JOURNAL OF MATERIALS SCIENCE 23 (1988) 1729–1734

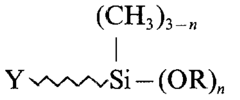
Adsorption of silane coupling agent on Co-γ-Fe_2O_3 and its effect on dispersibility

SHIGEO AOYAMA, KENJI SUMIYA, MASAHIRO AMEMIYA
Hitachi Maxell Ltd, Oyamazaki, Otokuni, Kyoto 618, Japan

The adsorption of a new type of silane coupling agent containing polyethylene oxide (EOS) on cobalt-modified iron oxide (Co-γ-Fe_2O_3) particles and its effect on dispersibility are examined by measuring the surface chemical properties. The EOS is adsorbed on Co-γ-Fe_2O_3 in the form of a monolayer and reduces the hydrophilicity of the surface of the particles with the adsorption. The surface hydrophilicity of EOS-treated iron foil (the iron foil has an ideal iron oxide surface) becomes lower with the increasing heat-treatment temperature. Heat treatment at 80° C or higher is required to achieve chemical bonding between EOS and the iron foil. By the same heat treatment, EOS polymerizes on the iron foil resulting in the formation of a polysiloxane network. The dispersibility of the particles in vinyl chloride–vinyl acetate–vinyl alcohol copolymer solution is improved dramatically by the surface treatment with EOS. The improvement in dispersibility is explained by considering the increase of the wettability of Co-γ-Fe_2O_3 for the solvent due to EOS treatment.

1. Introduction

Silane coupling agents have been widely used as adhesion promoters in fibre-reinforced plastic (FRP) since the 1960s [1, 2]. To date, many studies [2–6] have been conducted regarding the behaviour of silane coupling agents in composite materials. The general structure of silane coupling agents is described as



$$\begin{array}{c}(CH_3)_{3-n}\\ | \\ Y\sim\sim\sim Si-(OR)_n\end{array}$$

$n = 2$ or 3

where OR, an alcoxy group, hydrolyses in the presence of water to form silanols which, in turn, can both polymerize and react with hydroxyl groups on an inorganic material surface. The Y group, which is reactive with an organic polymer matrix, is generally composed of amino, acryl or epoxy groups. In this manner, the silanes can bind glass fibre to the organic polymer through a chemical bonding and improve the mechanical properties of FRP.

Recently, new types of silane coupling agents with a function different from adhesion promotion have been developed and applications of the new silanes as surface-treatment agents, specifically dispersant, lubricant or electro-conductive agent, are under investigation. The new silanes can repair organic groups to the substrate surface by chemical reaction between the silanol group derived from the hydrolysis of the OR group and the hydroxyl group on the substrate surface. However, there are few basic studies on the adsorption behaviour of these new silanes.

In this work, as a fundamental study of magnetic dispersion, the adsorption behaviour of the new type silane coupling agent containing polyethylene oxide (EOS), and its ability to improve dispersibility of fine Co-γ-Fe_2O_3 particles, were investigated.

2. Experimental details

2.1. Materials

The structure of EOS determined by the use of NMR is

$$RO(CH_2CH_2O)_nCH_2CH_2CH_2Si(OR')_3$$

Its impurities were not detectable. Acicular Co-γ-Fe_2O_3 having a coercivity of 600 Oe and the specific surface area of $39.5\,m^2\,g^{-1}$ were used as magnetic particles. A vinyl chloride–vinyl acetate–vinyl alcohol copolymer (PVCAL) and an equal mixture of methyl iso-butyl ketone and toluene was used as a binder resin and a solvent, respectively. In this study, an ultra-high purity iron foil having an Fe purity of 99.99%, and a thickness of 65 μm which had an ideal iron oxide surface, was used as a model for the magnetic particle surface. From ESCA measurement, it was confirmed that an iron oxide layer with a thickness of about 4.5 nm was formed on the surface of the iron foil.

2.2. Measurement of the EOS absorption amount

Silane coupling agents have been known to change their chemical structure during hydrolysis resulting in polymerization or reaction with the hydroxyl group on the surface of a substrate [3, 4]. Because X-ray fluorescence measurement can detect the number of silicon atoms which are not involved in hydrolysis or coupling reaction, this method is suitable for measuring the amount of silane adsorption on the particles.

