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The Effect of Functional Groups of Polymers on Dispersion of TiO_2 in Nonpolar Solvent

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Abstract

Dispersion of TiO_2 particles in methylcyclohexane was investigated through adsorption of polymers with various functional groups. The amount of adsorbed polymer was dependent on the kind of functional groups: The large amounts of adsorbed polymer perfectly covered the polar particle surfaces to form a thick adsorbed layer. The dispersions which had large amounts of adsorbed polymer were found to be more stable from the measurements of the rheological properties, the gloss, and the sedimentation rate.

It was confirmed that the adsorbed polymer layer played an important role to enhance dispersion stability and the polymer functional groups provided a significant effect.

Key-words : *Titanium dioxide, Polymer adsorption, Polymer functional group, Dispersion stability*

1. Introduction

An understanding of colloidal dispersion stability of fine particles in nonpolar solvent is very important for both theoretical and practical fields. Recently, the control of the stability of such a system has attracted considerable attention in many industrial applications such as paints, printing inks, cosmetics, magnetic tapes and ceramics¹⁾.

Fine particles having adsorbed polymer layer are known to improve dispersion stability due to steric repulsion. Many theoretical models have been suggested for this steric repulsion^{2~10)}, but there have not been sufficient experimental data, especially about the amount of solvent in the adsorbed layer. It is necessary to explain experimentally the nature of the adsorbed layer for the understanding of the steric repulsion mechanism and the stability of dispersions.

Polymers were adsorbed on fine particles by Řeháček's measurement method¹¹⁾. Applying his method, we can estimate not only the adsorbed amount of polymers, but also that of solvents. For a full description of the polymer adsorption phenomena on particle surfaces, the important parameters of the adsorbed layer, such as the adsorbed amount of

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polymer, the polymer concentration in the adsorbed layer, the total amount of the adsorbed layer, and the thickness of the adsorbed layer, are obtained by his method.

The aim of this paper was to experimentally explain the nature of the adsorbed polymer layer on TiO_2 particle surfaces. TiO_2 particles are utilized in many industries, for example, paints, printing inks and cosmetics. An understanding of the dispersion stability of these particles is vital for industrial applications. Also, we especially examined the effect of polymer functional groups in regard to the polymer adsorption phenomena on TiO_2 particle surfaces. In addition, the relationship between the nature of the adsorbed layer and the characteristics of concentrated dispersion was studied.

2. Experimental

2.1 Polymers

Four random copolymers were prepared by radical polymerization in methylcyclohexane, using azobisisobutyronitrile as an initiator. These copolymers contained *n*-butyl methacrylate and 2-ethylhexyl methacrylate as main components in the molar ratio of 1:1. Also three of them contained a small amount of a component which has a functional group such as acrylic acid, dimethylaminoethyl methacrylate, or glycidyl methacrylate. The characteristics and components of these copolymers are given in **Table 1**.

2.2 Pigment

TiO_2 particles, commercial grade R-780 were obtained from Ishihara Sangyo Kaisha, Ltd. The particles were coated with 3.8% Al_2O_3 and 3.4% SiO_2 . The particles were pretreated by drying at 80°C for over 12 h. The density, specific surface area, and particle size of the particles were 3.91 g/cm³, 20.2 m²/g (BET), and 0.31 μm , respectively.

2.3 Solvent

Analytical grade methylcyclohexane (MCH) was used.

2.4 Adsorption Measurement

Adsorbed amount of polymers on TiO_2 particles was measured by the difference in weight of polymers present in the solution before and after the adsorption process.

In a typical run, the mixtures of TiO_2 (30~50 g) and 50 g of polymer solutions of different concentrations (2.4~24.0 g/100 g) were agitated strongly using a paint shaker

Table 1 Characteristics of polymers used

Polymer	NON	AA	DM	GM
Components (mol%)				
<i>n</i> -butyl methacrylate	50.0	48.9	49.0	48.9
2-ethylhexyl methacrylate	50.0	48.8	48.9	48.8
acrylic acid	—	2.3	—	—
dimethylaminoethyl methacrylate	—	—	2.1	—
glycidyl methacrylate	—	—	—	2.3
Molecular weight $M_w(\times 10^5)$	1.1	0.9	1.0	1.0
Intrinsic viscosity $[\eta]$ (cm ³ /g)	20.9	12.8	19.3	20.2
Huggins constant K_H	0.853	2.448	1.039	0.974
Radius of gyration R_g (nm)	7.05	5.67	6.63	6.80

for 1 h at room temperature, then kept standing at 25°C for 12~18 h. Then, the mixtures were agitated strongly again for 1 h, and the dispersions were allowed to settle and centrifuged by a high-speed centrifuge (14,000~16,000 rpm). The concentration of the clear supernatant was measured by gravimetry.

