Studies on Interfacial Properties of Polyelectrolyte-Cellulose Systems. I. Formation and Structure of Adsorbed Layers of Cationic Polyelectrolyte-(Poly-DMDAAC) on Cellulose Fibers

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Synopsis

An investigation of the conditions for monolayer or multilayer formations of cationic polyelectrolyte on cellulose fibers using adsorption, hydrodynamic permeability, and electrokinetic measurements is described. ζ-potential measurements by streaming current method were made on polymer-treated fiber pads. Monolayer formations on cotton linter (CT) fibers and dissolving pulp (DP) and multilayer formation on carboxymethyl cellulose (CMC) fibers were demonstrated. Monolayer formation proceeds by electrostatic interaction and Van der Waals force until all the negative charges of the fibers are neutralized. After charge neutralization, adsorption proceeds by Van der Waals force until formation of a saturated monolayer is completed. Multilayer formation proceeds mainly by electrostatic force until all the carboxyls of the fibers are neutralized. The presence of excess negative charge due to unneutralized carboxyls at the point of monolayer formation on CMC is the prerequisite for further adsorption to form a saturated multilayer. Affinity of the interactions, configurations of the adsorbed polymer chains, thickness of monolayer and multilayer, the effect of polymer molecular weights, and the stoichiometry of charge neutralization are discussed. A multilayer adsorption model is proposed to account for the experimental data.

INTRODUCTION

Polyelectrolytes perform a wide variety of functions in paper-making processes. They are added to control drainage and formation properties; to assist in the retention of fiber fines, fillers, and additives; to improve initial wet web strength; to confer wet and dry paper strength; and to recover fiber from effluent water. These functions of the polymers depend upon the adsorption of the polymer by the fiber and upon their electrolyte properties as well as those of cellulose fibers. For these reasons, there has been a growing interest in cellulose-polyelectrolyte interactions.[1-5] Since cellulose fibers are negatively charged in aqueous suspensions, particular attention has been focused on cationic polymers to control surface charge of the fibers.

In order to study surface charge characteristics of the fibers as well as adsorption properties of the fibers, this work proposes to investigate the polyelectrolyte-cellulose systems by studying adsorption and electrokinetic phenomena. Since various factors come into play in polyelectrolyte-cellulose interactions, the system for investigation is very complex. With a view to simplify this system, experimental work was carried out on a simple model system, in which polymer chains exist only at fiber surface as irreversible adsorbed layers, and not in the adjacent bulk electrolyte solutions.

As for adsorption of polyelectrolytes, an extensive review of the factors affecting the adsorption on solid substrates has been made so far.[6] Structure of adsorbed polymer layers at solid-liquid interface in general has been reported so far in view of monolayer and multilayer formation for nonionic polymer-solid systems.[7] Further, multilayer adsorption of polymer molecules on a solid substrate from a statistical viewpoint has been reported.[8,9] However, detailed theoretical investigations as well as experimental work have not been made so far on the conditions of multilayer formation in the positively charged polymer-cellulose fiber systems. In addition to this, no attempt has ever been made to investigate the formations and structure of monolayer or multilayer of the polymer on the fiber surface from adsorption, together with electrokinetic data.

There are a number of works which established the correlations between ζ potential and concentration of cationic polyelectrolytes in polyelectrolyte-cellulose systems.[4,10–13] However, no detailed study has been performed to date on this system with particular emphasis on the configurational behavior of the polymer chains at fiber surfaces.

Under present circumstances, this work attempts to demonstrate from adsorption, hydrodynamic permeability, and electrokinetic measurements, the conditions that lead to the formations of monolayer or multilayer by cationic polyelectrolytes on cellulose fibers.

The structure of adsorbed layers and the factors affecting the formations of the layers will be discussed in terms of the effect of the molecular weight of the polymer, forces of interaction, and stoichiometry of charge neutralization.

EXPERIMENTAL

Materials

Cellulose Fibers

Three kinds of cellulose fibers were used. These are cotton linters (CT), acetate grade dissolving pulp (DP), and carboxymethyl cellulose (CMC) obtained from Hercules Powder, Canadian International Paper, and Whatman, respectively.