Initially, we made a calibration curve which indicated the relationship between detected intensity of silicon atoms originating from EOS and the additional amount of EOS adhering to the particles. The correlation coefficient of this calibration curve was 0.995.

The adsorption of EOS was achieved by dispersing Co-γ-Fe_2O_3 particles ultrasonically in an iso-propyl alcohol solution of EOS at various concentrations. The intensity of silicon atoms in the particles originating from adsorbed EOS was measured by X-ray fluorescence, and the EOS adsorption amount was obtained using the calibration curve.

2.3. Surface pressure–area curve measurement of EOS

Surface pressure (π)–area (A) curve of EOS was measured using a Wilhelmy-type surface balance for the purpose of obtaining the area occupied by an EOS molecule. The benzene solution of EOS was spread on 2 M NaCl aqueous solution, because EOS dissolves in pure water, and the salting out of EOS against NaCl aqueous solution was confirmed. After the evaporation of benzene, the barrier was pressed at a rate of 40 mm min^{-1}. During this process, the π–A curve was recorded automatically, and the area occupied by one EOS molecule was calculated from the curve obtained.

2.4. Dispersibility measurement of Co-γ-Fe_2O_3

In this experiment, EOS-treated Co-γ-Fe_2O_3 (treated by dispersing the particles in an iso-propyl alcohol solution of EOS) was previously heated at 80° C for 1 h in air to ensure the coupling reaction between EOS and the surface of particles had occurred [5, 6].

1 g EOS-treated particles were dispersed ultrasonically in 20 ml PVCAL solution. The amount of PVCAL adsorbed on the particles was calculated from the difference in solution concentration before and after dispersion. The final sedimentation volume of the particles in the same dispersion was also measured to estimate the dispersibility of the particles in a dilute binder solution. The magnetic paint was prepared with a more concentrated solution. PVCAL concentration and the content of particles in the magnetic paint were set at 13 and 80 wt %, respectively. The dispersibility of the particles which were treated in 1% iso-propyl alcohol solution of EOS was evaluated by transmission electron microscope (TEM) observation of a very thin coating of the magnetic paint on an acetylcellulose film.

2.5. Contact angle measurement

The value of the water contact angle on the surface of iron foil reflects its surface property. The increase of the water contact angle through surface treatment means that the character of the surface of the iron foil changes from hydrophilic to hydrophobic.

The surface treatment was made by dipping the iron foil in an iso-propyl alcohol solution of EOS at various concentrations. The water contact angle on the iron foil was measured using the droplet method. A droplet of water on the foil was enlarged by TV camera and was projected on to a cathode ray tube (CRT). The radius r_a, r_r and the height h_a, h_r of the enlarged droplet were measured. The contact angle, θ, was calculated from the following equations [7] (the subscript a and r represent advancing and receding, respectively)

$$\tan(\theta_a/2) = h_a/r_a, \quad \tan(\theta_r/2) = h_r/r_r$$

$$\cos\theta = (\cos\theta_a + \cos\theta_r)/2$$

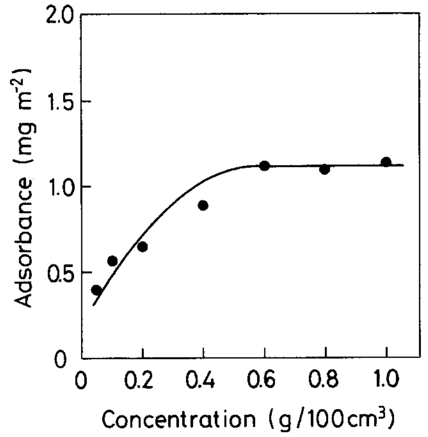


Figure 1 Relation between EOS adsorbance on Co-γ-Fe_2O_3 and initial concentration of iso-propyl alcohol solution of EOS.

2.6. FT–IR analysis

Fourier transform–infrared (FT–IR) analysis was used to examine the change in the chemical structure of EOS accompanied by heat treatment. A pellet composed of 1 mg EOS and 300 mg KBr was used for the analysis of EOS itself with and without heat treatment. EOS on the iron foil was analysed by attenuated total reflection (ATR) infrared spectra. The iron foil treated in 0.1% iso-propyl alcohol solution of EOS was placed at 45° with a germanium plate to obtain ATR spectra. Each spectrum was recorded at a resolution of 4 cm^{-1} with a total of 300 scans.

