

Dispersant-Ethyl Cellulose Binder Interactions at the Ni Particle-Dihydroterpineol Interface

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The interaction of a dispersant and a binder at the Ni particle surface is investigated to identify their influence on the dispersion stability of Ni particles in dihydroterpineol (DHT). Six different commercial dispersants are used to obtain a highly dispersed Ni suspension, and ethyl cellulose (EC) is used as a binder for the preparation of a Ni paste. The effectiveness of the dispersants on the dispersion stability of the Ni particles in DHT is evaluated by measuring the rheological behavior of the Ni suspension. Hypermer KD3 and RE610, among six different commercial dispersants, are found to be an effective dispersant for the Ni particles in DHT without EC. However, upon the addition of EC, different rheological behaviors of the Ni suspensions are shown according to the added dispersants. EC does not affect the rheological behavior of the RE610-stabilized Ni suspension. On the other hand, the addition of EC increases the apparent and relative viscosities of the Hypermer KD3-stabilized Ni suspension and causes a transition in rheological behavior from shear thinning behavior to shear thickening behavior. The adsorption results reveal that the deterioration in the stability of the Hypermer KD3-stabilized Ni suspension with the addition of EC is due to the partial displacement of the preadsorbed Hypermer KD3 by the EC. The influence of the interactions between the dispersant and binder on the dispersion stability of the Ni pastes is also confirmed via observations of the variations in the agglomerated particle size with the addition of EC.

I. Introduction

NICKEL (Ni) has been used as an internal electrode material of base metal electrode multilayered ceramic capacitors (BME-MLCCs).¹ The Ni electrode is screen printed onto the ceramic dielectric layer prepared by tape casting or coating. For the screen printing of the Ni inner electrode, various organic additives such as a dispersant and binder are added to the Ni suspension to formulate the Ni paste. To meet the downscaling that is required for the miniaturization of electronic devices, the thickness of the dielectric layer in the MLCCs is significantly decreased. Currently, the thickness of the sintered dielectric layer has decreased to under 1 μm . As the dielectric layer becomes thinner, the Ni inner electrode must also be reduced to increase the number of stacked layers. Accordingly, the configuration of even one Ni particle in the Ni inner electrode layer should be addressed. The dispersion state of the particle in the suspension is directly related to the resulting green microstructure.^{2–6} There-

fore, the stabilization of the Ni suspension has to be predetermined to obtain a homogeneous microstructure and to prevent the deterioration of the electrical properties. A dispersant is used to obtain a well-dispersed suspension in the preparation of a suitable paste for screen printing. In a non-aqueous system, it is widely adapted that dispersants are added to the suspensions to provide stability based on steric hindrance. Interpenetration or compression of the dispersant molecules on the particle surface during the particle encounter causes a decrease in the configurational entropy, which then provides a repulsive stabilizing force. This effect generally increases as the surface coverage and/or adsorbed layer thickness increases, and it requires that the dispersant has to be strongly anchored to the particle surface while extending into the solvent medium. In addition to the dispersant, a binder is commonly added to increase the strength of the green body for easy handling and storage. Additionally, the binder can provide improved wetting, delay of sedimentation, and increased viscosity to the suspension.⁷ Ethyl cellulose (EC) has been generally used as a binder in the paste industry to impart shear thinning and thixotropic characteristics to the paste for adaptability with screen printing.⁸ Cellulose contains a basic repeating structure of glucose and three replaceable hydroxyl groups for each unit. EC is prepared by substituting ethoxyl groups ($-\text{OC}_2\text{H}_5$) for hydroxyl groups ($-\text{OH}$) in cellulose. There have been reports^{9–11} that describe the effect of EC on the rheological behavior of the paste. These researches have focused mainly on the determination of the optimum binder concentration in order to maintain a suitable suspension viscosity. However, it was reported that competitive adsorption can occur when organic species with different surface affinities for the particle surfaces and molecular weight coexist in a suspension.^{12–20} The complex interactions between the dispersant and binder are expected to have a significant role in the dispersion stability of the suspension. Therefore, it is necessary to clarify the interactions between the dispersant and binder in the non-aqueous system and observe their influence on the dispersion stability of the non-aqueous Ni paste system.