CT and DP fibers were disintegrated and then subjected to fiber length fractionation to remove fines, since fines were observed to hinder appropriate pad formation for the electrokinetic measurements. CMC fibers were subjected to pretreatment according to the manufacturer's instruction.[14] This consists of two stages of pretreatment. In the first treatment, the CMC fibers were stirred into 15 volumes of 0.5N NaOH and left for 1 hr. Supernatant liquor was then decanted and the fibers were washed in a funnel until the effluent reached pH 8. The fibers were stirred into 15 volumes of 0.5N HCl and left for a further 30 min. This treatment was repeated followed by washing in a funnel until the filtered effluent was near neutral.

These fibers were washed three times with distilled water after pretreatment, i.e., disintegration and fractionation.

Polyelectrolyte

A quaternary ammonium polymer was selected as the cationic polyelectrolyte for the adsorption study, i.e., poly(1,1-dimethyl piperidinium-3,5-diallyl methylene chloride)(DMDAAC). Two molecular weights, M_n: ca. 50,000 and 200,000, were commercially available from Calgon Corporation and used as received. The dilute polymer solutions were prepared using distilled water. Monomer unit of the polymer is illustrated in Figure 1.

Adsorption Procedure

Air-dried 0.5 g (oven dry weight) of fiber was weighed into 50 ml of polymer solution and the tube was stirred for 24 hr at 25°C. After removal from the shaker, the tube was centrifuged for 15 min at 3500 r.p.m. The centrifuged sample was transferred into a glass filter, then washed with 1 l. of distilled water. The washed sample was transferred to a glass tube filled with 200 ml of distilled water and allowed to stand overnight. Then the sample was transferred into a glass filter, dried, and weighed. A portion of the dried sample was subjected to nitrogen analysis by the Kjeldahl method in order to determine the amount of polymer adsorbed (gram equivalents).

Polymer-treated fibers for electrokinetic and permeability measurements were prepared with the same fiber/solution ratio, i.e., 1/100. In this case, the ratio was 4 g fiber per 400 ml solution.

The amount of adsorbed polymer A is calculated according to the following formula:

$$A(\text{gram equivalent}) = b \times 10 \text{ mg}/14 \text{ geq/g fiber}$$
$$= 71.43b \times 10^{-5} \text{ geq/g fiber}$$

where b is the percent of N (nitrogen). This method gives the amount of polymer adsorbed irreversibly on the cellulose surface.

Determination of Carboxyl Content

Carboxyl contents of cellulose fibers were determined by a $NaHCO_3$—NaOH method (Wilson method).[15] Results are shown in Table I.

ζ Potential and Permeability Measurements

The suspensions of cellulose fibers with and without adsorbed polymers were prepared in dilute electrolyte (KCl) solutions and porous fiber pads were formed in a streaming current cell as illustrated in Figure 2. A continuous flow circuit was developed and attached to the apparatus developed by Chang and Robert-
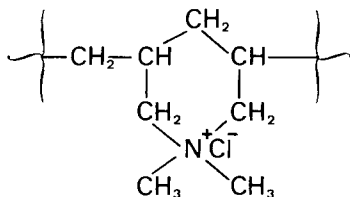

Fig. 1. Monomer unit of Poly-DMDAAC.

TABLE I
Hydrodynamic Variables and Carboxyl Contents of Fibers

Fiber	Specific surface area σ cm^2/g	Specific volume α cm^3/g	Carboxyl content —COOH $\times 10^{-5}$ geq/g	Density of carboxyl groups[a] —COOH/σ	
				$\times 10^{-9}$ geq/cm^2	$\times 10^{14}$/ cm^{2}[b]
CT	12,300	2.16	0.40	0.33	1.98
DP	8500	1.85	0.51	0.60	3.60
CMC	5950	1.66	19.6	32.9	197

[a] Density of carboxyl groups as calculated from specific surface area and carboxyl content of fibers.

[b] The number of carboxyl groups on unit surface area (k_2).

son.[11] The streaming current, the liquid permeability and the fiber conductivity were measured for five compression stages by this apparatus at successively higher concentrations as the pads were compressed.

Detailed results of ζ potential and conductivity measurements of the pads will appear in later publications of this series.

The zeta potential was calculated by means of the exponential form of the streaming current equation for a porous pad proposed by Chang and Robertson.[16]

$$I\eta L/pD = (A\zeta/4\pi)e^{-Bc} \qquad (1)$$

where I is the streaming current across the fiber pad, μA; η is the viscosity of liquid, poises; L is the length of the pad, cm; p is the pressure difference across the pad, dyn/cm^2; A is the cross-sectional area of the pad, cm^2; B is a constant; c is the solid concentration of the pad, g/cm^3; D is the dielectric constant, cgs; and ζ is the zeta potential, mV.