3. Results and discussion

3.1. Adsorption behaviour of EOS on Co-γ-Fe_2O_3

The relation between the amount of EOS adsorption on Co-γ-Fe_2O_3 and the initial concentration of EOS solution is shown in Fig. 1. When the concentration of the solution is less than 0.6%, the amount of adsorption varies in proportion with the concentration. At a concentration of about 0.6%, the amount of adsorption is saturated with about

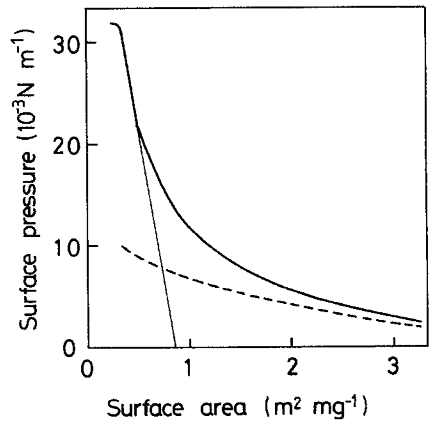


Figure 2 Surface pressure–area curve of EOS. Water phase: (——) 2 M NaCl aqueous solution, (– – –) distilled water. Spread from benzene solution.

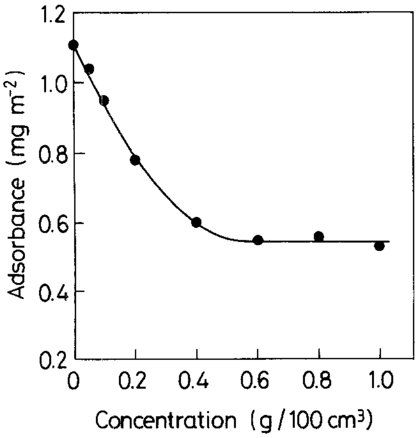


Figure 3 Relation between the saturated adsorbance of PVCAL on EOS-treated Co-γ-Fe_2O_3 and the concentration of EOS solution in the treatment of Co-γ-Fe_2O_3.

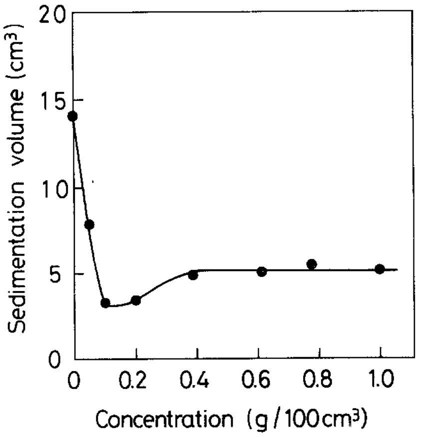


Figure 4 Relation between the sedimentation volume of EOS-treated Co-γ-Fe_2O_3 in PVCAL solution and the concentration of EOS solution in the treatment of Co-γ-Fe_2O_3.

1.1 $mg\,m^{-2}$. These changes in the amount of adsorption mean that EOS adsorbs on Co-γ-Fe_2O_3 in the form of a monolayer.

The π–A curve of EOS is shown in Fig. 2. The area occupied by one EOS molecule was calculated to be 0.82 $m^2\,mg^{-1}$ from this π–A curve. On the other hand, the area occupied by one EOS molecule calculated from the saturated adsorption amount, molecular weight of EOS and specific surface area of Co-γ-Fe_2O_3, was 0.9 $m^2\,mg^{-1}$. The good agreement of these two values indicates that the EOS molecule is arranged densely and is oriented perpendicular to the surface in the state of its saturated monolayer on Co-γ-Fe_2O_3 particles. On the surface of the 2 M NaCl aqueous solution, it is considered that for the EOS molecule orientation, the hydrophilic silanol group formed by the hydrolysis faces towards the solution surface and the polyethylene oxide chain faces outwards from the solution surface. When an EOS molecule follows the above mentioned adsorption conformation on the particle as well, the surface hydrophilicity of Co-γ-Fe_2O_3 particles becomes lower with EOS adsorption.