In this study, six commercial dispersants were added into Ni suspensions. An effective dispersant for Ni particles in DHT without EC was determined by evaluating rheological behavior. EC was added to the Ni suspension that was prestabilized by the addition of an effective dispersant to formulate the Ni paste. The stability of the resulting dispersion was investigated through rheological measurements and observations of the agglomerated particle size. The adsorption of the dispersant and binder was studied with diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) to clarify the influence of the interactions between the dispersant and binder on dispersion stability.

II. Experimental Procedure

A commercial Ni powder (Ni609S, Shoeni Chemicals Company, Tokyo, Japan) was used in the present investigation. The Ni

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Table I. The Information of Organic Materials

Name	Chemical structure	Functional group	Molecular weight (g/mol)
Dihydroterpineol (DHT)		-OH	156.269
Hypermer KD2	Polyether amine	COOH = CN	—
Hypermer KD3		COOH = CN	4090
Disperbyk111	Copolymer with acid number of 129 mg KOH/g	—	—
Disperbyk163	High molecular weight block copolymer with amine number of 10 mg KOH/g	—	—
Disperbyk180	Alkyloammonium salt of block copolymer with acid number of 95 mg KOH/g and base number of 95 mg KOH/g	—	—
RE610		-PO(OH) ₂	3460
Ethyl cellulose (EC)		-OH	142400

particle surface is composed of Ni (53.3%) and O (46.7%). Oxygen atoms on the Ni particle surface exist in the form of NiO (73%), Ni(OH)₂ (24%), and NiOOH (3%). This value was obtained by dividing the O1s peak. The powder had a nominal particle diameter of 300 nm and a BET-specific surface area of $3.74 \pm 0.04 \text{ m}^2/\text{g}$. To remove any physically adsorbed water and volatile organics adsorbed on the powder surface, the powder was vacuum dried at 130°C for 24 h. Dihydroterpineol (DHT) (Nippon Terpene Chemicals Inc., Kobe, Japan) was used as a suspending medium. Hypermer KD2 and KD3 (ICI Chemicals, London, UK), Disperbyk-111, -163, and -180 (BYK-Chemie GmbH, Wesel, Germany), and RE610 (Toho Chemical Co. Ltd., Tokyo, Japan) were used as dispersants. EC (Ethocel STD 45, Dow Chemical Corp., Russelville, AR) having an ethoxyl content of 48.0–49.5% by weight was used as a binder. The information of organic materials is summarized in Table I. X-ray photon spectroscopy measurements were carried out using an X-ray spectrometer. A MgK α X-ray (1253.6 eV) was used as a light source, and peak positions were internally referenced to the C 1s peak at 284.6 eV. This C 1s binding energy corresponds to the most intense carbon signal coming from the aromatic C–C carbons (excluding the carbons bonded to oxygens). The base pressure of the chamber was $\sim 2 \times 10^{-10}$ Torr and the electron takeoff angle was 90°. Suspensions were prepared by adding 50 wt% Ni powder into the DHT with 1 wt% dispersants based on the weight of the Ni powder. To establish an equilibrium dispersion system, the suspensions were ball milled for 4 h using 3 mm zirconia grinding media to ensure a thorough and uniform wetting and mixing of all the particles. After ball milling, ethyl cellulose binder with a mass fraction of 1% based on the Ni powder was added into the Ni suspension. Binder was added as a stock solution. The stock solution of the binder was made by dissolving EC in DHT at 80°C in the sil-

