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Interfacial Electrical Study on Deposition of Poly(vinyl acetate) Latex on Fibers*

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The amounts of poly(vinyl acetate) latex deposited on Nylon-6, polyacrylonitrile and cotton fibers were measured as functions of time and pH and compared with those of polystyrene and poly(ethyl acrylate) latices. The results were considered in terms of the interaction due to electrostatic force and van der Waals force.

The amounts of these latices deposited on Nylon-6 fiber decreased highly with increasing pH and it was found that the electrostatic interaction was a main factor for the deposition.

The amounts of polystyrene and poly(ethyl acrylate) latices deposited on polyacrylonitrile fiber and cotton fiber were high in spite of large repulsive interaction due to electrostatic force and slightly decreased for increase in pH, that is, an increase in electrostatic repulsive interaction. However, the amounts of poly(vinyl acetate) latex deposited on polyacrylonitrile fiber and cotton fiber were very low in spite of the almost same repulsive interaction as those of polystyrene and poly(ethyl acrylate) latices.

Based on these results, it is proposed that a steric repulsion due to water-soluble polymer layer, *e.g.*, poly(vinyl alcohol) layer which may be present on poly(vinyl acetate) latex surface, acts between the latex and polyacrylonitrile fiber or cotton fiber.

1 Introduction

The particle deposition onto fibers and the desorption of adhered particles are important in detergency, especially in removal of particulate soil. For the study on particle deposition or desorption, the use of polymer latices seems to be excellent because polymer latices consist of monodispersed spherical particles. From these points of view, the deposition of various polymer latices onto fiber has been studied^{1)~7)}.

In a recent study⁸⁾, we have dealt with the deposition of styrene-acrylamide copolymer latex onto polyamide (Nylon-6), polyester [poly(ethylene terephthalate)] (PET) and polyacrylonitrile (PAN) fibers. In the case of this latex, the deposition rates onto Nylon-6 fiber and PET fiber increased and those onto PAN fiber decreased with increasing acrylamide fraction

in latex particles. On the other hand, the viscometric measurements of this latex dispersions indicated that water-soluble polymer layer was present on the particle surface. On the basis of these results, the authors have introduced that a certain repulsive force, *e.g.* a steric repulsive force due to water-soluble polymer layers, acts between the latex particle and PAN fiber, in addition to the electrostatic force and van der Waals force.

Okamura *et al.* have reported that on the particle surface of poly(vinyl acetate) latex prepared in the presence of emulsifier, the hydrolysis takes place readily at room temperature and neutral pH, and poly(vinyl alcohol) is formed⁹⁾. This fact makes us to imagine the presence of water-soluble polymer layer, that is, poly(vinyl alcohol) layer on the particle surface. Thus, it is thought that the interaction between colloidal particles having water-soluble polymer layer and fibers can be further clarified by investigating the deposition of poly(vinyl acetate) latex onto fibers.

In this report, the deposition of poly(vinyl

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acetate) latex on PAN, Nylon-6 and cotton fibers is investigated and the amounts of latex deposited are compared with those of poly(ethyl acrylate) and polystyrene latices. The results obtained are considered in terms of the interaction due to electrostatic force and van der Waals force. In particular, regarding the deposition of poly(vinyl acetate) latex on PAN and cotton fibers, the operation of a steric repulsion due to poly(vinyl alcohol) layer on the particle surface is proposed, in analogy with styrene-acrylamide copolymer latex⁸⁾.

2 Experimental

2.1 Materials

Vinyl acetate (Katayama Chemical Ind.) and ethyl acrylate (Wako Pure Chemical Co., Ltd.) were distilled three times under reduced pressure. Potassium persulfate (Wako Pure Chemical Co., Ltd.) was recrystallized twice from water. Sodium chloride, sodium hydroxide, and hydrochloric acid (Wako Pure Chemical Co., Ltd.) were all analytical grade materials and were used without further purification. Distilled and deionized water was used throughout the experiments.

Poly(vinyl acetate) (PVAc) and poly(ethyl acrylate) (PEA) latices were prepared in the absence of emulsifier, using potassium persulfate as initiator^{10), 11)}. The polymerization conditions are shown in **Table-1**.

The particle sizes of PVAc latex and PEA latex were determined by electron microscopy and a soap titration method, respectively. Since these preparations were carried out at high monomer concentration, the mean particle diameters of the latices were relatively large. The

preparation of polystyrene (PS) latex was described in the previous paper¹⁾. The latices obtained were dialysed using well-boiled Visking dialysis tubing for about 1 week, and then electro-dialysed for about 1 week.

