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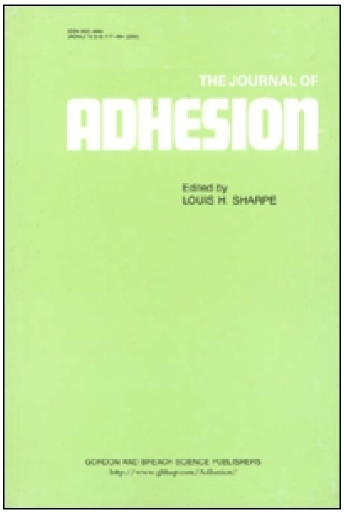

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Effect of a Side Chain Length of Polymer on Both the Adhesion and Dispersibility of γ-Fe_2O_3†

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Acrylic ester-acrylic acid copolymers were synthesized as model binder of magnetic paints. The dispersibility of γ-Fe_2O_3 was investigated as a function of the content of —COOH groups and the aliphatic side chain length. The following results were obtained. The saturated absorbance of copolymers on γ-Fe_2O_3 increased with the increase in content of —COOH groups, and then the dispersibility of γ-Fe_2O_3 was improved. However, when the content of —COOH group was over the 2 mol%, the saturated adsorbance of polymers was constant and the dispersibility of γ-Fe_2O_3 decreased with increasing number of carbon atoms in the acrylic ester side groups. However, the dispersibility of γ-Fe_2O_3 was explained by the difference in conformation of adsorbed polymers.

KEY WORDS Dispersibility; acrylic ester-acrylic acid copolymer; adsorption; interfacial tension; γ-Fe_2O_3; magnetic paint.

1 INTRODUCTION

The interaction between a polymer and an inorganic powder is one of the most important factors which controls the properties of composite materials, e.g., magnetic recording tape, paints, inks.

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etc. The need for high-density recording has grown along with the development of recording methods. Knowledge of magnetic materials such as co-containing γ-Fe_2O_3[1,2] and alloy powder[3,4] for high-density recording is far advanced. However, fundamental studies on the binder polymers which give high performance have clarified the interaction between γ-Fe_2O_3 particles and vinyl polymers by measuring the adsorption, the phase separation ability for particles in the concentrated solution, and the interfacial tension ($\gamma_{w/o}$) of polymer solution-water interface.[5–8]

The surface of γ-Fe_2O_3 was covered with a number of water molecules adsorbed both chemically and physically. Therefore, it was proved that the interface of γ-Fe_2O_3 surface-polymer solution can be substituted by the water-polymer solution interface.[5,7,8]

From these results, it was clarified that the polymer giving a lower interfacial tension of water-polymer solution interface ($\gamma_{w/o}$) has a higher interaction with γ-Fe_2O_3 surface.

Interaction between poly(acrylic ester-acrylic acid) copolymer and magnetic particles and the dispersibility of particles in magnetic paints were investigated as a function of the number of carbon atoms in the acrylic ester groups by using the adsorption, an interfacial tension ($\gamma_{w/o}$), and the magnetic properties measured by a Vibrating Sample Magnetometer (VSM).

2 EXPERIMENTAL

2.1 Materials

The γ-Fe_2O_3 particles have an average length of 0.25 μm, an average acicular ratio of 1/7, and a nitrogen surface area of 53.2 m^2/g.

Acrylic ester-acrylic acid copolymers were synthesized as model binders. Samples were twice purified by the solution-precipitation method. Acrylic acid content was measured by titration, and molecular weight was measured by GPC. Table I shows characterization of the polymers.

