Titanate coupling agent effects on nonaqueous Co_2Z ferrite suspensions dispersion

Hsing-I Hsiang · Jaw-Yue Tsai

Abstract Co_2Z ferrite powders with the chemical composition $3Ba_{0.5}Sr_{0.5}O·2CoO·12Fe_2O_3$ have superior high frequency magnetic properties. However, Co_2Z ferrite powders are difficult to apply to practical processes because of agglomeration induced by the strong magnetic attraction between particles. In this study, Co_2Z ferrite powder pretreatment using a titanate coupling agent—Neopentyl (dially)oxy tri(dioctyl)pyrophosphate titanate (Lica 38) on the sedimentation and rheological behavior is investigated. The bonding mechanisms between ferrite powder, Lica 38, and dispersant (KD1) are studied using diffuse reflectance Fourier transform infrared spectroscopy is used to explain the difference in the rheological and sedimentation behaviors of untreated and titanate coupling agent-modified ferrite powders. The affinity of Co_2Z ferrite and dispersants could be substantially enhanced by coating a titanate- coupling agent onto the ferrite surface. The coated layer could prevent particles from agglomerating from magnetic interaction.

Introduction

Magnetic components must be miniaturized to reduce device size in communication systems. The multilayer chip inductor was developed to increase the volume efficiency. They are important components in the latest products, such as notebooks, cellular phones, etc. The advantages of these chip devices over conventional

wire wound components are excellent magnetic shielding and miniaturization. This chip device can suppress high harmonic noise to the greatest extent. In today's market, equipment is diversifying and digital equipment is acquiring over-greater levels of performance. In this environment, device-processing speeds accelerate above 100 MHz. These trends have increased the complexity of the issues relating to noise suppression because the noise band increases to frequencies between 300 and 1000 MHz. In traditional multilayer chip inductors (NiCuZn ferrites), the impedance decreases rapidly between the 300 and 1,000 MHz bands because the Snoek limit [1] cannot suppress ultrahigh frequency EMI noise. Therefore, it is desirable to develop a material that has a resonance frequency higher than 1,000 MHz that can be used in making multilayer chip inductors.

Magnetoplumbite ferrites with hexagonal structures have revealed a higher dispersion frequency than that of nickel ferrites because of magnetoplumbite anisotropy [2]. Hsiang [3] observed that the multilayer chip inductors made of Co_2Z ferrite using the tape casting process exhibited excellent magnetic properties.

However, the ferrite particles tend to hold together, forming agglomerates because of the strong magnetic interactions between ferrite particles during tape casting slurry preparation. The agglomerates generally lead to the formation of microstructural defects in the green tapes, which affect the quality of magnetic devices. In this study, a titanate-coupling agent was adsorbed onto ferrite powder in the absence of dispersant during the first mixing stage. A commercial polymer dispersant was then introduced into the suspension during the second stage. The effect of the adsorbed titanate-coupling agent on dispersant adsorption, rheological

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and sedimentation behavior in nonaqueous Co_2Z ferrite suspensions was investigated. The bonding mechanisms between the ferrite powder, titanate coupling agent, and dispersant were studied using diffuse reflectance Fourier transform infrared spectroscopy to explain the difference in the rheological and sedimentation behaviors of untreated and titanate coupling agent-modified ferrite powders.

Experimental

Materials

The $3Ba_{0.5}Sr_{0.5} \cdot 2CoO \cdot 12Fe_2O_3$ ferrite powders used in this study were prepared following the method reported by Hsiang and Duh [4]. The Co_2Z ferrites were prepared from reagent-grade $BaCO_3$, $SrCO_3$, Co_3O_4 and Fe_2O_3, which were mixed and calcined at 1,200 °C for 2 h. The calcined powder used as the raw material was milled for 60 h using YTZ balls. Titanate coupling agent, tri(dioctyl)pyro-phosphato titanate-Lica 38 (Kenrich Petrochemicals Inc., USA) and a commercially available dispersant, KD1 (ICI surfactant, USA), were used without further purification. Ethanol and toluene were used as the solvent and prepared in a 60:40 ratio before use.