The fabrics of PAN fiber (Mitsubishi Rayon Co., Ltd.; Muslin), Nylon-6 fiber (Toray Co., Ltd.; Taffeta) and cotton fiber (Kanebo Co., Ltd.) were used. These fabrics were purified by the methods described previously^{1), 2)}.

2.2 Methods

Amounts of latex deposited. Similarly to the technique described previously^{1), 2)}, 2 g. weighed fabric (about 0.1×0.2 dm swatches) was immersed in 5×10⁻² dm³ latex dispersion (1 g·dm⁻³ solid content) for a prescribed time, and the amount of latex deposited was determined from the change in solid content of latex dispersion. The solid content was obtained by dry weight.

Electrokinetic measurements. The ζ -potentials of latex particles and the fibers were measured by the methods of microelectrophoresis and streaming potential, respectively, as described previously^{1), 2)}.

Deposition experiments and electrokinetic measurements were carried out as a function of pH at 25°C and 10⁻³ ionic strength. The pH was varied with hydrochloric acid sodium hydroxide. The ionic strength was adjusted with sodium chloride.

3 Result and Discussion

Fig.-1 shows the amounts of PVAc latex A and PS latex deposited on Nylon-6 fiber as a function of time at pH 3.1.

These amounts deposited increased with increasing deposition time, and 13.3 mg of PVAc latex and 7.5 mg of PS latex deposited on 1 g of fiber at 24 h. **Fig.-2** shows the amounts of PVAc A, PS, and PEA latices deposited on PAN fiber as a function of time at pH 3.1.

The deposition of PVAc latex on PAN fiber was markedly dif-

Table-1 Preparation of latices.

Latex	PVAc		PEA	PS
	A	B		
Vinyl acetate (M)	2.88	1.56	—	—
Ethyl acrylate (M)	—	—	1.85	—
Styrene (M)	—	—	—	0.501
KPS* (M)	1.5×10 ⁻²	1.0×10 ⁻²	0.4×10 ⁻³	2.48×10 ⁻³
Polymerization temp. (°C)	70	70	70	70
Polymerization time (h)	1.5	1.5	5	28.5
Particle diameter (μm)	0.59	0.48	0.38	0.46

*Potassium persulfate

Fig. 1 Amounts of latices deposited on Nylon-6 fiber as a function of time at pH 3.1, 10^{-3} ionic strength and 25°C .

Fig. 2 Amounts of latices deposited on PAN fiber as a function of time at pH 3.1, 10^{-3} ionic strength and 25°C .

ferent from those of other latices. The amounts of PVAc latex deposited were low and scarcely increased with the increase in deposition time. On the other hand, the amounts of PS latex deposited on PAN fiber increased with increasing time and they were higher than those on Nylon-6 fiber. **Fig. 3** shows the amounts of the three kinds of latices deposited on cotton fiber at pH 3.1. Though PVAc latex scarcely deposited on cotton fiber, PEA latex deposited readily.

If it is assumed that depositing particles are accommodated in a hexagonal close-packed array on the fiber surface, the amount of PVAc latex deposited on Nylon-6 fiber at 24 h corresponds to about 17 percentage of fractional coverage. In this calculation, the surface area of fiber was obtained from the diameter of monofilament (3 denier). Thus, the amounts of these latices deposited tend to increase even at 24 h of deposition time. This suggests that the amounts

Fig. 3 Amounts of latices deposited on cotton fiber as a function of time at pH 3.1, 10^{-3} ionic strength and 25°C .

of the latices deposited depend on the deposition rate and the deposition is irreversible under the conditions used.

Regarding the change in pH, **Table-2** shows the relation between the amounts of the latices deposited at 24 h and pH.

Table-2 The amounts of latices deposited at 24 h of deposition time, 25°C , and 10^{-3} ionic strength.

Fiber	pH	Amount of deposited latex (mg/g-fiber)		
		PVAc(B)	PS	PEA
Nylon-6	3.1	13.8	7.5	—
	4.8	1.0	0	—
	10.5	0.5	0	—
PAN	3.1	1.0	14.0	15.8
	5.3	1.0	12.6	10.9
	10.5	1.0	7.0	—
Cotton	3.1	2.9	9.6	16.5
	5.1	0.6	7.6	9.1
	10.5	0.5	5.8	—

In order to compare PVAc latex with PS and PEA latices, the results of PVAc latex B are shown, since the particle size is almost the same as that of PS latex. As shown in **Table-2**, the amounts of PVAc and PS latices deposited on Nylon-6 fiber decrease remarkably with increasing pH, and the latices scarcely deposit at alkaline pH. Though the amounts of PS and PEA latices deposited on PAN fiber are high and decrease with increasing pH, those of PVAc latex are almost constant for

the change in pH and low. The deposition on cotton fiber exhibited the same behavior as that on PAN fiber.