3.2. Dispersibility of EOS-treated Co-γ-Fe_2O_3

Decrease in the hydrophilicity of Co-γ-Fe_2O_3 particles due to the adsorption of EOS was checked by measuring the amount of PVCAL adsorbed. The amount of a binder resin containing hydroxyl groups, like PVCAL, which is adsorbed depends on the surface property of the particles [8]. The amount of binder adsorption decreases as the hydrophilicity of the surface of the particles becomes lower.

The relation between the saturated adsorption amount of PVCAL and the concentration of EOS solution in the treatment of Co-γ-Fe_2O_3 is shown in Fig. 3. The amount of PVCAL adsorbed decreases with the increasing treatment concentration up to 0.6%. With a concentration greater than 0.6%, the amount of adsorption shows a constant value. The decrease in the amount of PVCAL adsorbed indicates that the hydrophilicity of the particles is reduced by the adsorption of EOS. When the treatment concentration is above about 0.6%, there is no change in the amount of adsorption. This means that the formation of a monolayer of EOS is completed and there is no further reduction in the hydrophilicity.

The final sedimentation volume of EOS-treated Co-γ-Fe_2O_3 in PVCAL solution of 1% is shown in Fig. 4. When the concentration of the EOS solution in the treatment of Co-γ-Fe_2O_3 is above 0.1%, the sedimentation volume of the particles is remarkably reduced, and it is about 30% of that of untreated Co-γ-Fe_2O_3. In the case of magnetic paint, dispersibility was estimated by electron microscope observation. TEM photos of Co-γ-Fe_2O_3 particles dispersed in 13 wt % PVCAL solution are shown in Fig. 5.

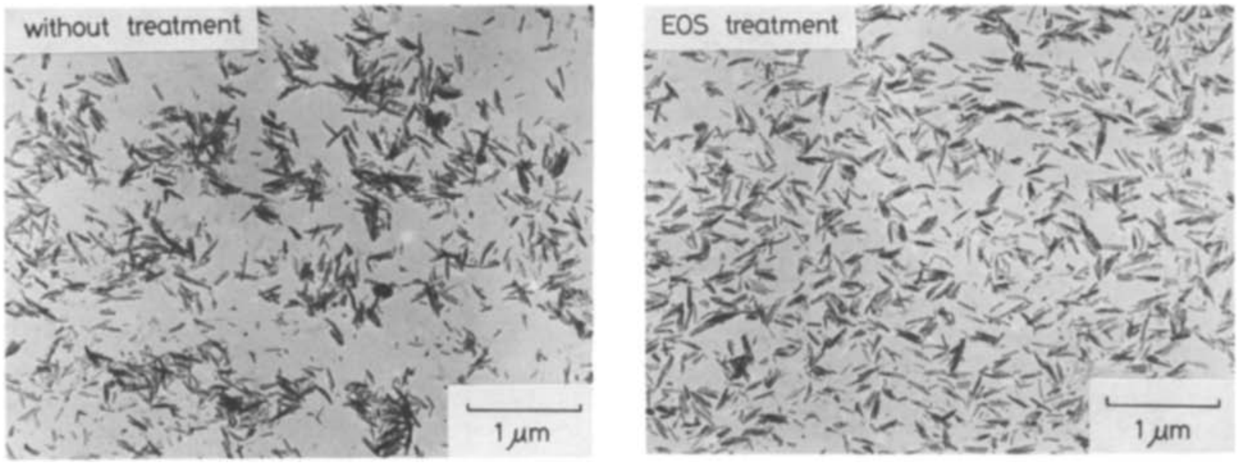


Figure 5 TEM photos of Co-γ-Fe_2O_3 with and without EOS treatment in magnetic paint.

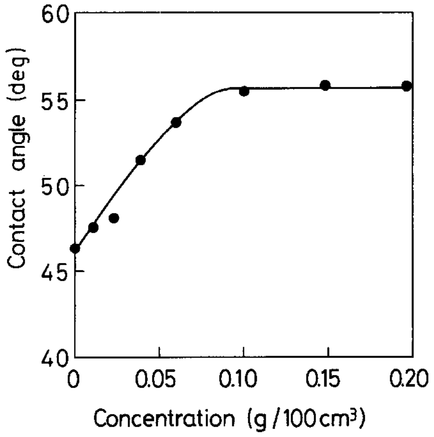


Figure 6 Relation between the contact angle of water on EOS-treated iron foil and the concentration of EOS solution in the treatment of iron foil.