2.2 The Measurements of adsorption

The adsorption of polymers on the γ-Fe_2O_3 surface was obtained by determining the change of concentration of the supernatant solutions. Glass tubes (25 cm^3 capacity) containing 20 cm^3 polymer

TABLE I
Characterization of the polymers used

Polymers	Molecular weight[a]	Carboxyl group mol%
Poly methyl acrylate (PMA)	33000	0
P(MA-AA[b])	34000	5.30
Poly ethyl acrylate (PEA)	100000	0
P(EA-AA)	31000	5.26
Poly buthyl acrylate (PBA)	30000	0
P(BA-AA)	62000	5.18
Poly 2-ethyl-hexyl acrylate (PEHA)	42000	0
P(EHA-AA)	118000	5.41
Poly lauryl acrylate (PLA)	200000	0
P(LA-AA)	170000	5.36
Poly stearyl acrylate (PSA)	29000	0
P(SA-AA)	98000	5.27

[a] Peak molecular weight obtained by GPC.
[b] AA: Acrylic acid.

solution and 2.0 g γ-Fe_2O_3 were subjected to 29 KHz ultrasonic waves for 30 min. After samples were shaken 24 hours and were allowed to stand for another 24 hours, the adsorbance were determined by the measurement of the concentration difference of the supernatant solutions.

2.3 The interfacial tension of the water-polymer solution interface

The interfacial tension $\gamma_{w/0}$ was measured by the du Nouy ring method. The adsorption of polymers at an interface between water and a polymer solution was achieved by placing 50 cm^3 of water into each of several du Nouy dishes and cautiously adding a similar volume of the polymer solution of the desired concentration. All measurements were carried out at 25°C. Since the interfacial tension of the water-polymer solution interface is slightly time dependent, $\gamma_{w/0}$ was measured after 3 hours of standing.

2.4 Measurements of magnetic properties and dispersibility of γ-Fe_2O_3 particles

The magnetic paint was prepared by a ball-milling process for 100 hours. The glass vessel (450 cm^3 capacity) contained 21.4 g polymer, 107.1 g solvent and stainless-steel balls.

The magnetic properties were measured by a Toei Kogyo Vibrating Sample Magentometer (VSM) specially designed for this study.

An attempt was made to evaluate the quality of dispersion of the particles in the magnetic paint under a low magnetic field. The rotation of particles in the paint can be traced by measuring the initial magnetization (M_i) to the saturated magnetization (M_s) and the holding time for the applied field of +50 Oe.[9] Figure 1 shows that the M_i/M_s of paint A increased with time; however, that of paint B remained constant and was equivalent to that of cobalt-containing γ-Fe_2O_3 powder itself. This means that particles in paint B were not well dispersed. In the case of paint A the M_i is given by

$$M_i = M_{im} + M_{io}$$

where M_{im} is the magnetization associated with removing the magnetic moment from the easy axis (=long axis of particles) and is

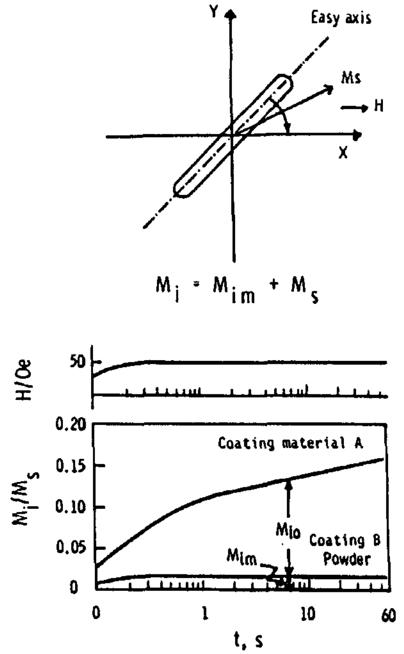

FIGURE 1 Relation between M_i/M_s and time of applied field of 50 Oe.

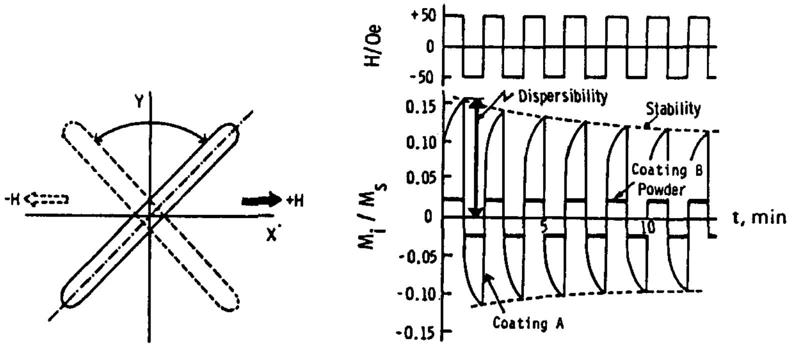

FIGURE 2 Vibration curve of M_i/M_s with a field of ±50 Oe at 1 minute intervals.

the quickly responding component. M_{io} is the magnetization associated with the orientation of particles and the slowly responding component. The particles should orient in the viscous magnetic paint.