Experimental procedure

Prior to surface modification, the Co_2Z ferrite powders were dried in an oven to remove moisture. The Co_2Z ferrite powders with the addition of Lica 38 and solvent were ball-mixed in polyethylene bottles for 16 h. The titanate-coupling agent concentration varied from 0.2 to 1.2% of the solid weight. After ball-mixing, the slurry was simultaneously agitated and dried at 80° C for 24 h. The surface modified Co_2Z ferrite powders were subsequently washed 3 times with ethanol to remove the nonadsorbed Lica 38.

Suspensions were prepared by mixing 30 vol% Co_2Z ferrite powders with solvent and KD1. KD1 was used at weight fractions ranging from 0.2 to 1.2%, based on the Co_2Z ferrite solids loads. To breakdown the agglomerates, the suspensions were sonicated for 15 min. using a high-energy ultrasonicator. The rheological behaviors of the examined suspensions were characterized using a cone/plate viscometer (Model DV-III, Brookfield, USA).

The suspensions were prepared using the process stated earlier, then allowed to stand undisturbed at room temperature for 200 h to achieve complete settling prior to the sedimentation studies. Sediment height was recorded and used as an indicator for Co_2Z ferrite powder dispersion.

The chemical characteristics of Co_2Z ferrite powders with and without Lica 38 treatment, adsorbed by KD1 were determined using Fourier transform infrared spectroscopy (Model DA 3.002, Bomem, Canada).

Results and discussion

Adsorption of Lica 38

Figure 1 shows the FTIR spectra of Lica 38. The main absorption bands at 1,215, 1,143, 1,045, and 928 cm^{-1}
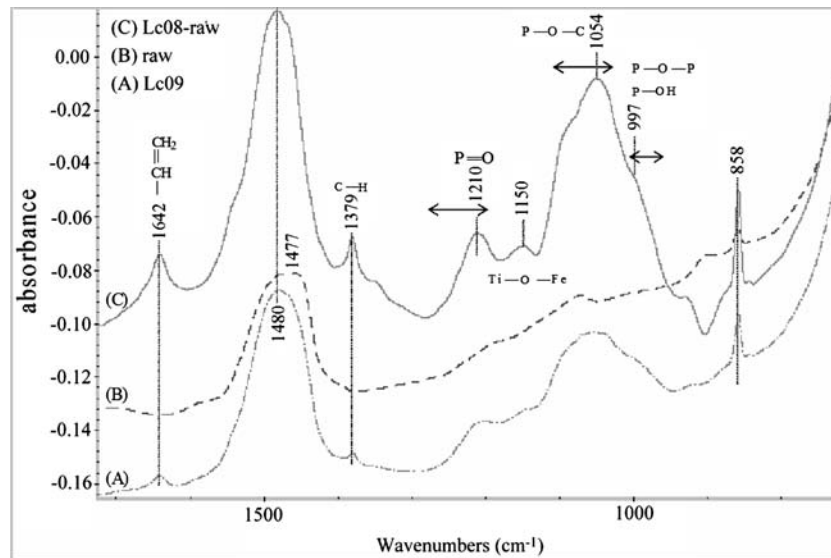
Fig. 1 FTIR spectra of Lica 38
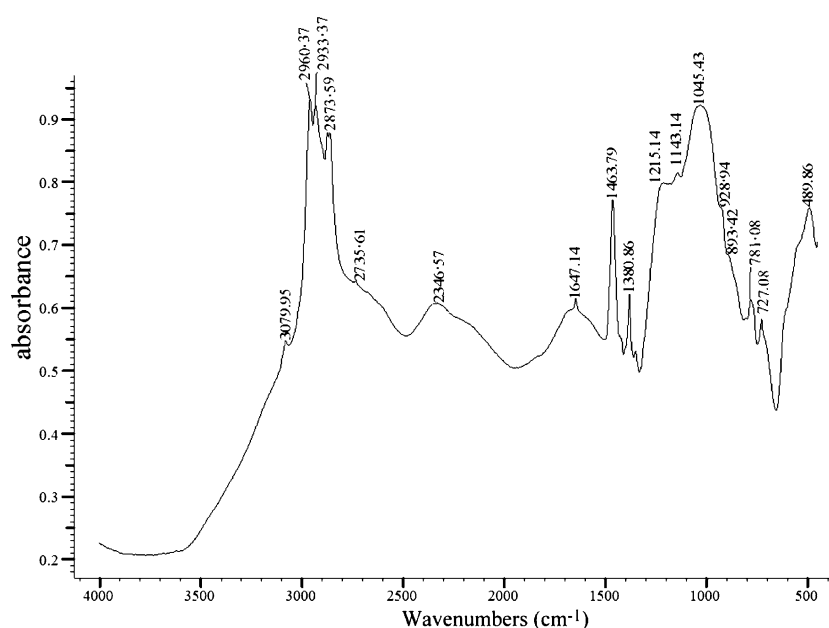
appearing in Fig. 1 are attributed to the P=O, Ti–O, P–O–C, P–O–P, and P–OH groups, respectively. The FTIR spectra of Co$_2$Z ferrite powders treated with 0.8 wt% Lica 38 are shown in Fig. 2. Spectrum A is the Lica 38-treated Co$_2$Z ferrite powder, spectrum B is Co$_2$Z ferrite powder, and the difference between spectrum of A and B is shown in spectrum C. The new peak at 1,150 cm^{-1} is observed. It is believed that the peak is related to the Ti–O–Fe linkage formed by breaking Ti–O–C and bonding with FeOH as reported by Singh et al. [5]. A significant reduction in O–H peaks at above 3,650 cm^{-1} associated with Fe–O–H for ferrite powder (Fig. 3A) are observed in Lica 38-treated Co$_2$Z ferrite powders (Fig. 3B–E). The absorption bands at 3,500–3,100 cm^{-1} shown in Fig. 3B–E result