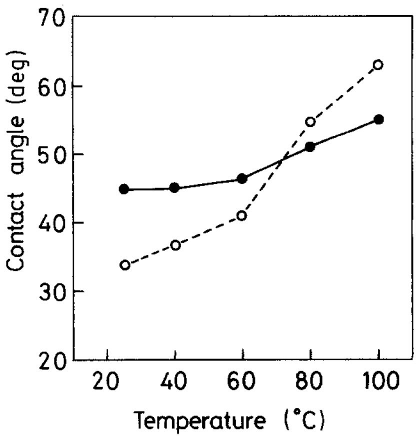


Figure 7 Contact angle dependence of water on EOS-treated iron foil on the heat-treatment temperature, (---) before dipping, (——) after dipping in boiling water for 5 min.

Flocculation observed in the untreated particles is not observed in the particles treated with EOS.

From these results, it is apparent that EOS can improve the dispersibility of Co-γ-Fe_2O_3 in PVCAL solution. Improvement of the dispersibility is explained by considering the increase in the wettability of the particles for the solvent, because the hydrophilicity of the particles is reduced appropriately by EOS treatment.

3.3. Surface hydrophilicity of EOS-treated iron foil

The relation between the contact angle of water on EOS-treated iron foil and the concentration of EOS solution used in the treatment of iron foil is shown in Fig. 6. In this experiment, the same heat treatment (80° C for 1 h) as that used in Co-γ-Fe_2O_3 particles was carried out to confirm the coupling reaction of EOS with the iron foil. The value of contact angle increases with increasing treatment concentration, and saturates to 55° at the treatment concentration of 0.1%. The increase in contact angle means that the adsorption of EOS reduces the hydrophilicity of the surface of the iron foil. Saturation of the contact angle indicates that EOS forms a monolayer on the surface of iron foil at the concentration of 0.1%. From these results, it is considered that the EOS molecule is adsorbed on the iron foil orienting its polyethylene oxide chain perpendicular to the surface to reduce the hydrophilicity. This EOS adsorption behaviour on the iron foil is the same as that observed in Co-γ-Fe_2O_3 particles.

The dependence of the contact angle of water on EOS-treated iron foil on the heat treatment temperature is shown in Fig. 7. In this experiment, EOS-treated iron foil was dipped in boiling water for 5 min after heat treatment to examine the strength of EOS adsorption on the iron foil. The dotted and solid lines represent before and after dipping, respectively. The EOS treatment concentration was fixed at 0.1%.

In the sample before dipping, the contact angle increases from 33° to 65° as the heating temperature is raised from 25 to 100° C. It is found that the surface property of EOS-treated iron foil depends on the heat treatment temperature in addition to treatment concentration. The contact angle on EOS-treated iron foils which are heated at 25 to 60° C is lower than that on the untreated foil. This suggests that not all the EOS silanol groups are adsorbed on the surface of the iron foil, and part of the silanol is exposed to the outside. Because of these unadsorbed silanol groups, it is considered that the surface of EOS-treated iron foil which is heated below 60° C indicates hydrophilic character (the silanol group is known to show a strong hydrophilicity [9]). A number of reports [5, 6, 9, 10] indicated that the reaction of the silanol group of silane coupling agents with the hydroxyl group on the substrate surface was initiated by heat treatment at about 60 to 100° C. In the case of EOS, the silanol group is expected to react with the hydroxyl group on the iron foil surface to form an Si–O–Fe bond [11] by heating.

In the sample after dipping, when the preheat-treatment temperature is less than 60° C, the contact angle increases to 45° which is the same as in the untreated foil. This phenomenon indicates that the EOS silanol groups do not react with the hydroxyl group at temperatures lower than 60° C, and this unreacted, namely physisorbed, EOS is easily removed by dipping in boiling water. On the other hand, when the treated foil is heated at 80° C or higher, the contact angle shows a slightly lower value than that before dipping, but shows a higher value than that of the untreated foil. Chiang and Koenig [5] reported that the amount of silane coupling agents which were removed from the silica surface by dipping in boiling water decreased with increasing heat treatment temperature. In our experiments, it is considered that EOS is not fully removed by boiling water in the case of heating above 80° C, because the coupling of EOS with the iron foil is initiated by the heat treatment at 80° C or higher. However, the coupling reaction is not completed even by heating at 80 to 100° C; EOS molecules which did not react but had been physisorbed, are assumed to be desorbed.