Figure 2 shows the vibration curve of M_i/M_s for A, B, and powder over a 1 minute interval. The curve of B did not involve the component M_{io} and coincide with that of the γ-Fe_2O_3 itself. The curve of A shows the large M_{io} component and the slower decay vibration (dotted line). The degree of decay was related to the stability of the paint. Since the amplitude of vibration of M_i/M_s for A increased with the dispersing time in the ball mill, the value at 1 minute can be used as a monitor of dispersion of magnetic particles in paint.

3 RESULTS AND DISCUSSION

3.1 Adsorption behavior of poly(acrylic ester-acrylic acid) copolymer on γ-Fe_2O_3

Figure 3 shows the adsorption of poly(acrylic ester-acrylic acid) copolymer which contains 5 mol% of acrylic acid. The adsorbance increases in the order of P(MA-AA), P(EA-AA) and P(BA-AA).

Figure 4 shows the effect of acrylic acid (AA) content of copolymer on the adsorbance. The adsorbance of copolymers saturated over 4 mol% of AA. Therefore, the following results were

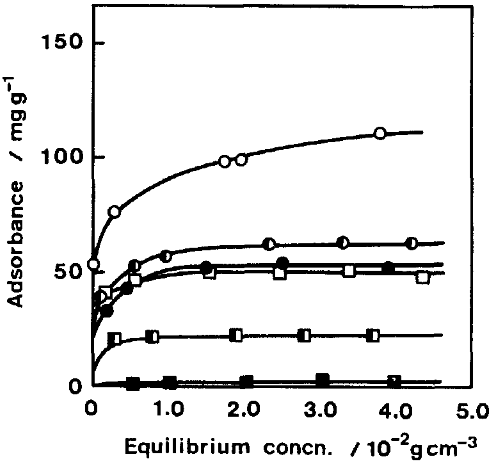

FIGURE 3 Adsorption isotherms of polymers on γ-Fe_2O_3 at 30°C: ○, P(MA-AA); ◐, P(EA-AA); ●, P(BA-AA); □, PMA; ◧, PEA; ■, PBA; AA content, 5 mol%.

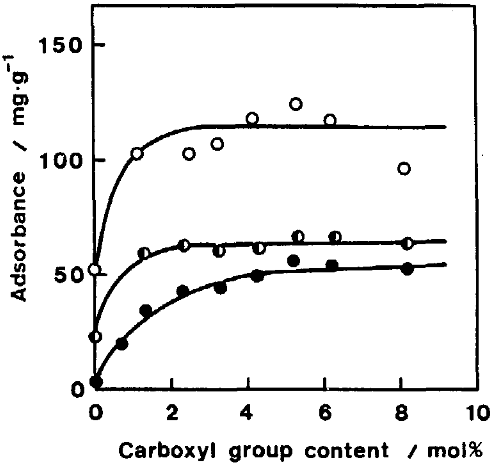

FIGURE 4 Effect of the carboxyl group content of alkylacrylate-acrylic acid copolymer on the saturated adsorbance of γ-Fe_2O_3: ○, P(MA-AA); ◐, P(EA-AA); ●, P(BA-AA).

obtained for the poly(acrylic ester-acrylic acid) copolymer containing 5 mol% acrylic acid.

Figure 5 shows the effect of the number of carbon atoms in the acrylic ester side group on the saturated adsorbance of polymer on the γ-Fe_2O_3 surface. The saturated adsorbance decreases significantly with increase in the number of carbon atoms in the acrylic ester side group, *i.e.* aliphatic side chain length. This means that the side chain bulkiness of the polymer affects the adsorbance of the polymers, and should affect the dispersibility of γ-Fe_2O_3 particles because of the difference in the conformation and solution properties at the γ-Fe_2O_3 surface-solution interface.