from the O–H group of Lica 38. The above results confirm that the adsorption of Lica 38 into the ferrite powders takes place through the formation of Ti–O–Fe bonding.

The relative integrated intensities of Ti–O–Fe bonding around 1,150 cm^{-1} with respect to the absorption peak belonging to ferrite powders at 858 cm^{-1} (A_{1150}/A_{858}) obtained from the Lica 38-treated ferrite powders are plotted against the Lica 38 amounts in Fig. 4. The A_{1150}/A_{858} value in Fig. 4 can be used as an indicator for Lica 38 adsorption onto the ferrite powder surface. The amount of Lica 38 adsorbed onto the surface of the ferrite powders increased with increasing Lica 38 addition into the slurry.
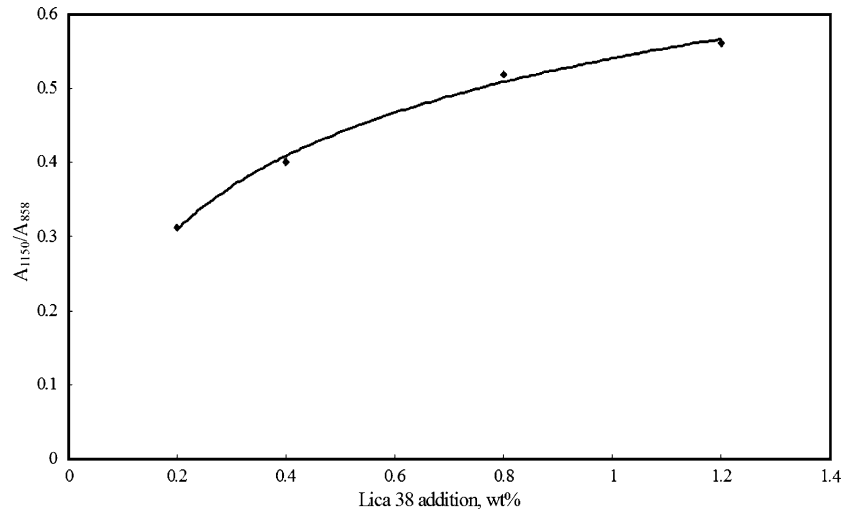

Fig. 2 FTIR spectra of Co$_2$Z ferrite powders treated with 0.8 wt% Lica 38 in the region 800–1800 cm^{-1}