The adsorbed amount of polymer was determined from the difference in the concentration of polymer solution before and after equilibration, using the relation

$$\Gamma_{ap} = M_o(C_o - C_e) \quad [1]$$

where Γ_{ap} is the apparent adsorbed amount of polymer per unit weight of particle (mg/g), M_o the total amount of polymer and solvent per unit weight of particle (mg/g), C_o the initial polymer concentration (g/100 g), and C_e the equilibrium polymer concentration (g/100 g).

2.5 Rheological Measurement

For the clarification of the relationships between the rheological properties and the adsorption measurements, the rheological measurement of both the dispersions and the polymer solutions was carried out with a cone-plate viscometer (Tokyo Keiki, EMD type).

2.6 Estimation of Gloss

To relate the dispersion of the particles in the system with the adsorption data, we have measured the gloss of the coating films obtained from dispersions. Specular gloss measurements at 60° optics were carried out on films coated on glass plates, using multiangle glossmeter (Suga Test Instruments, UGV-5 D type). Dispersion samples were prepared by using a paint shaker at room temperature for 1 h. The content of TiO_2 in coating films was 20 per cent of the total solid volume.

2.7 Sedimentation Rate Measurement

For the evaluation of the stability of the dispersions, the sedimentation rate was measured. The dispersions were poured into glass bottles (height: 80 mm, inner diameter: 45 mm), and the sedimentation level was recorded for 30 days. The dispersion samples were prepared by using the ball-milling process at room temperature for 30 h. These samples consisted of 50 wt% particles and 10 wt% polymers.

3. Results and Discussion

3.1 Nature of the Adsorbed Layer

For the investigation of the effect of polymer functional groups on the adsorption behavior, four random copolymers were prepared. Three of them, AA, DM, and GM had components of acrylic acid, dimethylaminoethyl methacrylate, and glycidyl methacrylate as polymer functional groups, respectively. The other copolymer did not contain a functional group (NON).

These four different polymers were adsorbed on TiO_2 from their methylcyclohexane solutions. The adsorption isotherms are presented as graphs of the apparent adsorbed amount of polymer as a function of the equilibrium polymer concentration as shown in **Figure 1**. All the isotherms showed a maximum in the adsorbed amount, followed

by a region so-called negative adsorption, where the concentration of the polymer solution after the adsorption is higher than the initial concentration. This behavior usually indicates that the adsorption of the solvent takes place, and that the experimental isotherm, known as the apparent isotherm, is the sum of two isotherms, one for polymer and the other solvent¹²⁾. In the dilute dispersion, the adsorbed amount of solvent is negligible, while in the concentrated dispersion, that of solvent is appreciable. In the analysis of such an isotherm for the adsorption of polymer from methylcyclohexane onto TiO_2 it is not easy to see why any adsorption of the nonpolar solvent should occur on the wet, polar particle surface, in competition with polymer. However, the difficulty is overcome by the suggestion that solvent is not adsorbed in competition with polymer, but that it is trapped within the adsorbed polymer molecule layer. Accordingly, it is considered that solvent adsorption is a consequence of polymer adsorption, not a competing process.

Moreover, the isotherms of respective systems showed a straight line of declining portion throughout the wide equilibrium polymer concentration range. It is required that not only the adsorbed amount of polymer but also the adsorbed amount of solvent and polymer conformation in the adsorbed layer are independent of the polymer concentration in the solution. Although this assumption cannot always be applied to a physisorption system, it is applicable to a chemisorption system^{11, 13~15)}.

For a full description of the polymer adsorbed layer on TiO_2 , it is necessary to measure important quantities: the intrinsic adsorbed amount of polymer Γ (mg/g); the concentration of polymer in the adsorbed layer C_a (g/100 g); the total amount of the adsorbed layer M_a ; and the thickness of the adsorbed layer δ (nm).

The parameters of the adsorbed layer were calculated by Řeháček's method¹¹⁾. According to his method, the apparent adsorbed amount of polymer per unit weight of particle, Γ_{ap} , is defined as:

$$\Gamma_{ap} = M_a (C_a - C_e) \quad [2]$$

where M_a is the total amount of the adsorbed layer containing polymer and solvent per unit weight of particle, and C_a is the polymer concentration in the adsorbed layer.