The left-hand side of the equation is plotted on semilogarithmic paper against concentration and the ζ potential is calculated from the $c = 0$ intercept obtained by extrapolating the linear plot using the least-squares method for five sets of data.

The hydrodynamic properties of the fiber, i.e., the specific volume α and the specific surface σ of the fiber were similarly calculated from the slope and in-
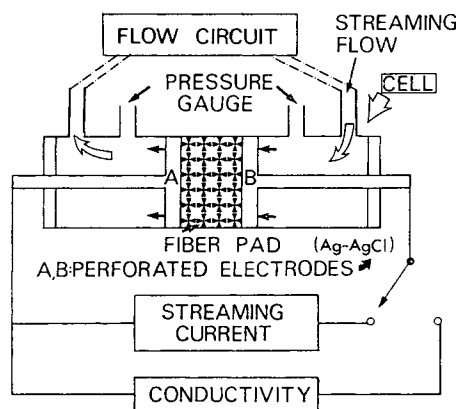

Fig. 2. Streaming current cell and experimental system.

tercept of the rectilinear form of the Kozeny-Carman equation by means of the least-squares method.[11,17]

$$(Kc^2)^{1/3} = (1/5.55\sigma^2)^{1/3}(1 - \alpha c) \tag{2}$$

where $K = Q\eta L/pA$ is the permeability coefficient of the pad; Q is the volume rate of streaming flow, cm^3/sec; α is the hydrodynamic specific volume, cm^3/g; and σ is the specific surface of the fibers, cm^2/g.

The results of hydrodynamic measurements are shown in Table I. Electronic computers of McGill University (IBM 360) and University of Tokyo (HITAC 8700) were used for processing the data.

RESULTS AND DISCUSSION

The experiments were designed to demonstrate adsorption and charge characteristics of three different fibers with monolayer or multilayer of the polymer from adsorption, permeability, and electrokinetic measurements.

Adsorption Isotherms

Adsorption isotherms of the polymer on CT are shown in Figure 3. The figure shows that the amount of adsorption is higher for the higher molecular weight sample of the polymer. However, no significant difference in the amount of adsorption was observed at the point of saturation. This means that the amount of adsorption of the polymer on the surface of CT is independent of molecular weight of the polymer when saturation adsorption is completed at ca. 1% of initial concentration of the polymer solution. This result suggests that the polymer segments are adsorbed on CT fibers with all the segments lying flat on the surface, which supports the monolayer hypothesis of polymer adsorption at the point of saturation adsorption (see Fig. 7).

Adsorption isotherms of the polymer on CMC are shown in Figure 4, in which it is shown that no significant difference in the amount of adsorption was observed at the lower initial concentration of the polymer. This indicates that the polymer segments are adsorbed with most of the segments lying flat on the surface (see Fig. 7).

However, at higher initial concentration of the polymer (0.5% to 1%), the amount of adsorption is higher for lower molecular weight polymers, suggesting that some of the polymer segments are adsorbed with loops or tails extending away from the fiber surface (see Fig. 5). The saturation adsorption occurs when the initial concentration of the polymer is between 0.5% and 1%.
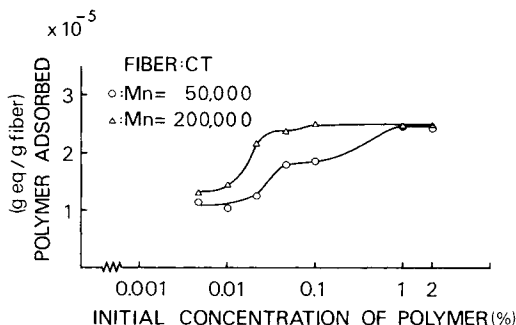