Fig. 3 FTIR spectra of Co$_2$Z ferrite powders treated with Lica 38 in the region 3000–3850 cm^{-1}
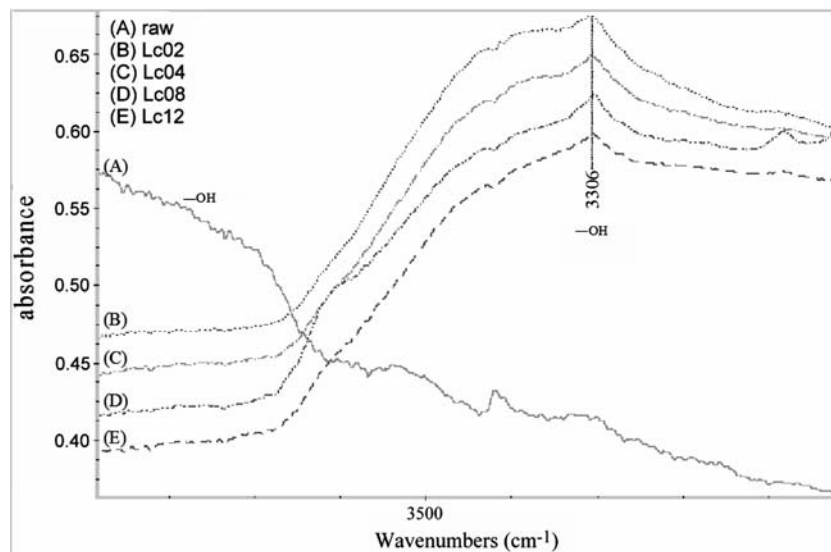
Fig. 4 Integrated intensity ratio, A_{1150}/A_{858}, for Lica 38 adsorption onto the surface of ferrite powders as a function of Lica 38 addition
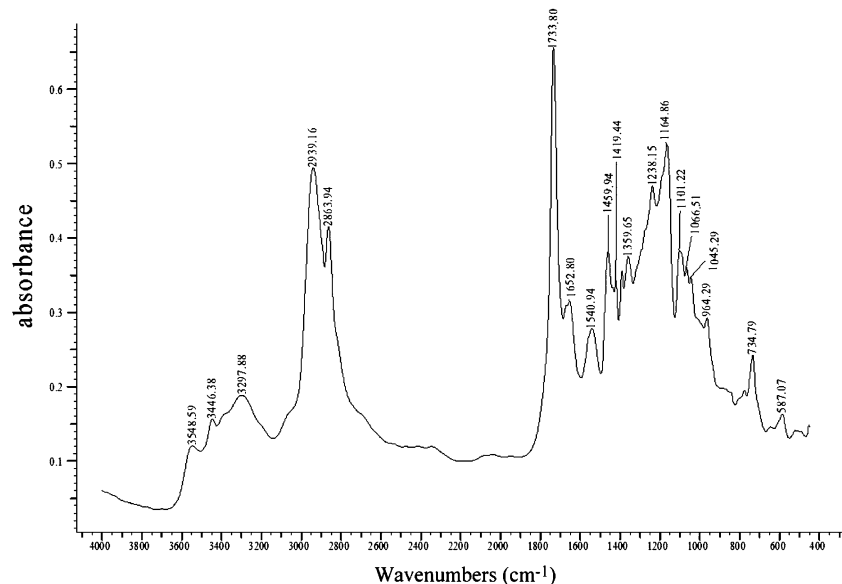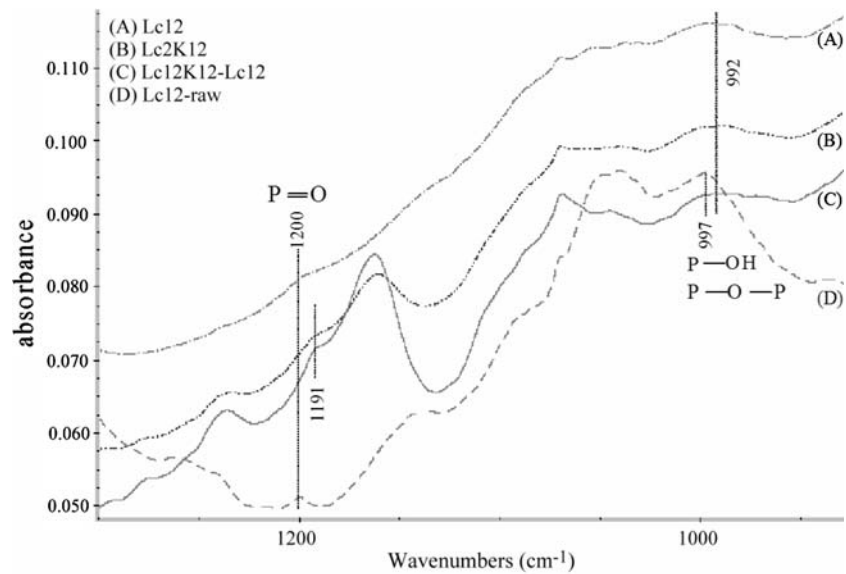