3.2 The dispersibility of γ-Fe_2O_3 particles in magnetic paint

Figure 6 shows the M_i/M_s curves for various paints. As mentioned in the experimental part, the dispersibility of γ-Fe_2O_3 particles ($D = M_i/M_s$) increases in the order P(MA-AA), P(EA-AA) and P(BA-AA), *i.e.* the same order of side chain length.

Figure 7 shows the effect of the carboxylic acid content of poly(acrylic ester-acrylic acid) copolymer on the dispersibility. Each

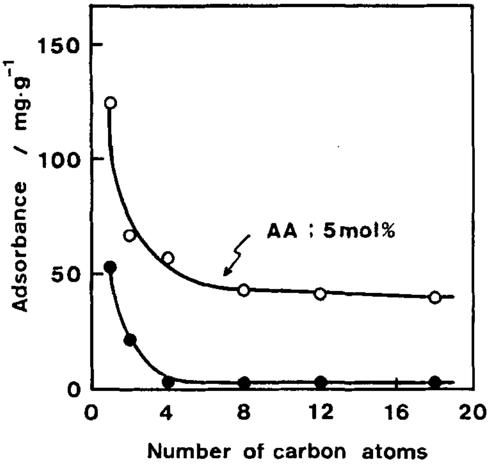

FIGURE 5 Effect of the number of carbon atoms of a side chain on the saturated adsorbance of polymers: ○, copolymer; ●, homopolymer.

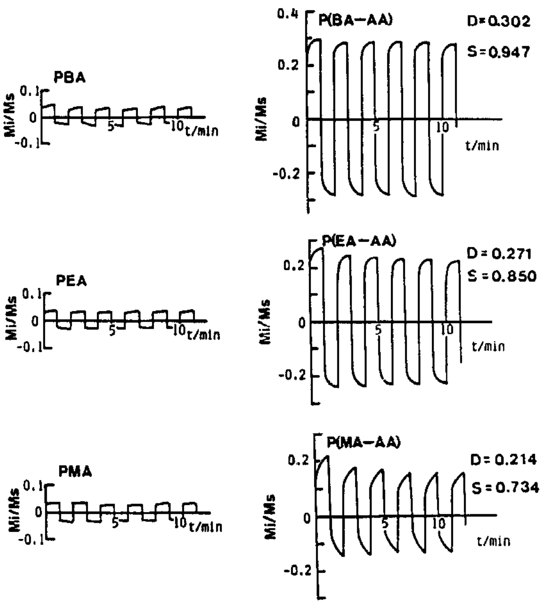

FIGURE 6 The M_i/M_s curves for various paints.

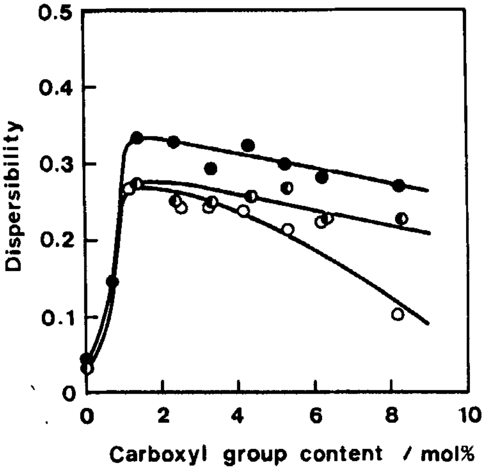

FIGURE 7 Effect of the carboxyl group content of alkylacrylate-acrylic acid copolymer on the dispersibility of a paint: ○, P(MA-AA); ◐, P(EA-AA); ●, P(BA-AA).

polymer has a maximum of dispersibility of γ-Fe_2O_3 in these polymer systems.

Figure 8 shows the effect of the aliphatic side chain length of acrylic ester side group on the dispersibility of γ-Fe_2O_3 as a function of carbon atoms in the acrylic ester side group. From these results, the homopolymer of acrylic ester with a different side chain length does not have high dispersibility. However, the dispersibility of γ-Fe_2O_3 using the poly(acrylic ester) with 5 mol% AA increases with increasing the number of carbon atoms *i.e.* the aliphatic side chain length.