icon bath. This slurry was then ball-milled for an additional 20 h at room temperature. The rheological behavior of the Ni suspensions was characterized using a concentric-cylinder viscometer (MCR300, Paar Physica, Stuttgart, Germany). The shear rate was increased from 1 to 700 s⁻¹ over 5 min. All viscosity measurements were performed at 20°C. We estimate the uncertainty associated with the measurement of rheological behavior under these experimental conditions to be $\pm 6\%$. The concentrated Ni suspension was diluted to 5 wt% and then agglomerated particles in the diluted Ni suspension were observed using a confocal laser scanning microscope (MRC-1024, Bio-Rad, Hercules, CA). The observation was repeated three times and then the results were averaged (uncertainty = $\pm 9\%$). In order to analyze the adsorption of the polymeric molecules on the Ni particle surface, DRIFTS (Thermo Nicolet 4700 FT-IR, Thermo Electron Co., Waltham, MA) measurements were taken. Samples for DRIFTS were prepared by mixing the dried Ni powders with KBr at a weight ratio of 10/90. Each DRIFTS spectrum was obtained by averaging 256 interferograms with resolution of 4 cm⁻¹. The as-collected spectra were converted by the Kubelka–Munk function in which the peak intensity is related directly with sample concentration.²¹ The IR spectra of the dispersant were obtained using the attenuated total reflection (ATR) technique. ATR-IR spectra were recorded on a Thermo Nicolet 4700 FT-IR spectrometer equipped with a commercial ATR accessory. Before the measurement, the Ge ATR crystal was cleaned using soap, water, and rinsed with acetone, and then dried by nitrogen. A spectrum was recorded with the cell empty to be used as a reference for subsequent experiments. Samples were made by drop-casting a thin film onto the Ge ATR crystal. Pure dispersants were used without any purification and dilution. Spectra were collected by coadding 256 scans at 4 cm⁻¹ resolution. We estimate the uncertainty

Table II. The Relative Viscosity of the Ni Suspension with Six Commercial Dispersants at a Constant Shear Rate of 20 s⁻¹

Dispersants	Relative viscosity
w/o	3.496
KD-3	2.291
KD-2	3.907
BYK111	3.813
BYK163	3.210
BYK180	2.977
RE610	2.382

associated with the results of IR spectroscopy under these experimental conditions to be $\pm 3\%$.

III. Results

(1) Rheological Properties of the Ni Suspension and Paste

Six commercial dispersants were compared for their efficiency to produce stable suspensions of Ni particles in DHT. The effectiveness of these dispersants was determined by measuring their rheological behavior. As the amount of dispersant was increased, viscosity decreased up to a dispersant mass fraction of 1%. Beyond this concentration, the suspensions, viscosity became nearly constant, indicating that the non-adsorbed dispersant does not deteriorate the suspension stability. All Ni suspensions presented a shear-thinning behavior with or without the addition of a dispersant, and the relative viscosity of the Ni suspensions with different dispersants was compared at a shear rate of 20 s⁻¹, which is shown in Table II. The relative viscosity of the Ni suspension without a dispersant was 3.50. Hypermer KD2 and Disperbyk-111 raised the viscosity of the Ni suspension compared to that without a dispersant. The relative viscosity of the Ni suspension prepared with Hypermer KD3 was 2.291 and the relative viscosity of the Ni suspension prepared with RE610 was 2.382. An examination of the individual effects of the dispersant on the suspension flow behavior indicated that the presence of either Hypermer KD3 or RE610 provided stability to the Ni suspension.

Figure 1 shows the effect of adding EC on the rheological behavior of Ni suspensions prepared with Hypermer KD3 and RE610. At a shear rate of 20 s⁻¹, the addition of EC decreases the relative viscosity of the RE610-stabilized Ni suspension from 2.382 to 1.922, while it increases that of the Hypermer KD3-stabilized Ni suspension from 2.291 to 3.216. The addition of EC influenced the rheological behavior as a function of the shear rate as well as the viscosity at a constant shear rate of 20 s⁻¹. For

the RE610-stabilized Ni suspension, the degree of shear thinning was maintained even after the EC was added. On the contrary, the addition of EC changed the rheological response of the Hypermer KD3-stabilized Ni suspension from shear thinning to shear thickening. A weak shear thickening behavior was observed at shear rates lower than 2 s⁻¹, while a shear thinning behavior was observed above a shear rate of 2 s⁻¹. This trend was similar to that of the rheological behavior of the Ni suspension prepared with only EC. Therefore, we hypothesized that the transition in rheological behavior from shear thinning to shear thickening for the Hypermer KD3-stabilized Ni suspension with the addition of EC was attributed to the interactions between the Hypermer KD3 and EC.