KD1 adsorption

Figure 5 shows the FTIR spectra for KD1. Intense of absorption bands at 1,733, 3,446, and 3,548 cm^{-1} due to the COOH and OH groups were observed in KD1. The FTIR spectra of Co$_2$Z ferrite powders treated with 1.2 wt% Lica 38 in the region 920–1,300 cm^{-1} before and after the addition of 1.2 wt% KD1 are shown in Fig. 6. Spectrum A gives the Co$_2$Z ferrite powders treated with Lica 38, showing that the absorption band at 1,200 cm^{-1} is associated with P=O and the absorption band at 992 cm^{-1} is due to P–OH or P–O–P. The FTIR result from Lica 38-treated ferrite powders with adsorbed KD1 is given in spectrum B. The difference in spectrums in Fig. 6, was obtained by subtracting spectrum B from spectrum A, and

shown as spectrum C. Spectrum D is the spectral difference for Lica 38-treated Co$_2$Z ferrite powder after subtracting the absorbance of pure Co$_2$Z ferrite powder. Comparing spectrum C and D, the bands at 1,200 and 997 cm^{-1} are observed to shift to 1,191 and 992 cm^{-1}, respectively. The FTIR spectra of Co$_2$Z ferrite powders treated with 1.2 wt% Lica 38 in the region 3,100–3,600 cm^{-1} before and after the addition of 1.2 wt% KD1 are shown in Fig. 7. The spectral difference in Fig. 7C, was obtained by subtracting spectrum B (Lica 38-treated Co$_2$Z ferrite powders with the addition of KD1) from spectrum A (Lica 38-treated Co$_2$Z ferrite powders). Spectrum D is the spectral difference in Lica 38-treated Co$_2$Z ferrite powder after subtracting the absorbance of pure Co$_2$Z ferrite powder. The band near 3,306 cm^{-1} related to

Fig. 5 FTIR spectra of KD1

Fig. 6 FTIR spectra of Co$_2$Z ferrite powders treated with 1.2 wt% Lica 38 in the region 920–1300 cm^{-1} before and after the addition of 1.2 wt% KD1


the P–OH group of Lica 38 shifts to 3302 cm^{-1}. The above results indicate that the adsorption of KD1 into the ferrite powders takes place through hydrogen bonding between the O–H groups in KD1 and P–OH groups in the Lica 38, as schematically shown in Fig. 8.
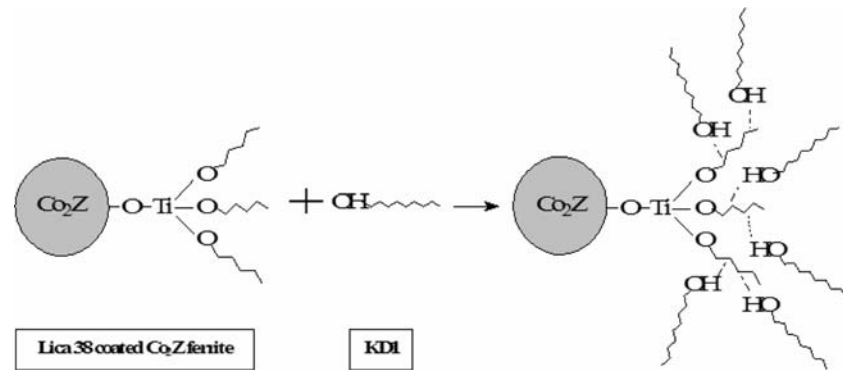
Figure 9 shows the FTIR spectra of Co$_2$Z ferrite powders treated with 1.2 wt% Lica 38 in the region 800–1,800 cm^{-1} before and after the addition of various amounts of KD1. The spectral difference obtained by subtracting the spectrum of Lica 38-treated Co$_2$Z ferrite powders with the addition of KD1 from the spectrum of Lica 38 (Fig. 9E), are shown in spectrums A–D. The new bands appearing in Fig. 9A–D all belong to KD1 groups, with the exception of the band near 856 cm^{-1}, which relates to