The adsorbed amount of polymer is usually obtained by

$$\Gamma_{ap} = M_0 (C_0 - C_e) \quad [1]$$

In the dilute dispersion, eq. 1 is correct; however, in the concentrated dispersion, taking into consideration the adsorbed amount of solvent, the adsorbed amount of polymer should be given by

$$\Gamma = M_0 C_0 - (M_0 - \Gamma - \Gamma_{solv}) C_e \quad [3]$$

where Γ is the intrinsic adsorbed amount of polymer and Γ_{solv} is the adsorbed amount of solvent. Using the following parameters

$$M_a = \Gamma + \Gamma_{solv} \quad [4]$$

$$C_a = \Gamma / M_a \quad [5]$$

we can obtain eq. 2.

The adsorption isotherms of respective systems gave a straight-line section of the declining portion. The point of intersection of the extrapolated straight line with the

Fig. 1 Relationship between the apparent adsorption amount Γ_{ap} and the polymer concentration in the supernatant

Fig. 2 Dependence of the reduced viscosity η_{sp}/C upon the polymer concentration in solution C

vertical intercept indicates the intrinsic adsorbed amount of polymer Γ (mg/g), while the point of intersection of the extrapolated straight line with horizontal intercept gives the concentration of polymer in the adsorbed layer C_a (g/100 g). The slope of the straight line section corresponds to the total amount of the adsorbed layer per unit weight of particle M_a (mg/g). When M_a is divided by the specific surface of particle S (m²/g) and the density of the adsorbed layer ρ_a (g/cm³), the thickness of the adsorbed layer δ (nm) can be calculated by :

$$\delta = M_a / (\rho_a \cdot S) \quad [6]$$

A summary of the parameters of the adsorbed layer obtained by using four different polymer is given in **Table 2**. The intrinsic adsorbed amount of polymer Γ was significantly dependent on the kind of polymer employed: It was the lowest in the case of NON, 23.1 mg/g, and the highest in the case of DM, 36.6 mg/g. These results indicate that polymer functional groups affect significantly the adsorption on TiO₂.

When strong interactions occur between particle surfaces and polymer molecules in solution, the intrinsic adsorbed amounts of polymer will increase. In this study, polymer functional groups are able to be put in order of the strong interaction on TiO₂, as follows :

$$DM > AA > GM > NON (\Gamma).$$

The concentration of polymer in the adsorbed layer C_a varied between 40.1 and 54.1%. These values indicate that the adsorbed layers contain substantial amounts of solvent.

The thickness of the adsorbed layer δ changed from 2.8 nm for NON to 4.5 nm for AA. These polymers are able to be put in order of the thick adsorbed layer, as follows :

$$AA > DM > GM > NON (\delta).$$

Table 2 Adsorption parameters for the adsorbed layer of polymers

	NON	AA	DM	GM
the intrinsic adsorbed amount of polymer Γ (mg/g)	23.1	31.1	36.6	28.0
the total amount of the adsorbed layer M_a (mg/g)	49.2	77.2	67.6	63.9
the concentration of polymer in the adsorbed layer C_a (g/g)	47.0	40.1	54.1	43.8
the adsorbed amount of solvent Γ_{solv} (mg/g)	26.1	46.1	31.0	35.9
the thickness of the adsorbed layer δ (nm)	2.8	4.5	3.9	3.7

The thickness of adsorbed layer δ is assumed to depend on the intrinsic adsorbed amount of polymer Γ , and the large amount of adsorbed polymer leads to a thick adsorbed layer. Also, the thickness of the adsorbed layer is assumed to depend on the solvation of the adsorbed layer by the solvent.

For the comparison between the solvation of adsorbed layer and the solvation of the polymer molecules in solution, the viscosity of polymer solutions was measured as given in **Figure 2**. The intrinsic viscosity $[\eta]$ of the polymer in methylcyclohexane is calculated by using Huggins relationship :

$$\eta_{sp}/C = [\eta] + K_H [\eta]^2 C \quad [7]$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity, and K_H the Huggins constant. The intrinsic viscosity of AA was the lowest, 13 cm³/g, and that of the others was higher and had almost the same value—roughly 20 cm³/g. Since the molecular weights of four polymers are practically equal, 1×10^5 , estimated by gel permeation chromatography, these results suggest that the solvation of polymer molecules in solution is the lowest in case of AA, and that of the other polymers is higher and practically equal. Further, these results envisage that the solvation of the polymer molecules in solution is different from that of the adsorbed layer by the solvent.

If the solvent is not adsorbed on particle surfaces but trapped within the adsorbed polymer molecules as mentioned above, these views support the important conclusion that the behavior of polymer molecules in the adsorbed layer is different from that of polymer molecules in solution. Therefore, when polymer molecules from solution adsorb on TiO₂ particle surfaces, it can be seen that the polymer conformations in the adsorbed layer are different from a random coil usually seen in solution^{16~18}). The extents of the transformation of polymer conformation are dependent on the kind of polymer functional groups: Compared with the radius of gyration of the polymer in the solution, the thickness of the adsorbed layer was smaller for all polymers. However, the ratio of thickness/radius of gyration is ordered as follows :

$$AA > DM > GM > NON$$

This means that the adsorbed polymers with functional groups are more extended than that without functional group.