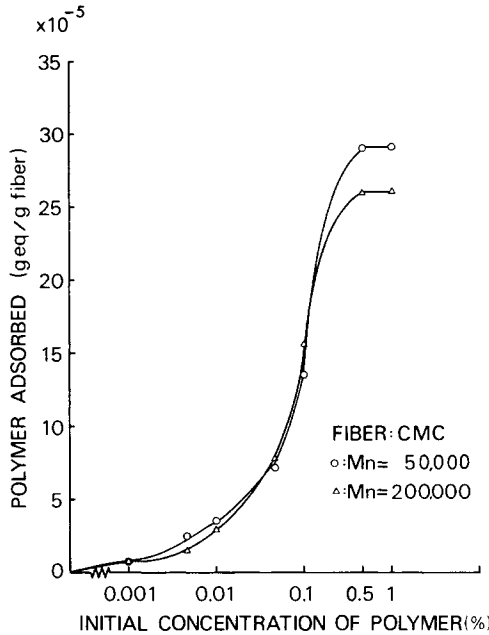Fig. 3. Adsorption isotherms of the polymer on CT.

Fig. 4. Adsorption isotherms of the polymer on CMC.

Affinity of the Polymers for the Fibers

Generally, polymer molecules are adsorbed on a solid surface from solution more or less as random coils. That is, some of the polymer segments are anchored on the surface and the rest of the segments extend into the solution by forming loops or tails as illustrated in Figure 5. The extent to which the segments are anchored to the surface is supposed to differ according to the affinity between polymer segments and a solid surface. Thus, the structure of an adsorbed polymer layer at a solid surface varies with adsorption affinity between the polymer and the surface.[18]

As illustrated in Figure 6, polymer chains tend to lie flat on a solid surface with increase in the affinity. That is, the fraction of anchored chains increases with increase in the affinity. In the interaction of cationic polyelectrolytes with cellulose fibers, the main factors affecting the affinity are supposed to be the cationic charge of the polymer and the negative charge of cellulose fibers.

Experimentally, it is known[18] that the adsorption affinity can be assessed from the initial slope of the adsorption isotherm as shown in Table II. The negative charge per unit area of the cellulose fibers is a function of the number of carboxyl groups per unit surface area (i.e., density of carboxyl groups, k_2), provided that the main origin of the negative charge is the carboxyl group.

The density of carboxyl groups is calculated from the specific surface area and the carboxyl content of the fibers as shown in Table I. The table indicates that
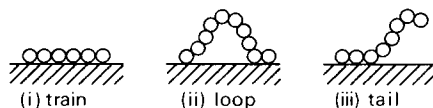

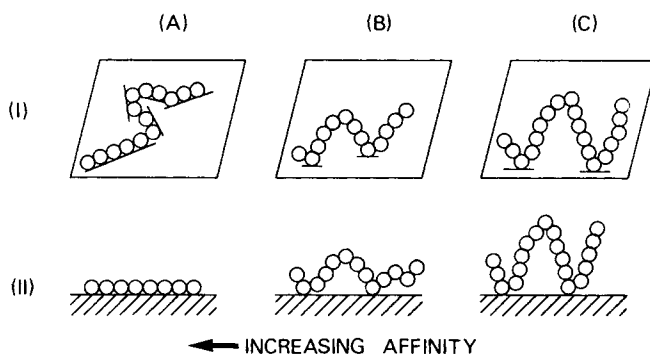Fig. 5. Configurations of an adsorbed polymer chain on a solid substrate.

Fig. 6. Affinity of adsorption vs adsorbed polymer chain configurations. (I) Three-dimensional model; (II) two-dimensional model. (a) Adsorbed as trains; (b) adsorbed as loops or tails; (c) adsorbed mostly as random coils. Adsorption affinity increases in the order of (c) < (b) < (a).

increasing order of magnitude of the density of carboxyl groups of three kinds of fibers is: CT < DP < CMC. This means that CMC has the highest affinity for the polymer among these three kinds of fibers.

Monolayer Formation and Apparent Molecular Area

Figure 7 shows the configuration of adsorbed polymer chains at solid surfaces with various affinities. If one considers an adsorbed polymer molecule to have both adsorbed and unadsorbed segments, then the following relationship holds for adsorption of polymers to solid surfaces in general:

$$P = P_a + P_u \tag{3}$$

where P is the degree of polymerization, i.e., the number of segments of one polymer molecule; P_a is the number of adsorbed (anchored) segments of one polymer molecule; and P_u is the number of unadsorbed (unanchored) segments of one polymer molecule.