ferrite powders. The relatively integrated intensities of the –COO group around 1,737 cm^{-1} with respect to the absorption peak belonging to ferrite powders at 856 cm^{-1} (A_{1737}/A_{856}) obtained from the various amounts of Lica 38-treated ferrite powders are plotted against the KDI amounts in Fig. 10. This indicates that the amount of KD1 adsorption onto the surface of the ferrite powders increased with increasing Lica 38 addition into the slurry. After coating Lica 38 onto the Co$_2$Z ferrite powders, the ferrite powder and dispersant affinity was dramatically increased. This maybe because the coupling agent adsorbed onto the surface provided more active sites (P=O, P–O–P, P–OH) that could interact with the dispersants.

Fig. 7 FTIR spectra of Co$_2$Z ferrite powders treated with 1.2 wt% Lica 38 in the region 3100–3600 cm^{-1} before and after the addition of 1.2 wt% KD1
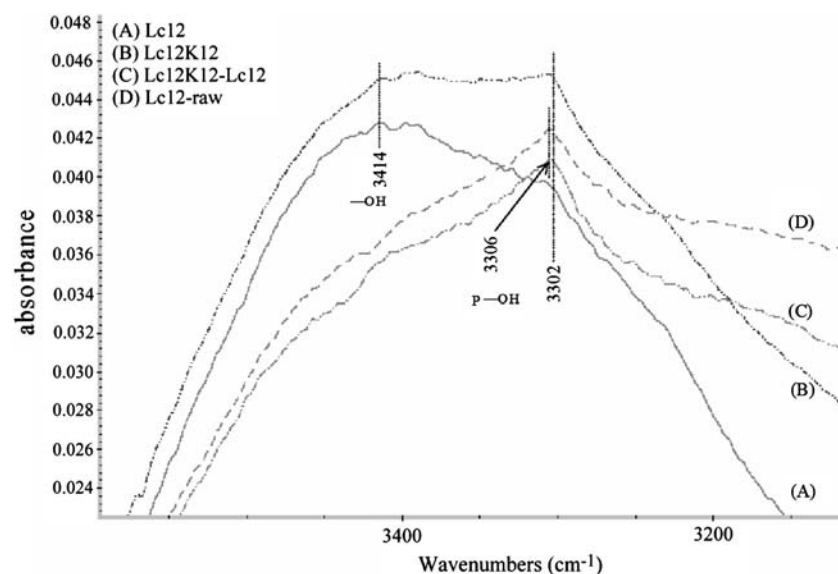
Fig. 8 Schematic of the adsorption mechanism of KD1 onto the surface of Lica 38-treated ferrite powders