3.4. Change in the chemical structure of EOS

Infrared spectra of EOS itself in a KBr pellet with and without heat treatment is shown in Fig. 8. In the original EOS spectrum, as shown in Fig. 8a, the strong

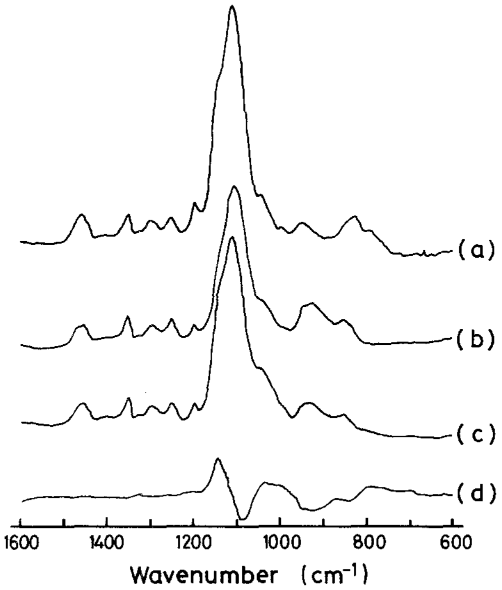


Figure 8 EOS FT–IR spectra in KBr pellet. (a) orginal, (b) heat treated at 80° C for 1 h in 1% aqueous solution, (c) heat treated (b) at 80° C for 1 h in air, (d) subtracted spectrum of (c) from (b).

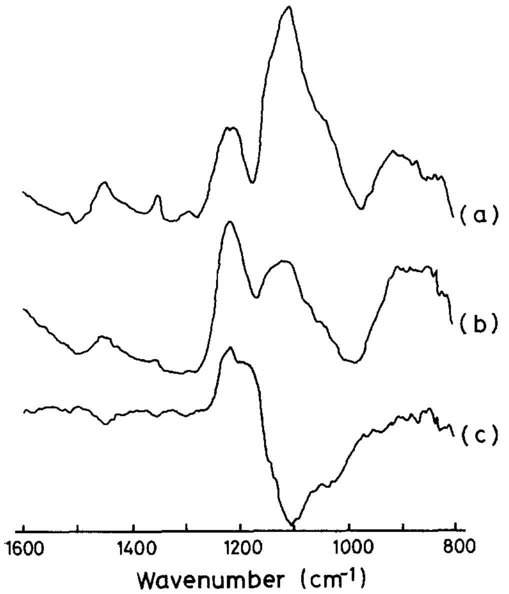


Figure 9 EOS FT–IR–ATR spectra on the iron foil. (a) No heat treatment, (b) heat treated (a) at 80° C for 1 h in air, (c) subtracted spectrum of (b) from (a).

band of ν(Si–O–C) [12] is seen at 1106 cm^{-1}. The weak band of ν(Si–OH) [5] is observed at 946 cm^{-1}. At 1140 cm^{-1} the ν(Si–O–Si) [6] band, which is a shoulder band of the Si–O–C peak, is observed. The presence of the Si–OH band means that EOS is slightly hydrolysed from the beginning. It can be seen from the existence of the Si–O–Si band that EOS polymerizes to form a polysiloxane bond.

The spectrum of EOS heated at 80° C for 1 h in an aqueous solution of 1% is shown in Fig. 8b . The intensity of the Si–OH band increases because of the promotion of hydrolysis by the heat treatment in aqueous solution. The existence of a strong peak at 1106 cm^{-1} means that the hydrolysis of EOS is not yet completed. Fig. 8c shows the infrared spectrum of EOS which was heated at 80° C for 1 h in air after heat treatment in aqueous solution. Fig. 8d shows the spectrum obtained by subtracting the spectrum in Fig. 8b from that in Fig. 8c. In Fig. 8d, the Si–OH band decreases, although the Si–O–Si band increases. This indicates that the polymerization of hydrolysed EOS is accelerated by heating in air. From these results, EOS was proved to polymerize by heat treatment and to form a polysiloxane network structure.