In addition to this, the following relationship is established:

TABLE II
Initial Slopes of Adsorption Isotherms

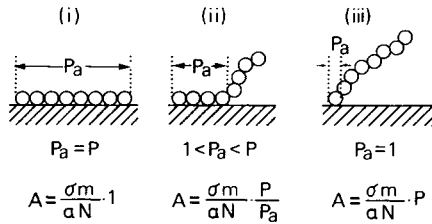| Fiber	Mn	Initial concentration of polymer (IC) %	Polymer adsorbed (PA) $\times 10^{-5}$ geq/g	Initial slope (PA)/(IC) $\times 10^{-5}$ geq/g/%
CT	50,000	0.005	1.14	228
		0.01	1.00	100
		0.05	1.79	35.8
	200,000	0.005	1.29	258
		0.01	1.43	143
		0.05	2.36	47.2
CMC	50,000	0.005	2.84	568
		0.01	3.55	355
		0.05	7.10	142
	200,000	0.005	1.42	284
		0.01	2.84	284
		0.05	7.81	156

Fig. 7. Schematic model for configurations of individual adsorbed polymer chain vs amount of adsorption. (i) Adsorbed with all the segments lying flat on the surface. The amount of adsorption A is independent of the degree of polymerization P. (ii) Adsorbed with part of the chain extending away from the surface. The amount of adsorption A is inversely proportional to the adsorbed fraction. (iii) Adsorbed with one chain end, leaving other segments extending away from the surface. The amount of adsorption is proportional to the degree of polymerization P.

$$A = (\sigma m/a\,N)\,P/P_a \tag{4}$$

where A is the amount of adsorption per unit weight of solid; σ is the specific surface area of solid; m is the molecular weight of monomer; a is the effective surface area occupied by an adsorbed polymer segment; and N is Avogadro's number.

The above two equations indicate that if P_a is equal to P, then the amount of adsorption A is independent of the degree of polymerization of polymer P, i.e., molecular weight of the polymer mP.

Since adsorption isotherms for CT show that the amount of adsorption at saturation is independent of molecular weight, the area of an adsorbed segment of the polymer on cellulose surface a can be calculated using model (i) in Figure 7.

The adsorption isotherms in Figure 3 show that the amount of adsorption at saturation is $A = 2.5 \times 10^{-5}$ geq/g. Specific surface area of CT is $\sigma = 12{,}300$ cm^2/g. Consequently, a is calculated by

$$A = (\sigma/a)(1/N) \tag{5}$$

where A is on a geq/g basis. The calculation gives $a = 8.2 \times 10^{-16}$ cm^2 = 8.2 Å^2.

Monolayer Formation and Surface Charge Characteristics

Since the density of carboxyls of CT is the lowest among these three kinds of fibers, CT is supposed to have the lowest affinity for the polymer. The molecular weight dependence of the adsorption isotherms on CT indicates that CT follows the adsorption pattern of $P_a = P$ at the point of saturation adsorption [see (i) of Fig. 7].

In view of the increasing order of magnitude of the density of carboxyl groups of these three kinds of cellulose fibers, namely, CT < DP < CMC, it is suggested that DP and CMC also follow the adsorption pattern of $P_a = P$.

Experimental evidence for monolayer formation for CT is that the amount of adsorption is independent of molecular weight at the point of saturation. The evidence for DP is that ζ potential values are constant independent of molecular weight of adsorbed polymer at the point of saturation adsorption as shown in Figure 8. A theoretical calculation for CMC below gives $A = 1.2 \times 10^{-5}$ geq/g for monolayer formation ($P = P_a$).

$$A = \frac{\sigma}{a}\,1/N = \frac{5950}{8.2 \times 10^{-16}} \times \frac{1}{6 \times 10^{23}} = 1.2 \times 10^{-5}$$
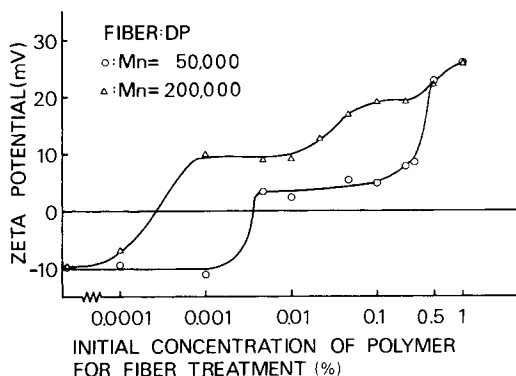
Fig. 8. ζ potential of monolayer-formed DP. Medium: 10^{-4} M KCl aq.

