suspensions when using branched PEIs with a molecular weight ranging from 300 to 70,000 and linear PEI with Mw of 1400.

suspensions was first investigated. Fig. 2 shows the relationship between the shear stress and shear rate of each suspension containing branched PEIs with a molecular weight (Mw) ranging from 300 to 70,000. The shear stress decreased with an increase in the Mw ranging from 300 to 1800, although the suspension flow properties diverged from Newtonian law. The branched PEIs with the Mw 300 and 600 did not reduce the shear stress at the lower shear rate (<5 1/s) compared to the suspension without a dispersant. When the PEIs with the Mw greater than 10,000 were used, the shear stress at all shear rates ranging from 1 to 100 1/s decreased remarkably, and the slope of the relationship between the shear stress and shear rate of the suspensions approached about 1.0.

Fig. 3 shows the apparent viscosity at the same shear rate (10 1/s) of each $Al_2O_3$ suspension. It is more obvious that the apparent viscosity decreased with an increase in the Mw up to 10,000, and the branched PEIs with the Mw ranging from 10,000 to 70,000 displayed a lower viscosity compared to that of the others. The optimum molecular weights of branched PEIs for the minimum viscosity and Newtonian flow property on dense $Al_2O_3$ ethanol suspension were determined over the range from 10,000 to 70,000.

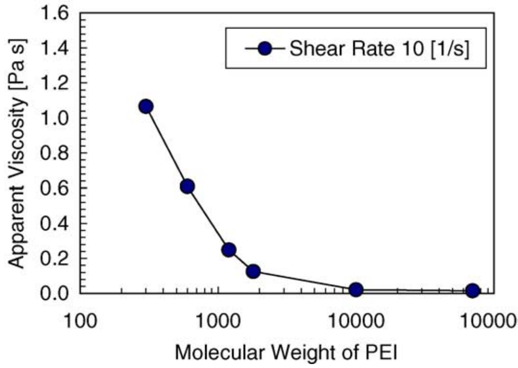


Fig. 3. The apparent viscosity at the same shear rate (10 1/s) on the $Al_2O_3$ ethanol suspensions as a function of the molecular weight of branched PEIs.

The affect of the molecular structure of the PEI on the viscosity of the $Al_2O_3$ ethanol suspensions was examined using the linear PEI with Mw of 1400. The relationship between the shear stress and shear rate of the suspension containing each PEI is also shown in Fig. 2. When the linear PEI was used, the value of the shear stress was observed that the linear PEI located between branched PEIs with 600 and 1200. The linear PEI did not reduce the share stress of the suspension as well as the branched PEIs with Mw of 1200 and 1800. This result was the same as that of the SiC ethanol suspensions with the linear and branched PEIs in our previous work.[20] The viscosity of the $Al_2O_3$ ethanol suspension depended on the molecular structure and weight of the PEI.

### 3.2. *Adsorption properties of PEIs on $Al_2O_3$ particle*

The amount of adsorption of the branched and linear PEIs on the $Al_2O_3$ surface was investigated, because the surface interaction between particles will be promoted by a polymer dispersant adsorbed on a particle. Fig. 3 shows the amount of the adsorption of the branched PEIs and the linear PEI when using an excess amount of the PEIs. The amount of adsorption did not significantly change with the molecular weight, though it gradually increased from 0.8 to 1.4 $mg/m^2$ with an increase in the Mw ranging from 300 to 70,000. As for the difference between branched and linear structure of PEI, the amount of the adsorption of the linear PEI with Mw of 1400 was almost the same as that of the branched PEIs with the same molecular weight.

The adsorption properties of branched PEIs on the $Al_2O_3$ particles were similar to those on the SiC particles in our previous work.[20] The adsorption structure on the $Al_2O_3$ surface was examined by the equation from Perkel and Ullman[21] which was established between the amount of adsorbed polymer ($\Gamma$) and the molecular weight (Mw).

$$\Gamma = K \times \mathrm{Mw}^{\alpha} \qquad (1)$$

Since the adsorption constant $\alpha$ was determined to be about 0.1 from the approximate curve for Fig. 4, the adsorption of branched PEI on the $Al_2O_3$ surface followed a head-tail model and adsorption near model independent of the molecular weight.