(2) Agglomerated Particle Size

Variations in the dispersion stability by adding EC can be verified through confocal laser scanning microscopy (CLSM). The concentrated Ni suspension was diluted to 5 wt% and then the agglomerated particles in the diluted suspension were observed by CLSM. The influence of the EC on the prestabilized Ni suspension prepared with Hypermer KD3 or RE610 was evaluated through a direct comparison of the micrographs for the Ni suspensions with and without EC, which are shown in Fig. 2. The diluted Ni suspension without a dispersant had a highly agglomerated suspension structure. The Ni suspensions that were prepared with RE610 or Hypermer KD3 were well dispersed and each particle could be individually differentiated. The addition of EC increased the agglomerated particle size of the Hypermer KD3-stabilized Ni suspension, which is characteristic of an unstable suspension, whereas the RE610 still provided dispersion stability to the Ni suspension. The agglomerated particle size was estimated by taking measurements with a ruler; these are summarized in Table III. The trend corresponded well with the observed rheological behavior.

(3) Adsorption of the Dispersant and Binder Onto the Ni Particle Surface

The neat dispersant was characterized by ATR spectroscopy to observe the characteristic peak of dispersant. The as-received Ni and Ni powder adsorbed with the dispersants and binder were characterized by DRIFTS to clarify the interactions between the dispersant and binder as well as their influence on the rheological behavior. In Fig. 3, a sharp peak at 1735–1750 cm⁻¹ for the Ni powder adsorbed with Hypermer KD3 (Fig. 3(b)) was attributed to the C=O of the ester group in Hypermer KD3, which corresponded well with the peak of neat Hypermer KD3 (Fig. 3(a)). In comparison, for the powder adsorbed with Hypermer KD3 and EC (Fig. 3(c)), the DRIFTS peak intensity at 1735–1750 cm⁻¹ decreased by about 40%. This indicated that the concentration of Hypermer KD3 on the Ni particle was decreased by the addition of EC.

In Fig. 4, the IR spectra of neat RE610 (Fig. 4(a)) exhibited strong peaks at 1244 and 829 cm⁻¹, which are assigned to P=O and P-OH, respectively, and also showed P-O-R vibrations at 1088 and 982 cm⁻¹. The overall DRIFT spectra features of the RE610-adsorbed Ni (Fig. 4(b)) and the RE610- and EC-adsorbed Ni (Fig. 4(c)) were virtually the same, which indicated that the concentration of the RE610 on the Ni particle was maintained even after EC was added.

IV. Discussion

(1) The Effectiveness of Dispersant

The relatively high effectiveness of the RE610 and Hypermer KD3 can be explained in terms of the anchoring group and tail structure. The linear type of a phosphoric ester consists of a phosphonic acid head group, hydrophilic oxyethylene (CH₂-CH₂-O) repeating units, and hydrophobic alkyl chains. RE610 is an aromatic-type phosphate ester with a benzene ring which is located following (CH₂-CH₂-O) units.^{22,23} The phosphonic acid

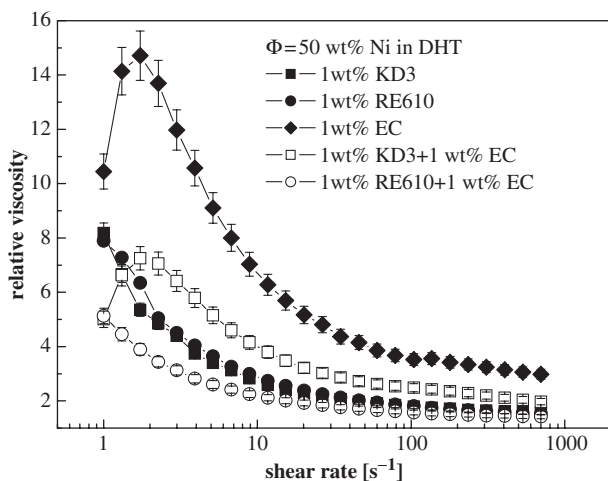


Fig. 1. The rheological behavior of the Ni suspension with dispersants in the presence of ethyl cellulose.