In the previous paper, we have investigated the dispersibility of γ-Fe_2O_3 by means of interfacial tension ($\gamma_{w/o}$), and a surface pressure-area method of the Langmuir type. We proposed that the polymer having a stronger interaction with an γ-Fe_2O_3 surface gives a large adsorbance and a lower interfacial tension ($\gamma_{w/o}$). On the basis of these results, the relationship between the adsorbance and the dispersibility of γ-Fe_2O_3 in this study is a little different from previous results. That is, the polymer having a long aliphatic side chain in acrylic ester with 5 mol% AA has a high dispersibility of γ-Fe_2O_3 in spite of a lower adsorbance.

Figure 9 shows the effect of content of AA in poly(acrylic

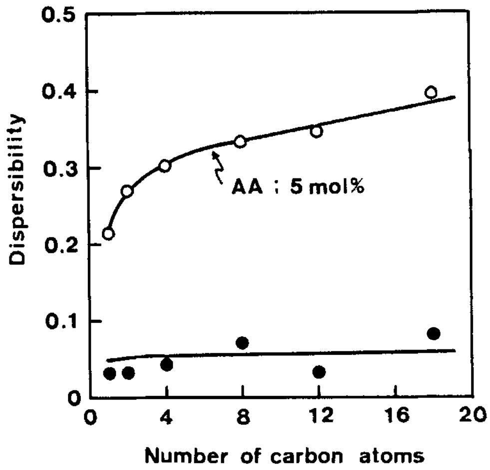

FIGURE 8 Effect of the number of carbon atoms of a side chain on the dispersibility of a paint: ○, copolymer; ●, homopolymer.

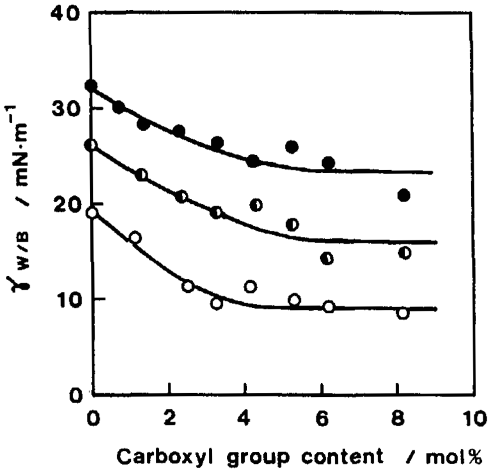

FIGURE 9 Effect of the carboxyl group content of alkylacrylate-acrylic acid copolymer on the interfacial tension at the water/benzene interface: ○, P(MA-AA); ◐, P(EA-AA); ●, P(BA-AA).

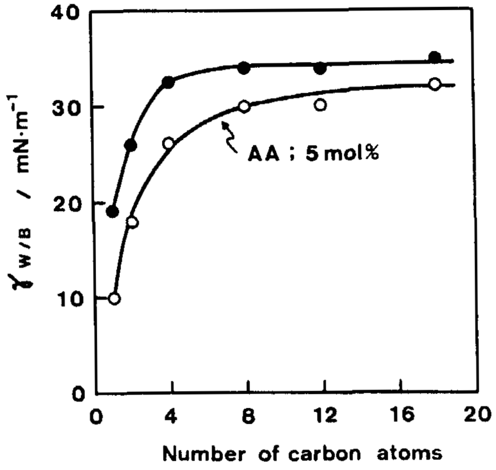

FIGURE 10 Effect of the number of carbon atoms of a side chain on the interfacial tension of polymers at the water-benzene interface: ○, copolymer; ●, homopolymer.

ester-acrylic acid) copolymer on the interfacial tension at the water-polymer solution interface. $\gamma_{w/0}$ decreases with increasing AA content. This agreed with the behavior of partially-sulfonated polystylene.[10]

The $\gamma_{w/0}$ of a longer side chain, *e.g.* P(BA-AA), is lower than that of a shorter side chain (P(MA-AA)). This means that the interaction of P(BA-AA) at the water-benzene interface is weaker than that of P(MA-AA), and the adsorbance of P(BA-AA) on the γ-Fe_2O_3 surface is smaller than that of P(MA-AA). This behavior agreed the results shown in Figure 3.