The decrease of adsorption intensity in the band at 1082 cm^{-1} due to Si–O–C in Fig. 8d is based on the presence of unhydrolysed EOS. Ordinary silanes are reported to hydrolyse easily in the presence of water [5, 12]. The low ability of EOS to hydrolyse is attributed to its structure, the polyethylene oxide chain. The C–O bond existing in the polyethylene oxide chain has a relatively strong hydrophilic character and attracts water molecules [13]. Therefore, the functional group in EOS (–SI(OR′)$_3$) is relatively stable in opposing hydrolysis.

ATR spectra of EOS on the iron foil are shown in Fig. 9. In this figure, (a) and (b) represent before and after heat treatment at 80° C for 1 h in air, respectively. Fig. 9c shows the spectrum after subtracting the spectrum in Fig. 9a from the spectrum in Fig. 9b. In Fig. 9c, it is found that the Si–O–Si band at 1180 to 1210 cm^{-1} increases on heat treatment, although the Si–O–C band at 1101 cm^{-1} decreases on heat treatment. This tendency, accompanied by the heating, was also observed in the case of EOS itself. Consequently, these results show that EOS can polymerize and form a polysiloxane network on the iron foil by heat treatment at 80° C or higher. This indicates the formation of a stable hydrophobic layer on the surface of the iron foil. The shift of the Si–O–Si band to slightly higher wavenumbers compared with EOS itself is expected to originate from the Si–O–Fe bond [11, 14].

4. Conclusions

The adsorption of a new type of silane coupling agent (EOS) on Co-γ-Fe$_2$O$_3$ particles and its effect on dispersibility were examined by measuring the surface chemical properties. The following results were obtained.

1. EOS was adsorbed on Co-γ-Fe$_2$O$_3$ particles in the form of a monolayer.
2. The surface hydrophilicity of EOS-treated iron foil was reduced with increasing EOS treatment concentration and heat-treatment temperature.
3. The coupling reaction between EOS and the iron foil and the polymerization of EOS to form a polysiloxane network on the iron foil were initiated by heat treatment at 80° C or higher.
4. The dispersibility of the particles in vinyl chloride–vinyl acetate–vinyl alcohol copolymer solution was improved dramatically by the surface treatment with EOS. The improvement of the dispersibility was explained by considering the increase in the wettability of Co–γ–Fe$_2$O$_3$ for the solvent due to EOS treatment.

Acknowledgements

The authors wish to thank Professor S. Hirano of Nagoya University for his valuable discussion and Mr M. Yoshiya for his assistance in FT–IR analysis.

References

1. H. YOSHIOKA, *Setchaku Kyokai Shi* **21** (1985) 252.
2. A. T. DIBENDETTO and D. A. SCOLA, *J. Colloid Interface Sci.* **64** (1978) 480.
3. B. ARKLES, *Chem. Tech.* December (1977) 766.
4. J. D. MILLER and H. ISHIDA, *Langmuir* **2** (1986) 127.
5. C. H. CHIANG and J. L. KOENIG, *J. Colloid Interface Sci.* **83** (1981) 361.
6. H. ISHIDA and J. L. KOENIG, *ibid.* **64** (1978) 555.
7. K. SUMIYA, T. TAII, K. NAKAMAE and T. MASTUMOTO, *Setchaku Kyokai Shi* **18** (1982) 345.
8. T. SATO, *Shikizai Kyokai Shi* **47** (1974) 385.
9. H. ISHIDA and J. L. and KOENIG, *J. Colloid Interface Sci.* **64** (1978) 565.
10. R. L. KAAS and J. L. KARDOS, *Polym. Engng. Sci.* **11** (1971) 11.
11. M. GETTINGS and A. J. KINLOCH, *J. Mater. Sci.* **12** (1977) 2511.
12. C. H. CHIANG, H. ISHIDA and J. L. KOENIG, *J. Colloid Interface Sci.* **74** (1980) 396.
13. T. KONDO and S. SUZUKI, in "Koroido to Kaimen no Kagaku (Colloid and Interface Science)" (Sankyo Shuppan, Tokyo, 1983) p. 51.
14. F. J. BOERIO, L. H. SCHOENLEIN and J. GREIVENKAMP, *J. Appl. Polym. Sci.* **22** (1978) 203.

Received 22 June
and accepted 27 August 1987