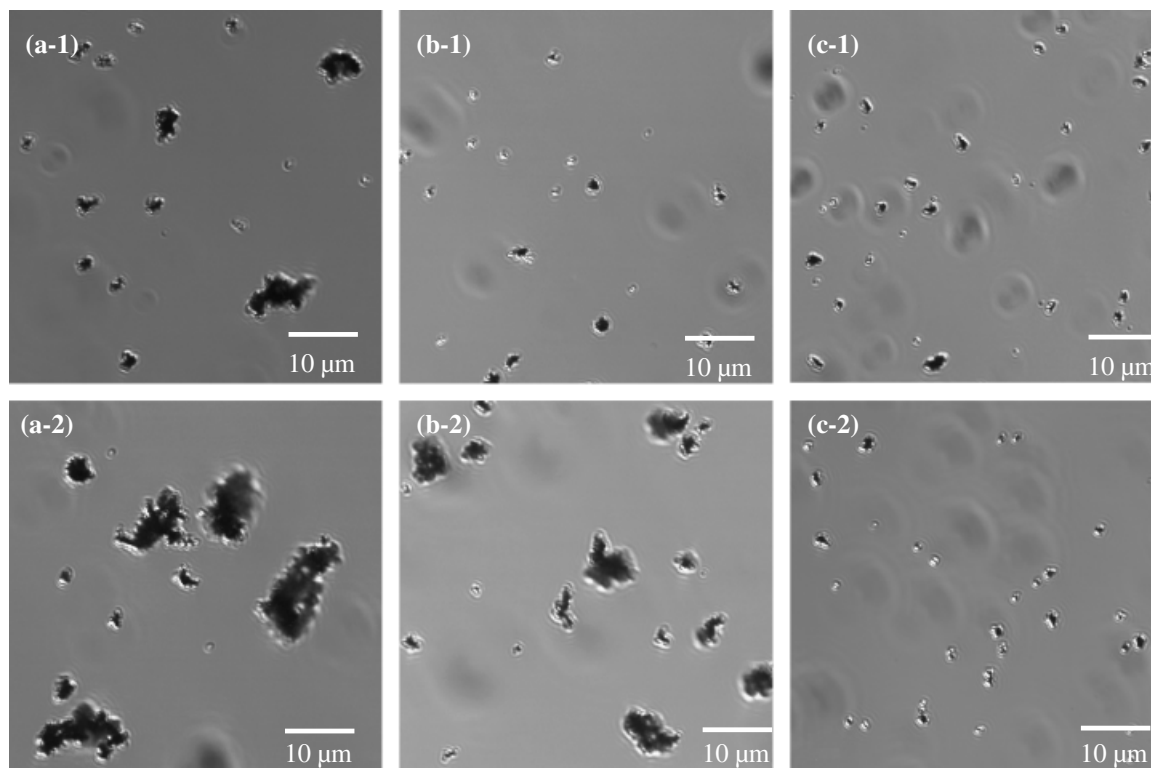


Fig. 2. Confocal micrographs of a diluted Ni suspension: (a-1) dihydroterpineol, (a-2) EC, (b-1) Hypermer KD3, (b-2) Hypermer KD3+EC, (c-1) RE610, and (c-2) RE610+EC. EC, ethyl cellulose.

head group interacts strongly with the basic hydroxyl group on the metal oxide surface via acid–base interactions.^{24,25} Additionally, a molecule with a phosphonic head group has been used for self-assembled monolayer (SAM) formation because of its strong affinity for metal oxide surfaces. In case of a SAM consisting of 4-phosphonobutyric acid or 2-phosphonopropionic acid on oxidized titanium foils, the carboxylic acid groups extrude into the air, which indicates a preferential attachment of the phosphonic acid group to the metal oxide surface.^{26,27} It can be considered that phosphonic acid has a stronger affinity for the metal oxide surface than carboxylic acid. The non-ionic surfactants containing a (CH₂–CH₂–O) repeating unit are highly soluble in solvents which enable hydrogen bonding.²⁸ It is expected that the tail of RE610 easily stretches out into the DHT due to the OH group in the DHT molecule.

Hypermer KD3 is a polyimine ester copolymer²⁹ consisting of carboxylic acid³⁰ and imine^{29,31} functional groups, and polyester stabilizing moieties.³² It can be strongly adsorbed to metal oxide particles via acid–base interactions, provided particles are sus-

pending in a non-polar solvent with dispersion stability.^{33–35} In addition, it was reported³⁶ that Hypermer KD3 provides a steric barrier of about 9–15 nm which is sufficient to stabilize the sub-micron-sized alumina particles in the non-polar solvent, decalin. Therefore, the obvious decrease in the viscosity of the Ni suspension resulting from the addition of RE610 and Hypermer KD3 was attributed to the strong affinity for the Ni particle surface and the tail structures.

