Effect of Water on Adsorption Behavior at Polymer/γ-Fe$_2$O$_3$ Interface

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Effect of Water on Adsorption Behavior at Polymer/γ-Fe$_2$O$_3$ Interface*

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The adsorption behavior of a hydroxylated polymer onto γ-Fe$_2$O$_3$ particles in a tetrahydrofuran/water solvent system was investigated. The saturation adsorption of the polymer decreased with an increase in the water content of the solvent system, and the degree of dispersion of the magnetic particles in the paint also decreased. It was shown that the water located not at the interface between the particles and the solution but in the solution. Water interacted with the polymer and increased the radius of gyration of the polymer in solution. Thus, the polymer did not interact with the particles, and the particles were prevented from having a high dispersion.

INTRODUCTION

A magnetic recording medium consists of inorganic magnetic particles and an organic polymeric binder. To prepare a high-density magnetic recording medium, dispersion of magnetic particles in the polymeric binder in very important, in addition to the properties of magnetic particles themselves. The dispersion is controlled by the interaction between polymeric binder and magnetic particles. We have reported that, under normal conditions, the surfaces of magnetic particles are hydrophilic and are fully covered with water molecules adsorbed chemically and physically.[1] Therefore, the adsorption behavior of the polymeric binder on the surface of the magnetic particles can be viewed as adsorption at the interface between a polymer solution and a water phase. It is possible to evaluate the interaction force between a polymer and magnetic particles by means of measurement of an interfacial tension between water and polymer

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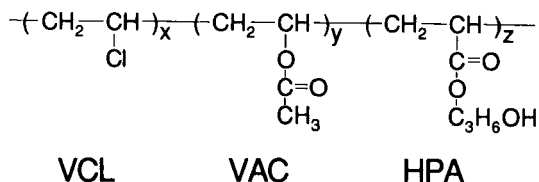
solution. A polymer which consists of a hydrophobic molecular chain including a small amount of hydrophilic functional groups is an excellent binder for magnetic coatings.[2]

The presence of water in magnetic paint is an interesting subject not only from an industrial but also from a chemical standpoint because the interaction behavior between polymer and magnetic particles may change with the water content of the solvent. In this paper, we report the effect of added water on both the interaction behavior of polymeric binder with magnetic particles and on the dispersion of magnetic particles in magnetic paint.

EXPERIMENTAL

Materials

General grade γ-Fe_2O_3 particles having a specific surface area measured by B.E.T. method of $30\,m^2/g$, a coercivity of 650 Oe and a saturated magnetization of 78 emu/g were used as magnetic particles. A hydroxylated vinyl chloride polymer (VAGF; Union Carbide Corporation, USA) was used as a polymeric binder. The chemical structure of the polymer is as follows.

$$-(CH_2-\underset{\underset{Cl}{|}}{CH})_x\ (CH_2-\underset{\underset{\underset{CH_3}{|}}{\overset{|}{C}=O}}{\underset{|}{CH}})_y\ (CH_2-\underset{\underset{\underset{C_3H_6OH}{|}}{\overset{|}{C}=O}}{\underset{|}{CH}})_z-$$

VCL   **VAC**   **HPA**

Here the polymer has a average degree of polymerization of 475 and consists of vinyl chloride (VCL), vinyl acetate (VAC) and hydroxypropylacrylate (HPA) units of 89, 3 and 8 mol%, respectively. Thus, the polymer has a hydroxyl group content of 38 units per molecule. Solvents were prepared by addition of distilled water to tetrahydrofuran (THF), which was of extra pure reagent grade.

Measurement

The dispersibility of magnetic particles in paint was measured by using a rotation-vibration method[3]. The magnetic paint, which contained 28 wt% of the γ-Fe_2O_3 particles, 7 wt% of the polymer and 65 wt% of the solvent mixture was prepared by agitating on a paint shaker for 10 hours. The measurement was carried out by using a Vibration Sample Magnetometer (VSM; Toei Kogyo, Japan). A low magnetic field of $+50\,Oe$ or $-50\,Oe$ was applied to the paint sealed in a cylindrical sample tube at 1-minute intervals as shown in Figure 1(a), and the change in the magnetization of the paint was measured.