As described in the previous papers^{(1)~(4), (6), (7)}, the deposition phenomena of latex particles on fibers can be considered by the coagulation theory of colloidal particles. That is, the deposition is mainly influenced by the interaction between a latex particle and the surface of fiber. In this study, therefore, the observed phenomena of the three kinds of latices were considered from these points of view.

In general, the interaction energy between a latex particle and the fiber can be estimated by the incorporation of electrostatic interaction energy and van der Waals interaction energy. The electrostatic (double layer) interaction energy (V_E) is calculated by the equation (1)⁽²⁾, as the energy between a sphere and the flat plate.

$$V_E = \frac{a\epsilon}{4kT} \left[(\phi_1^2 + \phi_2^2) \ln \frac{\exp(2\kappa H) - 1}{\exp(2\kappa H)} + 2\phi_1\phi_2 \ln \frac{\exp(\kappa H) + 1}{\exp(\kappa H) - 1} \right] \quad (1)$$

where a is the radius of a latex particle, ϵ is the dielectric constant of medium, k is the Boltzmann constant, T is the absolute temperature, H is the distance between a latex particle and the fiber, κ is the Debye-Hückel parameter, and ϕ_1 and ϕ_2 are surface potentials of a latex particle and the fiber, respectively.

The interaction energy of van der Waals forces (V_A) is calculated by the equation (2)⁽³⁾.

$$V_A = -\frac{A}{6kT} \left[\frac{2a(H+a)}{H(H+2a)} - \ln \frac{H+2a}{H} \right] \quad (2)$$

where A is the Hamaker constant. As A , 5×10^{-21} J was used on the basis of the value for polystyrene in water⁽¹⁴⁾.

Using ζ -potentials as surface potentials in Eq (1), the electrostatic interaction energies were calculated. The ζ -potentials of the latices measured are shown in **Fig.-4**, as a function of pH. The ζ -potentials of the latices were negative at all pH. These negative values increased with increasing pH and exhibited the constant ones at alkaline pH. The constant values increased in the order : PVAc < PS < PEA.

Fig.-4 ζ -Potentials of latices as a function of pH at 10^{-3} ionic strength and 25°C.

Fig.-5 ζ -Potentials of fibers as a function of pH at 10^{-3} ionic strength and 25°C.

The ζ -potentials of the fibers are shown in **Fig.-5**, as a function of pH. The ζ -potential of Nylon-6 fiber was positive at acidic pH and exhibited the isoelectric point at pH 4.3. The negative ζ -potential at alkaline pH increased with increasing pH. The negative ζ -potentials on PAN fiber and cotton fiber increased with increasing pH in the region of acidic pH to neutral pH, and those were constant at alkaline pH.

Based on these ζ -potentials, the electrostatic interaction energies were calculated as a function of separation distance between a latex particle and the fiber. The total interaction energies (V_T) due to V_A and V_E calculated at pH 3.1 are shown in **Fig.-6**.

V_T between Nylon-6 fiber and the latices are attractive energies because the ζ -potentials are opposite in sign. In the case of PAN fiber

Fig.-6 Total interaction energy between latex particles and fibers as a function of separation distance at pH 3.1, 10^{-3} ionic strength and 25°C.

and cotton fiber, V_T have maximum values (V_{Tmax}) at a certain separation distance. Therefore, the deposition of the latices on the fibers seems to be mainly influenced by the magnitude of V_{Tmax} . V_{Tmax} between the latices and the fibers are shown in **Table-3**, as a function of pH.

Table-3 V_{Tmax} between latex particles and fibers at 25°C and 10^{-3} ionic strength.

Fiber	pH	PVAc (B)	V_{Tmax} PS (kT)	PEA
Nylon-6	3.1	<0	<0	—
	4.8	189	181	—
	10.5	1759	1876	—
PAN	3.1	67	65	54
	5.3	121	163	97
	10.5	189	189	153
Cotton	3.1	46	45	38
	5.1	171	116	137
	10.5	227	220	186

V_{Tmax} of PVAc and PS latices for Nylon-6 fiber increased highly with increasing pH. In the case of PAN fiber and cotton fiber, V_{Tmax} of the three kinds of latices increased gradually with increasing pH and those values were approximately same at each pH. From these results, it is supposed that the depositing amounts of the latices decrease with increasing pH regardless of the kind of fiber or latex, and those of PVAc B, PS, and PEA latices on PAN fiber or cotton fiber are almost same at same pH.