Table III. Agglomerated Particle Size Obtained from Estimated Measurements Based on the Confocal Laser Scanning Micrographs

Dispersants	Binder	
	Without EC	With EC
Average observed linear dimension		
w/o	2.439	3.865
KD3	1.427	2.675
RE610	1.396	1.284
Maximum observed linear dimension		
w/o	11.250	15.625
KD3	3.750	8.750
RE610	2.688	2.399

EC, ethyl cellulose; unit, μm.

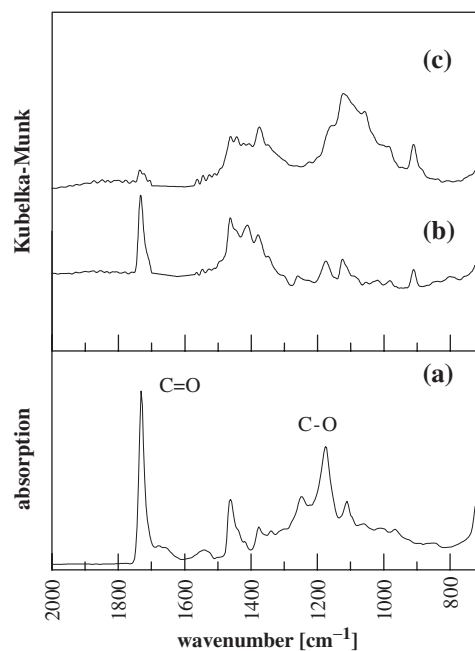


Fig. 3. Attenuated total reflection spectra of neat Hypermer KD3 (a), and diffuse reflectance Fourier transform infrared spectroscopy spectra of the Ni powder with an adsorbed layer of Hypermer KD3 in the absence (b)/presence (c) of ethyl cellulose.

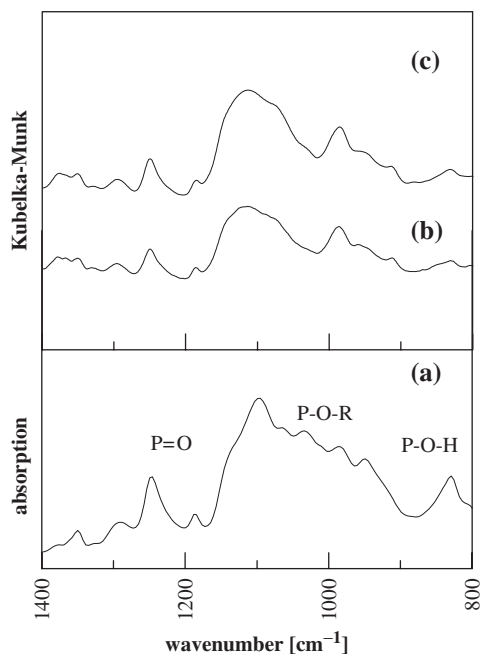


Fig. 4. Attenuated total reflection spectra of the neat RE610 (a), and diffuse reflectance Fourier transform infrared spectroscopy spectra of the Ni powder with an adsorbed layer of RE610 in the absence (b)/presence (c) of ethyl cellulose.

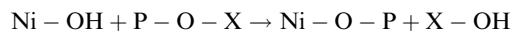
(2) The Influence of the Dispersant–Binder Interactions on the Rheological Behavior

In a particle dispersion, shear thickening results from the three-dimensional network structure that consists of particles bridged by flexible polymer coils.³⁷ Two particles can be bridged by a flexible polymer coil when the polymer chains do not have a very strong affinity for the surface and the coil size in the solution is comparable to the particle diameter.^{37,38} It was experimentally found that the rheological behavior of a suspension is changed from a shear thickening to a shear thinning behavior by altering the solvent system and using a polymer with a stronger affinity.³⁹ The rheological response to an increase in the shear rate of the KD3-stabilized Ni suspension changed from shear thinning behavior to shear thickening behavior upon the addition of EC (see Fig. 1). This implied that the affinity of the adsorbed polymer either decreased or the coil size of the adsorbed polymer increased by the particle size.