The adsorption test was carried out as follows. $20.0\,cm^3$ of polymer solution and $2.00\,g$ of γ-Fe_2O_3 particles were mixed in a glass tube ($25\,cm^3$ capacity). The sample tube was shaken for 24 hours and was allowed to stand for an additional 48 hours. The temperature was maintained at 25°C. The adsorption of the polymer on the magnetic
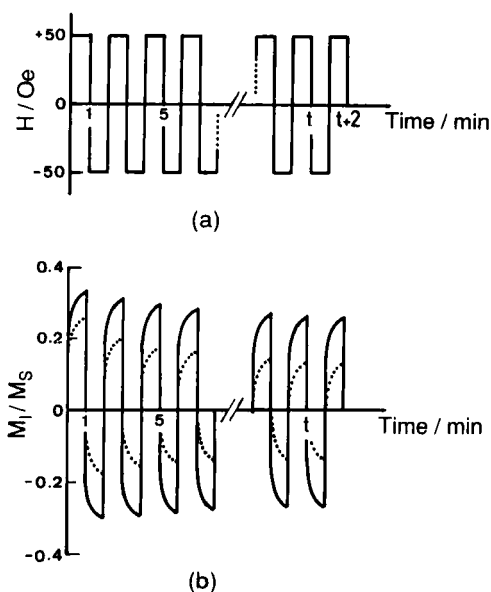
FIGURE 1 Applied magnetic field and typical examples of data for the rotation-vibration method. (a) Magnetic field applied to a paint. (b) Examples of vibration curves of M_t/M_s. A well-dispersed paint gives vibration curves such as the solid line, and a paint whose dispersion is inferior gives vibration curves such as the dotted line.

particles was determined by the difference in polymer concentration of the supernatant solutions before and after the adsorption test. The polymer concentrations were determined by measuring the solid content of the supernatant solutions.

The desorption test followed the adsorption test for which the initial polymer concentration was $3.5 \, g/100 \, cm^3$ and for which the water content of the solvent was zero. After adsorption, $5 \, cm^3$ of the supernatant solution was replaced by the same volume of solvent (containing 0–2 wt% water), and the sample tube was shaken and was allowed to stand for 48 hours at 25°C. The desorption was determined by measuring the polymer concentration of the supernatant solutions (as above) before and after the desorption test.

The amount of water in the polymer solution was measured by using the Karl Fischer method. Intrinsic viscosity of the polymer solutions was measured by using Ubbelhode's method. The ^1H nuclear magnetic resonance (NMR) spectra were collected on a Bruker AC250 spectrometer operating at 250 MHz at room temperature. Tetrahydrofuran-d^8 (d^8-THF, of purity above 99.5%) was used as a solvent, and tetramethylsilane was used as an internal reference.

RESULTS AND DISCUSSION

Dispersibility

As mentioned previously, a rotation-vibration method was used to determine the dispersibility of the magnetic particles in the paint. The principle of the rotation-

vibration method is as follows. A change in magnetization of the paint in an alternating magnetic field, as shown in Figure 1(a), is controlled both by a magnetization of magnetic particles themselves and by orientation of the magnetic particles in the paint. The degree and rate of orientation are related to dispersion of the magnetic particles in the paint. The dispersibility of magnetic particles in the paint and the stability of the dispersion are given by equations (1) and (2).

$$\text{Degree of dispersion} = M_I(1)/M_S \tag{1}$$

$$\text{Stability of dispersion} = M_I(t)/M_I(1) \tag{2}$$

where $M_I(1)$ and $M_I(t)$ are magnetizations of the paint after applying the alternating magnetic field shown in figure 1(a) for 1 minute and for t minutes, respectively, and M_s is the saturation magnetization of the magnetic particles. Figure 1(b) shows typical examples of the change in M_I/M_S of a paint during the measurement.

Figure 2 shows the relationship between the degree of dispersion of the magnetic particles and the water content of the THF-water solvent system. The degree of dispersion shows a plateau below 0.3 wt% water content in the solvent and then decreases rapidly with an increase in water content over 0.3 wt%. The magnetic particles cannot be dispersed above 2 wt% of water.