Based on the results, regardless of the variation in the molecular weight of branched PEIs and the difference between branched and linear structure of PEI, the amount of all adsorbed the PEIs is almost the same; nevertheless, the viscosity of the $Al_2O_3$ ethanol suspension greatly changed with the molecular structure and weight of the PEI. Because it seems that the steric repulsion between particles promotes a dominant dispersibility of particles in a non-aqueous system, the surface interactions between $Al_2O_3$ particles were examined using a colloidal probe AFM to analyze the effect

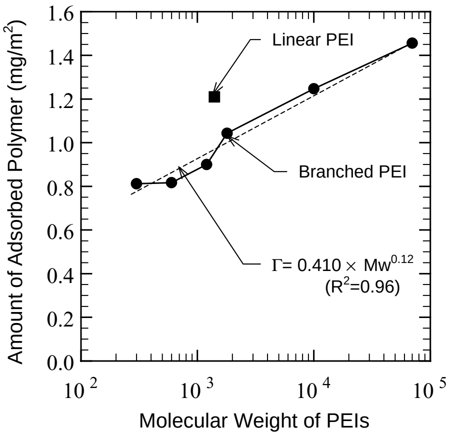


Fig. 4. The amount of adsorption of the branched PEIs with a molecular weight ranging from 300 to 70,000 and the linear PEI with Mw of 1400 on $Al_2O_3$ particle in ethanol suspension.

of the molecular structure and weight of the PEI on the suspension behavior.

### *3.3. Surface interaction between $Al_2O_3$ particles adsorbed polymer*

Fig. 5 shows the force curve between an α-$Al_2O_3$ colloidal probe and polished α-$Al_2O_3$ substrate in the ethanol solutions. From the force curve without a polymer dispersant, the electrostatic repulsive interaction based on DLVO theory was observed at the relatively long surface distance >8 nm, and van der Waals-type attractive forces appeared at a distance of about 3–5 nm. However, when the branched PEIs with Mw of 600 and 1800 and the linear PEI with Mw of 1400 were added to the solution, the electrostatic repulsive interaction disappeared at the relatively long distance >8 nm. The repulsive interaction of the branched PEI with Mw 600 and 1800 appeared at a short distance of <8 nm, although the short-range repulsive force of the linear PEI without a branched chain almost disappeared. This short-range repulsive force clearly depends on the steric repulsion of the branched chain of the dispersant.

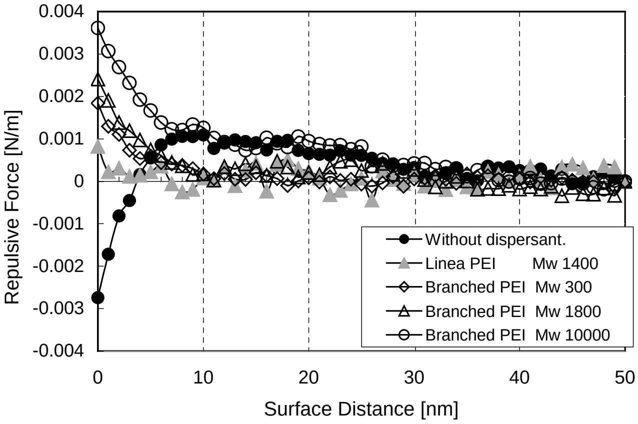


Fig. 5. The repulsive force curve between the $Al_2O_3$ colloid probe and substrate in the ethanol solutions with the branched and linear PEIs and without a dispersant.

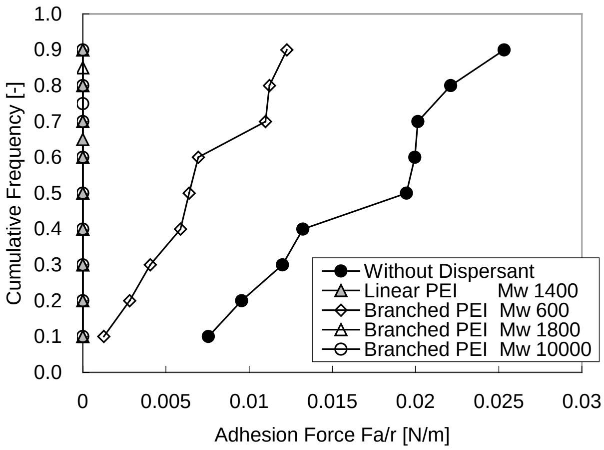


Fig. 6. The adhesive strength distribution between the $Al_2O_3$ colloid probe and substrate in the ethanol with the branched and linear PEIs and without a dispersant.

On the other hand, the repulsive interaction of the branched PEI with Mw 10,000 continued to gradually increase from a long distance to a short distance of <8–10 nm and was significantly larger at a short distance of <10 nm compared to that of the branched PEIs with a low Mw. The longer branched chain of the PEI with the increase in the molecular weight would cause the repulsive force. This large repulsive force is also the steric interaction of the adsorbed polymer on the $Al_2O_3$ surface.