Fig. 9 FTIR spectra of Co_2Z ferrite powders treated with 1.2 wt% Lica 38 in the region 800–1800 cm^{-1} before and after the addition of various amounts of KD1
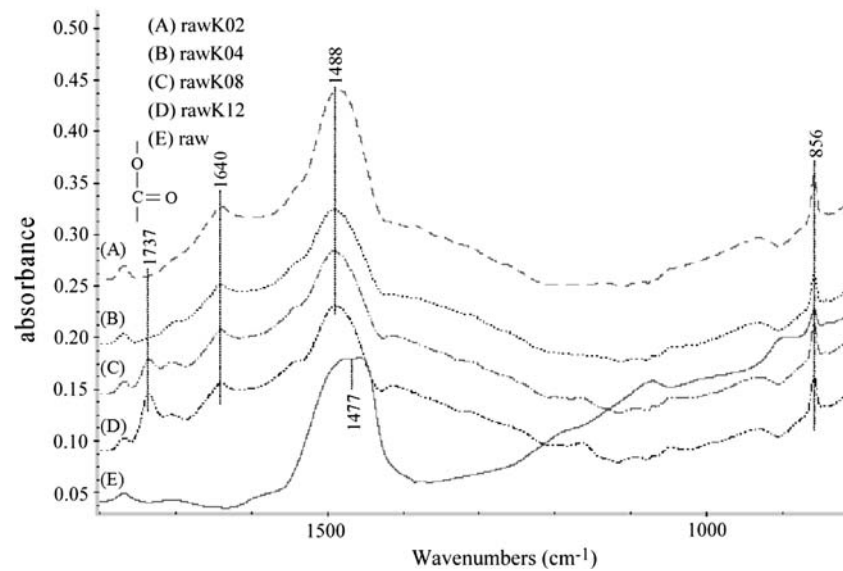
Fig. 10 Integrated intensity ratio, A_{1737}/A_{856}, for KD1 adsorption onto the surface of Lica 38-treated ferrite powders as a function of KD1 addition
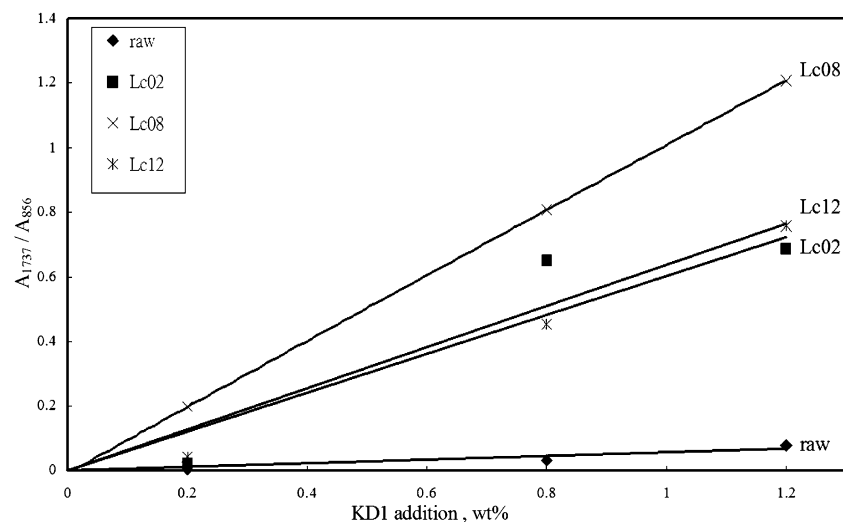

Rheological and sedimentation behaviors

The dispersion of non aqueous Co_2Z ferrite suspensions were assessed by measuring their rheological and sedimentation behaviors. Figure 11 shows the viscosities at a constant shear rate $\gamma = 7.6$ s^{-1} for the Lica 38-treated ferrite powders added with various amounts of KD1. The sedimentation heights of the Lica 38-treated ferrite powders for increasing KD1 concentration in solvent are given in Fig. 12. For all