Adsorption

Figure 3 shows the adsorption isotherms of the polymer on the magnetic particles in the THF-water solvent system. When the water content of the solvent system is below 1 wt%, the adsorption of the polymer increases with the equilibrium concentration of the polymer but shows a plateau above an equilibrium concentration of *ca.* $1.0g/100cm^3$. On the other hand, the adsorbance takes zero or negative values in the solvent containing water at 2 wt% concentration or above.

Figure 4 shows the relationship between the saturation adsorption of the polymer on the magnetic particles and the water content of the solvent system. Addition of water
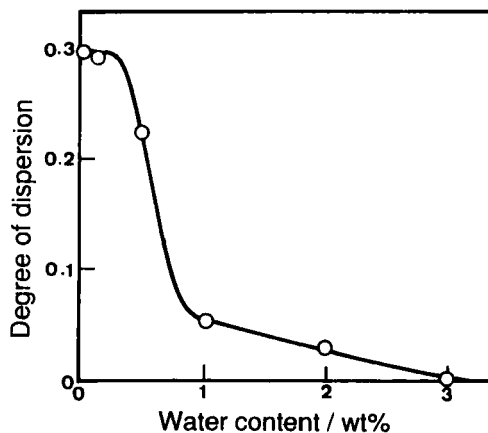
FIGURE 2   Relationship between the dispersibility of the magnetic particles measured by the rotation-vibration method and the water content of the solvent system.
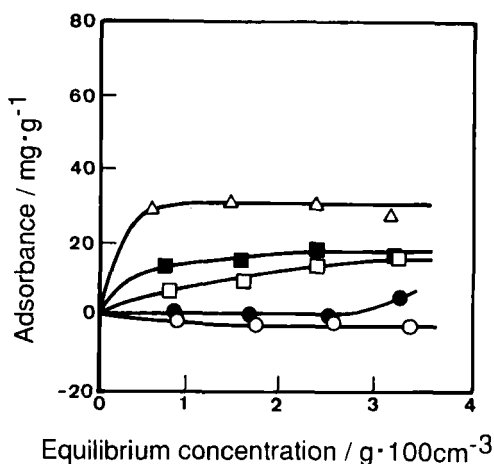
FIGURE 3   Adsorption isotherms of the polymer on the magnetic particles in THF-water solvent system. Volume of added water to THF: $\triangle$, 0.0 wt% ; $\blacksquare$, 0.5 wt% ; $\square$, 1.0 wt% ; $\bullet$, 2.0 wt% ; $\circ$, 3.0 wt% .

prevents the polymer from adsorbing on the magnetic particles. The saturation adsorption decreases with an increase in water content, and the polymer cannot adsorb on the magnetic particles when there is over 2 wt% of water in the solvent system.

The magnetic particles which we used have a hydrophilic surface. Thus, the surface of the magnetic particles and a hydroxyl group of the polymer can form a hydrogen bond. This interaction introduces both the large amount of adsorption of the polymer on the magnetic particles and the high dispersibility of the magnetic particles in the paint. THF does not prevent this interaction because a THF molecule has an ether group which is less hydrophilic than a hydroxyl group of the polymer. Therefore, both the
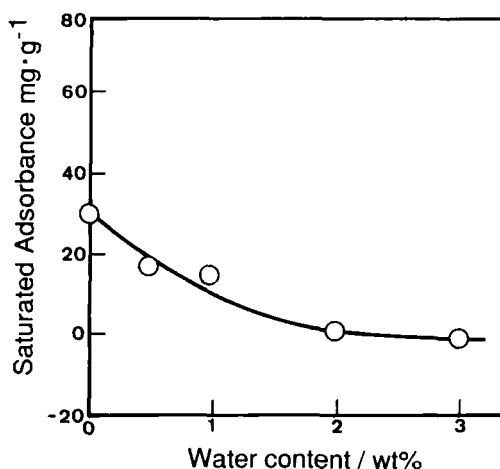
FIGURE 4   Relationship between the saturation adsorbance of the polymer on the magnetic particles and the water content of THF-water solvent system.

dispersibility of the magnetic particles and the adsorption of the polymer take the highest value at a water content of 0 wt% in the solvent system.