Preadsorbed Hypermer KD3 was desorbed by the addition of EC (see Fig. 3), which resulted in a decrease in the concentration of Hypermer KD3 at the interface between the Ni particles and DHT. In general, the diffusivity of a polymer with a lower molecular weight is higher than that of a higher molecular weight polymer,¹⁴ and thus, upon the coaddition of Hypermer KD3 and EC, the Hypermer KD3 ($M_w = 4090$ g/mol) can diffuse and is adsorbed faster than the EC ($M_w = 142\,400$ g/mol). However, thermodynamically, the polymer with the higher molecular weight is preferentially adsorbed onto the particle surface compared with that of lower molecular weight.^{13,14} When the molecular weights differ by a factor of 2 or more but the affinity of two molecules for a particle surface is similar,¹⁵ a complete detachment of the shorter chains from the adsorbed site occurs. However, Hypermer KD3 can be strongly adsorbed on the Ni particle surface via an acid–base interaction between the carboxylic acid and imine of the Hypermer KD3 and the Ni particle surface. On the other hand, EC is weakly adsorbed on the Ni particle surface via hydrogen bonding⁴⁰ between the hydrogen groups on the macromolecular chains and the oxygen atoms on the Ni particle surface. Consequently, the preadsorbed Hypermer KD3 molecules are partially displaced from the surface by EC even though EC has a molecular weight 34 times larger than

that of Hypermer KD3. This yielded results that were similar to previous results reported by Lewis *et al.*¹⁹ regarding the competitive adsorption between MFO fish oil and PMMA. Such a phenomenon occurs when the segmental adsorption energy difference dominates over the chain length differences.¹³ At low concentrations of dispersant at the interface between the particle and solvent medium, dispersant that is attached to one particle can bridge itself to available sites on a second, nearby particle, forming a so-called polymeric bridge, which results in flocculation. Therefore, it can be concluded that polymeric bridging leads to the shear thickening of the Hypermer KD3-stabilized Ni suspension which was induced by the addition of EC.

In contrast, the addition of EC did not change the rheological behavior of the RE610-stabilized Ni suspension (see Fig. 1). The intensity of the IR characteristic peak of RE610 had not changed even after the EC was added (see Fig. 4), which implied that the RE610 concentration at the interface between the Ni particle and DHT was maintained to some extent. Phosphonic acid derivatives are anchored via both the coordination of the phosphoryl oxygen (P = O) to Lewis acid sites and condensation reactions between the surface hydroxyl groups and P–OX (X = H, Me₃Si, Et, etc.) groups.⁴¹ After the anchoring of RE610 on the Ni surface, a relative decrease of the R–OH vibration peak was observed compared with the P = O stretching bond, suggested that condensation of Ni–OH and P–O had occurred, according to



Even after EC was added, the concentration of RE610 at the interface between the Ni particles and DHT was maintained because its functional group, phosphonic acid, had a stronger affinity for the metal oxide surface than even a carboxylic acid.^{27,28} Polymer bridging can be hindered by the presence of an immobilized layer which can prevent other polymer chains from reaching the solid surface of the particle and by polymer molecules which might be capable of taking the adsorption site that is newly produced by the desorbing polymer chain.³⁸ Therefore, it can be considered that RE610 acts as an immobilized layer against EC or can immediately occupy any vacant adsorption site. Consequently, the addition of EC cannot alter the rheological properties of the RE610-stabilized Ni suspension.

V. Conclusions

The interaction of a commercial dispersant and the EC binder on the particle surface and its influence on the dispersion stability of the Ni suspension were investigated. The rheological behavior of the Ni suspension with the commercial dispersants was characterized to evaluate the effectiveness of the commercial dispersants. Both Hypermer KD3 and RE610 provided an effective stabilization of the Ni suspension without EC. However, upon the addition of EC, the Hypermer KD3 deteriorated the rheological behavior of the Ni suspension, whereas the RE610 still provided dispersion stability to the Ni suspension. It was confirmed from a DRIFTS analysis that these results are attributable to the competitive adsorption between the dispersant and binder molecules. It was found that the RE610 in the presence of the EC retained a stronger anchoring and higher affinity on the Ni particle surface than that of the Hypermer KD3 in the presence of EC. Furthermore, because RE610 contains a phosphate ester, additional dispersion stability was imparted to the Ni suspension. These results will impact the preparation of the Ni paste and the dispersant selection when using EC as a binder for the fabrication of multilayer ceramic packages.

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