Adsorption isotherms in Figure 4 show that the amount of adsorption for CMC at the point of monolayer formation is almost independent of polymer molecular weights.

Table III shows the surface charge characteristics of the three kinds of polymer-treated cellulose fibers when saturated monolayers are formed. The data are calculated based on the assumption that the polymer molecules are closely packed (condensed monolayer) in the surface layer with surface coverage of almost 100%. The data for three kinds of surfaces are compared on unit area basis. The calculation follows below.

The area occupied by an adsorbed polymer segment a is $a = 8.2 \times 10^{-16}$ cm^2 = 8.2 Å^2 as calculated in the preceding section for CT. Therefore, the number of adsorbed segments per 1 cm^2 of fiber surface k_1 is $k_1 = 1/a = 1/(8.2 \times 10^{-16})$ = 12.2×10^{14}.

The number of adsorbed segments on gram equivalent basis is $k_1/N = 12.2 \times 10^{14}/(6 \times 10^{23}) = 2.03 \times 10^{-9}$ geq/cm^2.

Affinity and Monolayer Formation

Concentrations of the polymers required to form monolayers are lower for the fiber with higher negative surface charge density (or density of carboxyls), i.e., 0.002% for CMC, 0.5% for DP, and 1% for CT. These results indicate that fibers with lower affinity for the polymer require higher initial concentrations of the polymer to form a monolayer.

Conditions for Monolayer and Multilayer Formations

Table III shows that for CT and DP, the number of adsorbed polymer segments accomodated per 1 cm^2 of the fiber surface (k_1) is larger than the number of carboxyl groups on 1 cm^2 of the fiber surface (k_2). This results in excess positive surface charge density at saturated monolayer formations for CT and DP.

On the other hand, for CMC the number of adsorbed polymer segments accomodated per 1 cm^2 of CMC surface (k_1) is smaller than the number of carboxyl groups per 1 cm^2 of CMC fiber surface (k_2). This leads to an excess negative surface charge density at the point of monolayer formation. The results from electrokinetic measurements in Table III show that CT and DP with monolayers of the polymers are positively charged and the CMC with monolayer is still negatively charged.

TABLE III
Surface Charge Characteristics of Monolayer-Formed Fibers

Fiber	Adsorbed layer at saturation	Density of carboxyl groups (k_2) ×10^{14}/cm^2	Number of adsorbed polymer segments (k_1) ×10^{14}/cm^2	k_1 vs k_2	Surface excess at monolayer-formed fibers ×10^{14}/cm^2	ζ potential in 10^{-4} M KCl aq.		Concentration of polymer required to form monolayer %	Polymer adsorbed on monolayer-formed fibers ×10^{-5} geq/g
						Fiber only mV	Fiber with monolayer (Mn = 50,000) mV		
CT	Monolayer	1.98	12.2(2.03)[a]	$k_1 > k_2$	$k_1 = 10.2$	−18.1	+23.7	1.0	2.5
DP	Monolayer	3.60	12.2[b](2.03)[a]	$k_1 > k_2$	$k_1 = 8.60$	−10.0	+22.5	0.5	1.7
CMC	Multilayer	197	12.2[b](2.03)[a]	$k_1 < k_2$	$k_2 = 185$	−20.5	−3.4	0.002[c]	1.2[d]

[a] Value in parentheses refers to the amount of polymer adsorbed on gram equivalent basis per unit surface area of fibers (i.e., ×10^{-9} geq/cm^2).
[b] On the basis of flat monolayer hypothesis, the equal numbers of adsorbed polymer segments may be theoretically contained in unit surface area of CT, DP, and CMC, because k_2 increases in the order of CT < DP < CMC.
[c] This value gives the amount of adsorption (1.2×10^{-5} geq/g) on adsorption isotherm on CMC (see Fig. 4).
[d] This value is obtained by entering $k_1 = 12.2$ into $k_1\sigma/N$, where $\sigma = 5950$ cm^2/g.

Thus, the results of electrokinetic measurements, together with the theoretical calculations of the surface charge of three kinds of fibers with polymer monolayer, indicate the possibility of monolayer formation for CT and DP: multilayer formation for CMC.