The relation between the amounts deposited in **Table-2** and V_{Tmax} in **Table-3** was considered. In the case of Nylon-6 fiber, the amounts of PVAc and PS latices deposited decrease highly with increasing V_{Tmax} , though the amount of PVAc latex is larger than that of PS latex at no repulsive energy. In particular, these latices scarcely deposit on Nylon-6 fiber in the presence of high V_{Tmax} . This suggests that the electrostatic interaction is an important factor for the deposition of latex on Nylon-6 fiber. On the other hand, the amounts of PVAc latex deposited on PAN fiber and cotton fiber are almost constant and low in spite of the variation in V_{Tmax} . Additively, from the comparison of **Table-2** and **Table-3**, it seems that the amounts of PS and PEA latices deposited on PAN fiber and cotton fiber depend slightly on V_{Tmax} , though the amounts deposited decrease with increasing V_{Tmax} . That is, the amounts of PS and PEA latices deposited on PAN fiber and cotton fiber are larger than those on Nylon-6 fiber, in spite of high V_{Tmax} .

The above-mentioned results regarding PAN fiber and cotton fiber suggest the operation of other interaction forces in addition to the electrostatic force and van der Waals force. In regard to PVAc latex prepared in the presence of emulsifier, Okamura *et al.*⁹⁾ have reported that the hydrolysis takes place readily on the particle surface at room temperature and neutral pH, and poly(vinyl alcohol) is formed. Though PVAc latex used in this study was prepared in the absence of emulsifier, the formation of poly(vinyl alcohol) seems to be caused by potassium persulfate used as initiator. That is, poly(vinyl alcohol) layer may be present on the particle surface of PVAc latex, and this poly(vinyl alcohol) layer seems to influence on the deposition of PVAc latex on PAN fiber and cotton fiber. Recently, the authors⁸⁾ have found that on the deposition of styrene-acrylamide copolymer latex on PAN fiber, a certain repulsive force acts between the latex particle and PAN fiber, besides the electrostatic force. As this repulsive force, a steric repulsive force due to water-soluble polymer layer, which is present on the particle surface, has been introduced. Thus, in analogy with styrene-acrylamide co-

polymer latex, a steric repulsive force due to poly(vinyl alcohol) layer may act between PVAc latex particle and PAN fiber or cotton fiber, as schematically represented in Fig.-7(A).

(A) : PVAc (B) : PS and PEA

Fig.-7 Schematic representation of interaction between PAN or cotton fiber and latex particles.

It is thought that because of this repulsive force, the amounts of PVAc latex deposited on PAN fiber and cotton fiber are almost constant and low in spite of the variation in V_{Tmax} . On the other hand, a certain attractive force seems to act between PS or PEA latex particle and PAN fiber or cotton fiber, besides the electrostatic force and van der Waals force. For example, a force due to bridging may act, as represented in Fig.-7(B). It may be attributed to this force that the amounts of PS and PEA latices deposited on PAN fiber and cotton fiber are larger than those on Nylon-6 fiber, in spite of high V_{Tmax} .

Furthermore, in order to consider the influence of poly(vinyl alcohol) layer of PVAc latex particle, the PVAc latex B particles deposited on Nylon-6 fiber were observed by scanning electron microscopy. A typical photograph is given in Fig.-8, together with that of PS latex. PS latex particles deposit on Nylon-6 fiber connected to each other, e.g., like a rosary, as described in the previous paper⁶⁾. However, in the case of PVAc latex, it was observed that

(A) : PVAc (B) : PS

Fig.-8 Scanning electron micrographs of latex particles deposited on Nylon-6 fiber at pH 3.1, 24 h of deposition time and 10^{-3} ionic strength.

many particles tended to deposit as individual particles. Because of the steric repulsive force due to poly(vinyl alcohol) layer, PVAc latex particles may deposit as individual particles. This supports the influence of poly(vinyl alcohol) layer mentioned above for the deposition of PVAc latex.

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ポリ酢酸ビニルラテックスの繊維への付着性に関する界面電気的研究

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ポリ酢酸ビニルラテックスのナイロン-6, ポリアクリロニトリル及び木綿繊維への付着量を時間及び pH に関して測定し, ポリスチレン及びポリアクリル酸エチルラテックスの結果と比較した。結果を静電力及びファンデルワールス力による相互作用の点から考察した。

ナイロン 6 繊維への付着量は, pH の増加と共に急激に減少し, 静電的な相互作用が付着に対する主たる因子