Figure 10 shows the effect of the number of carbon atoms in the acrylic ester side group on the interfacial tension. The interfacial tension ($\gamma_{w/0}$) increases with increasing number of carbon atoms in the acrylic ester. This means that the content of polymer segments at the water-benzene interface with increasing side chain length in acrylic ester group decreased owing to its high bulkiness. The dispersibility of γ-Fe_2O_3 by adsorbed polymer increased with increasing side chain length of the ester group as shown in Figures 7 and 8. On the basis of the previous paper, the properties and structure of the γ-Fe_2O_3-polymer solution interface were the most important factor for the dispersibility of γ-Fe_2O_3.

Figure 11 shows the schematic representation of the conformation of poly(acrylic ester-acrylic acid) adsorbed at the γ-Fe_2O_3-polymer solution interface. From the previous results,[7,8] we concluded that the loop-anchor type adsorption of polymer at the γ-Fe_2O_3 surface is the most important factor, because a certain length of the loop segment solvates the solvent strongly and then the solvation layer at the γ-Fe_2O_3 surface acts as a protecting layer for the aggregation of γ-Fe_2O_3 particles owing to its entropy effect. On the basis of this concept, in the case of the shorter side chain length the polymer strongly adsorbed due to the acrylic acid group and the carbonyl group in the ester group because the C=O group has an interaction to the γ-Fe_2O_3 surface. On the other hand, in the case of the long side chain length, *e.g.* acrylic stearate, the adsorption of polymer is prevented by the long aliphatic side chain, which is solvated with hydrophobic solvent. Therefore, in the case of the long side chain, the adsorbed long aliphatic side chain acts as an excellent protecting layer owing to the solvation layers, despite its small adsorbance.

Consequently, it is reasonable to conclude that the adsorption of

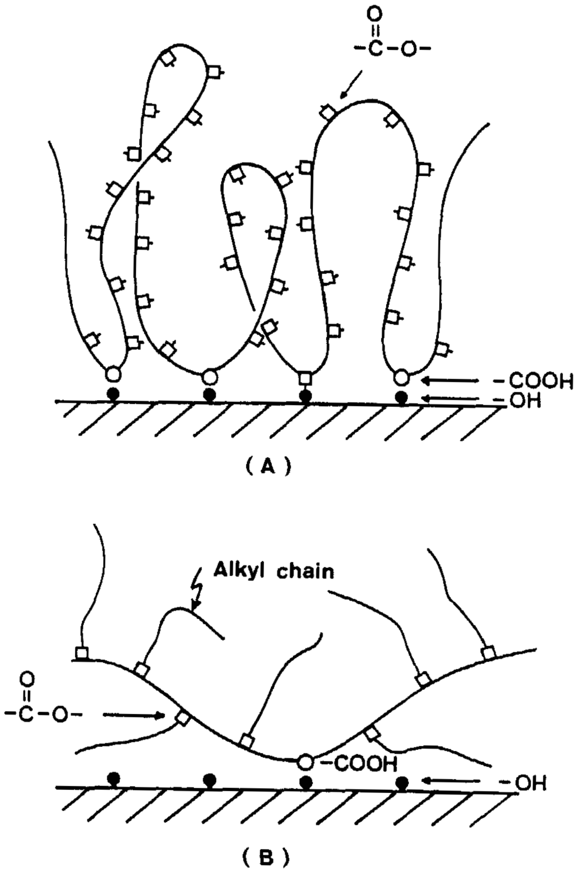

FIGURE 11 Schematic representation of alkylacrylate-acrylic acid copolymer adsorbed at the solvent/γ-Fe_2O_3 interface.

polymer which has a long aliphatic side chain solvated with a hydrophobic solvent provides a protection layer for aggregation of γ-Fe_2O_3 and the binder.

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