A water molecule has the same hydrophilic functional groups, hydroxyl groups, as the polymer. Thus the presence of water in the solvent system may change the characteristics of the interaction behavior between the surface of the magnetic particles and the polymer. Two effects of additional water are considered to explain the results of the dispersibility and the adsorbance (See Figures 2 and 4): one is a competitive adsorption of a water molecule and the polymer, and the other is a change of the characteristics of the polymer solution.

The Amount of Water in Solvent

Table I shows the water content of the solvent system before and after the adsorption test. The water content of the solution after adsorption is nearly equal to that before adsorption. This result shows the added water exists not at the surface of the magnetic particles but in the solution. Thus, the added water does not adsorb on the surface of the magnetic particles. This result also indicates that the surface of the magnetic particles used was probably fully covered with water molecules before the adsorption test. Therefore, the change of the characteristics of the polymer solution by addition of water is more important in the system than the competitive adsorption of a water molecule and the polymer.

Intrinsic Viscosity

Figure 5 shows the relationship between the intrinsic viscosity of the polymer solution and the water content of the solvent system. The intrinsic viscosity increases slightly below 1 wt% of water and levels off over 1 wt%. Flory's equivalent sphere model[4] proposed equation (3).

$$[\eta] = \phi \cdot (6 \cdot \langle S^2 \rangle)^{3/2}/M \tag{3}$$

where $[\eta]$ is an intrinsic viscosity, $\langle S^2 \rangle$ is the mean square radius of gyration of a polymer molecule, M is a mean molecular weight of polymer and ϕ is a constant.

TABLE I
Water content of the solvent system before and after the adsorption test

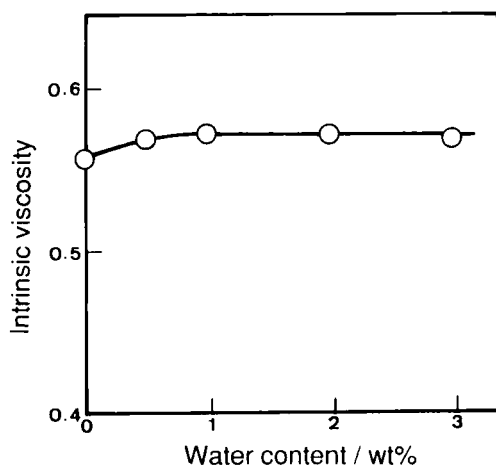| The amount of water added to solvent, wt%	Water content of solution, wt%	
	Before adsorption test	After adsorption test
0	0.02	0.08
0.5	0.52	0.57
1.0	0.99	1.01
2.0	1.90	1.91
3.0	2.91	2.86

FIGURE 5   Relationship between the intrinsic viscosity of the polymer solution and the water content of THF-water solvent system.

Equation (3) gives the relationship between the radius of gyration of a polymer molecule in solution and the intrinsic viscosity of the polymer solution. Increase in $[\eta]$ indicates expansion of the polymer molecule when M is a constant. In general, expansion of the polymer molecule corresponds to solubility of the polymer in solvent. In this study, though addition of water lowered solubility of the polymer, it introduced an increase in $[\eta]$, which showed expansion of the radius of gyration of the polymer molecule in the solvent system. Therefore, the change of the radius of gyration suggests a change of the solvation behavior; that is, formation of an interaction between the polymer and water molecules added to the solvent.

Solvation Structure and Adsorption Behavior

Figure 6 shows a schematic representation of the solvation structure of the polymer and the interaction between the particles and the polymer. In the absence of water, THF molecules may have a weak interaction with all units of the polymer chain, and the hydroxyl groups of the polymer can interact with the surface of the magnetic particles instead of THF molecules, because the interaction between the hydroxyl groups and the surface is stronger than that between the hydroxyl groups and the THF molecules. In the presence of water, on the other hand, water molecules may form some clusters and interact with the hydroxyl groups of the polymer chain. Therefore, the radius of gyration of the polymer chain is such that the polymer wraps the cluster of water, and the hydroxyl groups of the polymer locate at an inner part of the coil. This solva- tion structure leads to the expansion of the coil and prevents the polymer from interacting with the surface of the magnetic particles. Thus, the hydroxyl groups are not concerned with the adsorption of the polymer onto the magnetic particles. As a result, the adsorption of the polymer and the dispersibility of the magnetic particles decrease with addition of water.
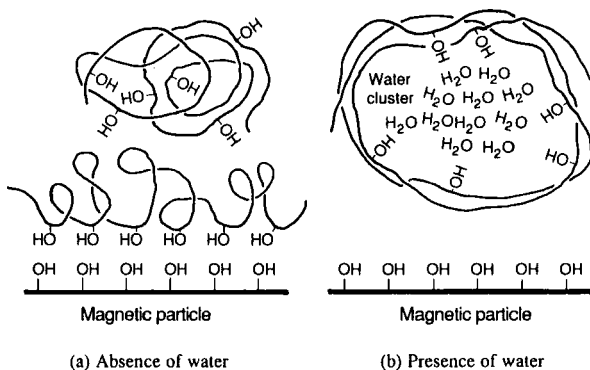
(a) Absence of water   (b) Presence of water