Fig. 11 The viscosities at constant shear rate $\gamma = 7.6 \text{ s}^{-1}$ for the Lica 38-treated ferrite powders as a function of the concentration of KD1
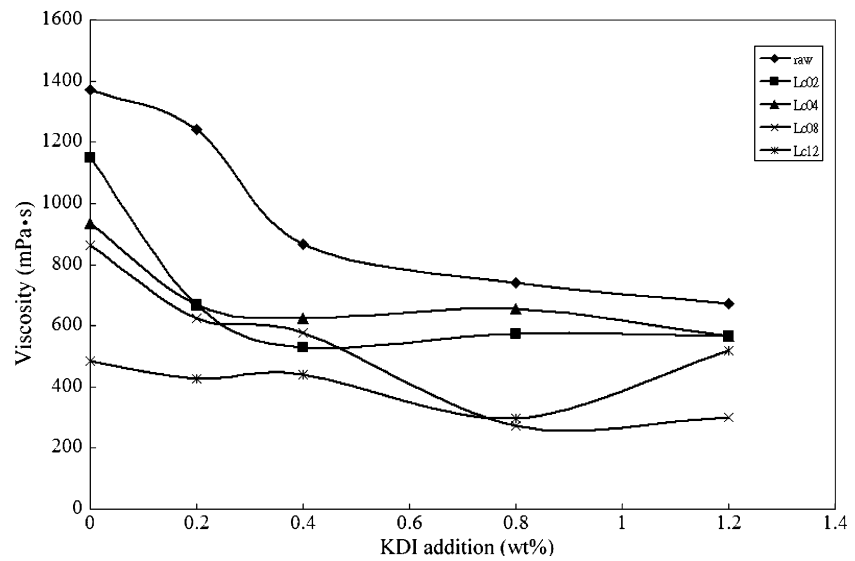
Fig. 12 The sedimentation heights of the Lica 38-treated ferrite powders for increasing KD1 concentration in solvent
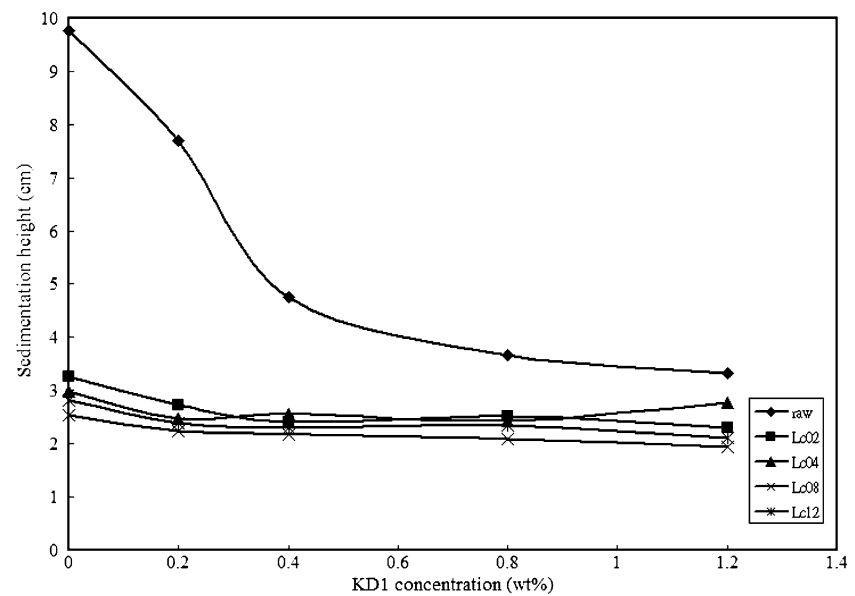
KD1 concentrations investigated, the Lica 38-treated ferrite powders yielded much lower viscosities and sedimentation heights than those without Lica 38 pre-treatment. This indicates that coating Lica 38 onto the ferrite powders can provide a surface coverage on the particle surface and effectively prevent the particles from agglomerating from the magnetic interaction. For 0.2 and 0.4 wt% Lica 38-treated ferrite powders, the viscosities and sedimentation heights decreased initially, then followed little dependence on the KD1 concentration as the KD1 concentration increased above 0.4 wt%. Clearly, full and monolayer coverage of Lica 38 onto ferrite powders was not formed for 0.2 and 0.4 wt% Lica 38-treated ferrite powders, as shown in Fig. 4. Therefore KD1 can adsorb onto the surface

of 0.2 and 0.4 wt% Lica 38-treated ferrite powders at KDI concentrations below 0.4 wt%, which improves the dispersion. The viscosities and sedimentation heights of 0.8 wt% Lica 38-treated ferrite powders decreased with increasing KD1 concentration and yielded lower viscosities than 1.2 wt% Lica 38-treated ferrite powders at higher KD1 concentration (above 0.8 wt%). This may be due to the higher adsorption amounts of KD1 onto the surface of 0.8 wt% Lica 38-treated ferrite powders than that for 1.2 wt% Lica 38-treated ferrite powders, as shown in Fig. 10. As the KD1 concentration increased above 0.8 wt% for 1.2 wt% Lica 38-treated ferrite powders, the excess KD1 resulted in polymer bridging for the observed increased viscosity.

Conclusion

1. The Ti–O–Fe covalent bond was formed through the interaction of the Ti–O bond in Lica 38 and FeOH onto the surface of ferrite powders.
2. The adsorption of KD1 onto the surface of Co_2Z ferrite powders takes place through hydrogen bonding between the hydroxyl groups on the surface of the ferrite powders and the KD1 hydroxyl groups.
3. After coating Lica 38 onto the Co_2Z ferrite powders, the affinity of the ferrite powders and dispersants was dramatically increased. This maybe because the coupling agent adsorbed onto the surface provided more active sites that could interact with the dispersants than raw material powders.
5. The affinity of Co_2Z ferrite and dispersants could be substantially enhanced through coating a titanate-coupling agent onto the ferrite surface. The coating layer prevented particles from agglomerating due to the magnetic interaction.

References

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