Fig. 6 shows the adhesion strength distribution between the $Al_2O_3$ colloidal probe and substrate. The adhesion strength between the $Al_2O_3$ colloidal probe and substrate had a wide distribution in ethanol without a dispersant, and the adhesion force was from 0.007 to 0.25 μN/m. When the polymer dispersant was added to the suspension, the attractive force was reduced and disappeared. Interestingly, the adhesion force in ethanol containing the branched PEI with Mw of 600 displayed a lower value than that without a dispersant. It seems that the branched PEI with relatively low molecular weight cannot adsorb on all surfaces, because the amount of adsorption of the PEIs with a low molecular weight was smaller than that of the others. If the dispersant adsorbs more firmly and completely on the entire surface of a particle, it will protect perfectly the direct contact between particle surfaces.

## 4. Discussion

Based on the previous results, the action mechanism of the polymer dispersant on the dense $Al_2O_3$ suspension

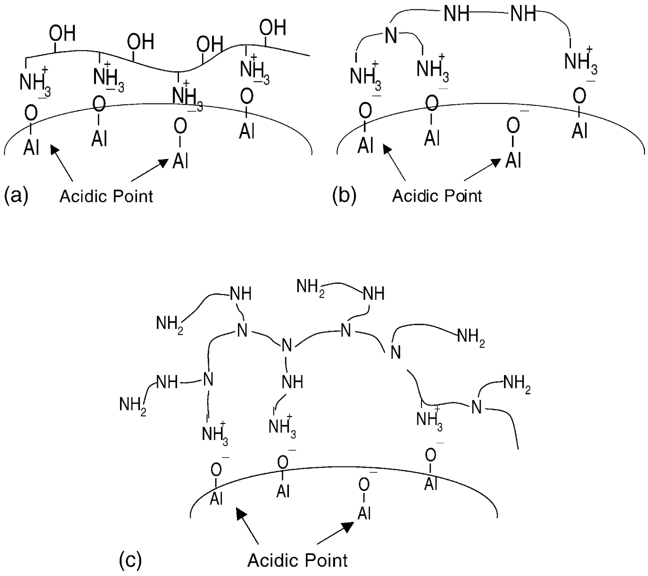


Fig. 7. The schema of the effect of the molecular structure and weight of polymer dispersant adsorbed on $Al_2O_3$ surface: (a) linear PEI, (b) branched PEI with low molecular weight and (c) branched PEI with high molecular weight.

behavior in ethanol is discussed. The effects of molecular structure on each adsorbed polymer dispersant on the $Al_2O_3$ surface are shown in Fig. 7. It seems that the basic amino groups in the PEIs adsorb at the acid group on the surface by the acid-base reaction. Because the linear PEI does not have a branched chain with amino groups, the molecular structure of the PEI adsorbed on the surface would be in a plane as shown in Fig. 7a. The branched PEI with Mw 300 and 600 would be adsorbed in the plane without sufficient thickness to accelerate a steric effect as shown in Fig. 7b, because the branched PEIs lack a sufficient branched chain because of a low degree of polymerization (about 5–10). These adsorbed molecular structures will reduce the adhesion force between solid surfaces without accelerating the steric force of the dispersants. The polymer dispersant adsorbed on the particles also protects the direct contact between particle surfaces in a non-aqueous system, regardless of the adsorption configuration of a dispersant.

On the contrary, as the molecular weight of the branched PEI increases, its branched chain is more lengthened and complicated. Fig. 7c shows the molecular structure on an adsorbed PEI with high molecular weight on the $Al_2O_3$ surface. The PEI will be formed by a loop and train structure, which accelerates a steric effect. Moreover, it seems that the branched PEI with Mw 10,000 has branched long chains that are not able to adsorb on a surface. The non-adsorbed long chains promote the steric repulsive force between solid surfaces. The increase in steric repulsive force by the formation of the loop and train structure and the non-adsorbed long branched chain will facilitate the dispersion of aggregates in a suspension and decrease the suspension viscosity.

## 5. Conclusions

The action mechanism of a polymer dispersant on dense $Al_2O_3$ ethanol suspension was investigated using a colloidal probe AFM and branched and linear polyethyleneimine. To obtain the minimum viscosity and Newtonian flow property of the dense ethanol suspension, the optimum molecular weights of the branched PEIs were determined over the range from 10,000 to 70,000. The linear PEI with Mw 1400 did not reduce the suspension viscosity compared to the branched PEI with the same Mw. The amount of adsorbed PEI did not significantly change regardless of the molecular structure and weight of the PEIs. Based on the surface interaction between α-$Al_2O_3$ solids, the branched chain of the branched PEI adsorbed on the $Al_2O_3$ surface facilitated the short-range steric repulsive force between particles, which appeared at about 3–5 nm in surface distance. This short-range steric interaction increased with an increase in molecular weight of the PEI and reduced the viscosity of the ethanol $Al_2O_3$ suspension.

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