It is also important to discuss interaction between surface site of TiO₂ and functional groups of the polymers. Since being coated with silica and alumina, TiO₂ has acidic and

basic sites on the surface. When DM and AA are adsorbed on the TiO_2 surface of TiO_2 , it is easily understood that DM is adsorbed on it through acid-base interaction between acidic site of TiO_2 and functional group of DM, while AA is adsorbed because of the basic site of TiO_2 . The detail studies in the interaction of acid-base on TiO_2 are in progress.

3.2 Properties of the Dispersions and the Adsorbed Layer

The investigation of the dispersions by various methods brought to interesting relationships among adsorption, gloss, sedimentation rate, and the rheological properties of the dispersions.

In the dispersions containing low-concentration polymer solutions before reaching the adsorption maximum, the adsorbed layer is not thoroughly formed and the system is often flocculated. The dispersion/solution viscosity ratios of various dispersions having a specific pigment concentration were high at first as shown in **Figure 3**, and the fluidities of the dispersions were not sufficient. From the concentration at which the adsorption reached maximum, the viscosity ratios were independent of the solution concentration, indicating that the nature of the adsorbed layer is hardly affected by the polymer concentration in the solution.

In detailed viscosity measurements, a high consistency of the dispersion was accompanied by deviations from the Newtonian behavior during the flow, as shown in **Figure 4**. The extent of deviation from the Newtonian behavior was the largest in the case of NON, and smallest for DM. This result agrees with the order of the intrinsic adsorbed amount of polymer, that is, a larger the intrinsic adsorbed amount of polymer tends to stay closer to the Newtonian behavior. In nonpolar systems, it is said that the source

Fig. 3 Dependence of dispersion/solution-viscosity ratio η_{ap}/η_0 upon the polymer concentration in dispersion C_0 .

Fig. 4 Relationship between the shear rate and the shear stress of dispersions

of the stability of the dispersion is the steric repulsion of the adsorbed layer ²⁻¹⁰). For the stabilization of the systems, it is necessary that the adsorbed polymer perfectly covers the polar particle surface and the thick adsorbed layer is formed. If the adsorbed layer is not thoroughly formed, the system is flocculated, and deviates from the Newtonian behavior during the flow. Accordingly, it is suggested that a larger adsorbed amount of polymer, a perfect coverage of the polar particle surface, and a thicker adsorbed layer stabilize the system well.

Also, to relate the dispersion of the particles in the system with the adsorption data, we have measured the specular gloss values. The plot of the gloss versus the adsorbed amount of polymer given in **Figure 5** clearly illustrates that the gloss increases gradually with increasing adsorbed amount of polymer. Usually, the flocculation of pigment particles causes reduction in gloss. These findings also indicate that the dispersibility of the pigment particles in the system having larger adsorbed amounts of polymer is better than that in the system having small adsorbed amounts of polymer.

Moreover, to evaluate the dispersion stability in long term the sedimentation rate was measured. **Figure 6** shows that the sedimentation rate decreases with increasing adsorbed amount of polymer. It is clear that the adsorbed polymer contributes to improve dispersion stability, and the effect of polymer functional groups is significant on the polymer adsorption onto TiO_2 surfaces.

4. Conclusions

The effect of polymer functional groups in regard to the polymer adsorption phenomena on TiO_2 particle surfaces was investigated. The amount of adsorbed polymer was dependent on the kind of polymer functional groups. This result suggested that the strength of interactions between particle surfaces and polymer functional groups had influence

Fig. 5 Dependence of the gloss of coating film upon the adsorption amount Γ . The contents of particles in coating film are 20 per cent of the total solid volume

Fig. 6 Dependence of the sedimentation rate upon the adsorption amount Γ . The sedimentation rate values are taken as a 30-day average

on polymer adsorption. Also, the adsorbed layer contained substantial amounts of solvent. The thickness of the adsorbed layer was assumed to increase when the adsorbed amount of polymer and the solvation of the adsorbed layer increased. Then, the polymer conformations in adsorbed layer were altered from random coil in solution. The extents of the transformation of polymer conformation were dependent on the kind of polymer functional groups. The large amount of adsorbed polymer and the thick adsorbed layer could enhance the dispersion stability. This fact was confirmed by the measurement the rheological properties, the gloss, and the sedimentation rate.

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