The polarity of excess surface charge on monolayer-formed CT and DP is positive, and the positively charged fiber surfaces are likely to repel the positively charged polymer molecules. Thus, further adsorption of the polymer onto the monolayer-formed CT and DP will not occur.

On the other hand, the polarity of excess surface charge on monolayer-formed CMC is still negative, and the negatively charged CMC fiber surface tends to attract positively charged polymer segments.

Then, further adsorption of the polymer is supposed to proceed until excess negative charge due to unneutralized carboxyls is neutralized by multilayer formation of the polymers.

This hypothesis is supported by the experimental fact that gram equivalent weight of adsorbed polymer at the end point of multilayer formation (w_1) is close to the carboxyl content of CMC on gram equivalent basis (w_2), where $w_1 = 29 \times 10^{-5}$ and 26×10^{-5} geq/g for Mn: 50,000 and 200,000, respectively; and $w_2 = 19.6 \times 10^{-5}$ geq/g.

Possible explanations for the reason why w_1 is larger than w_2 would be that (i) some of the polymer segments are adsorbed without charge neutralization, and (ii) some of the carboxyls are present inside porous structure of fibers and thus nonaccessible to the polymer segments.

Thickness of Monolayer

The thickness of monolayer of adsorbed polymer on cellulose surface is calculated from the adsorption data on CT provided that the close-packed segment model is applicable in the calculation as shown in Figure 9. The figure shows that the area of one adsorbed polymer segment a is $a = 8.2 \times 10^{-16}$ cm^2. The thickness of monolayer δ is $\delta = a^{1/2} = 2.86 \times 10^{-8}$ cm = 2.86 Å. The volume of one segment v is $v = a^{3/2} = 23.5 \times 10^{-24}$ cm^3 = 23.5 Å^3. From the above calculations, a possible close-packed monolayer adsorption model for CT and DP is schematically shown in Figure 9.
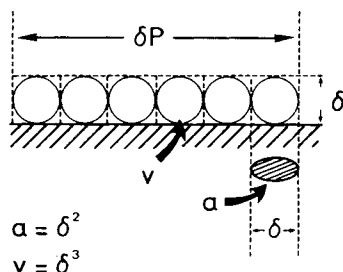

Fig. 9. Possible close-packed monolayer adsorption model for CT and DP. δ: monolayer thickness (=2.86 Å), a: area occupied by one adsorbed polymer segment (=8.2 Å^2), V: volume of one adsorbed polymer segment (=23.5 Å^3), δP: length of an adsorbed polymer chain.

Thickness of Multilayer

The adsorption isotherms for CMC show that the amount of adsorption at saturation for Mn: 50,000 and 200,000 are ca. 29 and 26 ($\times 10^{-5}$ geq/g), respectively. Table III shows that the amount of polymer segments contained in one anchored layer is 2.03×10^{-9} geq/cm^2.

If the multilayer on CMC is assumed as a combination of the monolayers as shown in the simplified model (I) in Figure 10, then the number of layers calculated from the amount of adsorption on CMC is as follows:

for Mn: 50,000,

$$\frac{(29 \times 10^{-5})/5950}{2.03 \times 10^{-9}} = 24.01 = \text{ca. 24 layers}$$

for Mn: 200,000,

$$\frac{(26 \times 10^{-5})/5950}{2.03 \times 10^{-9}} = 21.5 = \text{ca. 22 layers}$$

where 5950 cm^2/g is the specific surface area of CMC fibers as shown in Table I.

Since the thickness of monolayer is 2.86 Å, the thickness of multilayer is as follows: The thickness of multilayer equals (the number of layers) $\times$ (the thickness of monolayer). Consequently, the thickness of multilayers are as follows: for Mn: 50,000: $24 \times 2.86 = 68.6$ Å; for Mn: 200,000: $21.5 \times 2.86 = 61.5$ Å.

It is also seen from Table III that the number of monolayers of the polymer required to neutralize all the negative charges of carboxyl groups of CMC is calculated by k_2/k_1. $k_2/k_1 = (197 \times 10^{14})/(12.2 \times 10^{14}) = 16.2$ layers. Therefore, the thickness of multilayer in this case is $16.2 \times 2.86 = 46.3$ Å, provided that each layer is adsorbed flat on the fiber surface and all the carboxyls are present on the external surface of CMC fibers. The above calculations have shown that the thickness of multilayer calculated from the saturated amount of adsorption (68.6 and 61.5 Å) are larger than that calculated from carboxyl groups of CMC fibers (46.3 Å). This means that some of the polymer segments are adsorbed on the fiber surface without neutralizing negative charges of carboxyl groups of fibers; this probably leads to the formation of loops or tails (Fig. 5).