FIGURE 6   Schematic representation of the solvation structure of the polymer and the interaction between the particles and the polymer.

NMR Spectra

Table II shows the values of the chemical shift of the hydrogen atoms in the THF molecules. The values are effectively constant even in the presence of the polymer or water. Table III and Figure 7 show the chemical shift of hydrogen atoms in the water molecules in the presence of d^8-THF. A sharp absorption peak at 2.621 ppm is observed in the absence of the polymer. The presence of the polymer causes the peak to divide in to three peaks into and shift to 2.687 ppm (main peak). This result shows that the polymer forms a strong interaction with water in the solution. Only hydroxyl groups in the polymer can have a strong interaction with water.

Desorption

Desorption of the polymer from the magnetic particles was not observed under the experimental conditions used in this study. This result shows either that the polymer

TABLE II
Chemical shift in ^{1}H-NMR spectra for THF molecules

Polymer content, wt%	Water content, wt%	Chemical shift, ppm
0	0	3.578, 1.727
0	2	3.581, 1.729
5	0	3.580, 1.730
5	2	3.580, 1.730

TABLE III
Chemical shift in ^{1}H-NMR spectra for water molecules

Polymer content, wt%	Chemical shift, ppm		
0	–	–	2.621
5	2.687,	2.786,	2.621

The solvent contains 98 wt% d^8-THF and 2 wt% water.

Chemical shift / ppm
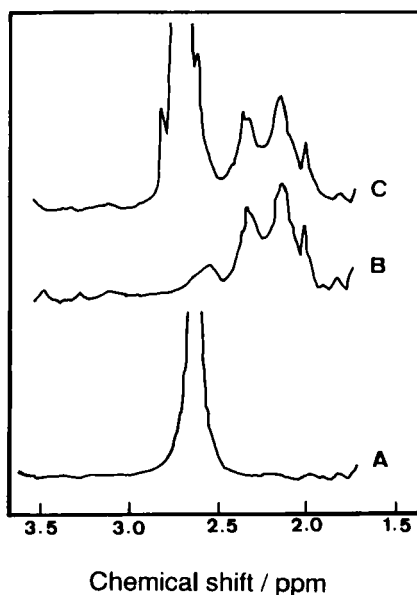
FIGURE 7 ¹H-NMR spectra of the polymer solution. A. The solvent contains 98 wt% d⁸-THF and 2 wt% water. B. 5 wt% polymer solution whose solvent does not contain any added water. C. 5 wt% polymer solution whose solvent contains 2 wt% of added water.

interacts with the magnetic particles more strongly than water or that it is difficult for water to disrupt the adsorption structure of the polymer on the magnetic particles. This result also explains why addition of water causes the adsorption of the polymer onto the magnetic particles to decrease; *i.e.*, the change results from the solvation structure of the polymer rather than from the competitive adsorption of a water molecule and the polymer onto the magnetic particles.

CONCLUSION

The adsorption of a hydroxylated vinyl chloride polymer in THF solution onto magnetic γ-Fe_2O_3 particles was decreased by addition of water to the THF solvent, and the degree of dispersion of the magnetic particles in the paint decreased as a consequence. Additional water caused a strong interaction between the hydroxyl groups of the polymer and the water molecules and resulted in the expansion of the polymer coil in the solvent. Thus, the decrease in the adsorption was explained by the change in the solvation structure of the polymer.

Acknowledgement

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