Consider one negative point charge of cellulose fibers (point A), and one positive point charge in nth adsorbed layer (point B) as illustrated in model (I) of Figure 10 for the electrostatic interaction between the negatively charged fibers and the positively charged polymers. Then, the electrostatic force acting between these two points is represented by F_n:
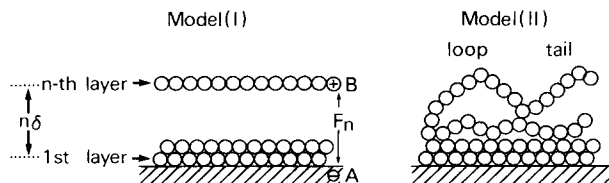

Fig. 10. Multilayer adsorption models. Model (I): A simplified model where multilayer consists of piled up monolayers and free from loops or tails. Model (II): A possible multilayer model where loops or tails due to entropic effect is taken into account. This model may be applicable to adsorption of poly-DMDAAC on CMC.

$$F_n = ke^2/(nl)^2 \tag{6}$$

where e is the electron charge, n is the number of layers, l is the layer thickness, and k is a constant.

Since electrostatic force is inversely proportional to the square of the distance between the two oppositely charged points, the electrostatic force acting between them decreases with increase in the distance of separation. Therefore, it is suggested that the electrostatic force acting between the cellulose surface and the adsorbed layer of polyelectrolyte decreases as the sequentially adsorbed layers are separated from the fiber surfaces.

The segments of polyelectrolytes are then likely to form loops or tails rather than forming anchored segments (trains) layers probably due to predominance of the hydrolyzing power of the polymer segments and the entropic effects over the electrostatic force as illustrated in model (II) of Figure 10.

Multilayer Adsorption Model

Silberberg[8] has proposed a multilayer adsorption model by using a statistical treatment of adsorbed polymer chains on a solid substrate. The Silberberg model successfully accounts for segmental distributions in surface layers. However, this Silberberg's model deals with adsorption of nonionic polymers from dilute solution onto a solid substrate, and not refers to charged polymer systems.

In view of the above, an attempt was made to propose an adequate model capable of accounting for polymer chain configurations for the multilayer formation in terms of charge neutralization between the positively charged polymer molecules and the negatively charged fiber surfaces.

Dependence of the molecular weights, and carboxyl contents of the adsorption isotherms for CMC indicates that the polymer chains are adsorbed on CMC surface with the segments almost lying flat on the cellulose surface in the lower adsorbed layers and with loops or tails in the higher adsorbed layers as illustrated in model (II) of Figure 10.

Force of Interaction for Adsorbed Layer Formations

For the interaction of cationic polyelectrolytes with cellulose fibers, a dual mechanism is proposed, in which the primary adsorption occurs to the point of charge neutrality probably due to an ion exchange mechanism, and the secondary adsorption takes place probably due to Van der Waals force or hydrogen bonding.[13]

In the case of monolayer formation on CT and DP, both electrostatic and Van der Waals forces appear to come into play in the adsorption process. After all the negative charges of the fibers are neutralized, adsorption proceeds only by Van der Waals force until a saturated monolayer is completed. Thus the dual mechanism theory is supported by the results from monolayer formation.

In the case of multilayer formation on CMC, electrostatic force is predominant in adsorption. Since the density of carboxyls of CMC is far higher than those for the other two kinds of fibers, electrostatic force would be dominant in the adsorption on CMC.

In view of this, the polymer adsorption on CMC proceeds mainly by this

electrostatic force until all the negative charges are neutralized. An active site hypothesis by Bobalek[18] claims that adsorption capacity of a substrate is a function of the number of active sites for adsorption. If the carboxyls on CMC are regarded as the active sites for adsorption, the active site hypothesis appears to explain the polymer adsorption on CMC.

Although the Van der Waals force universally functions in adsorption systems, it is inversely proportional to the seventh power of the distance, whereas electrostatic force to the square of the distance. This means that Van der Waals force is negligible compared with electrostatic force. Accordingly, the dual mechanism theory holds less for the polymer adsorption on CMC compared with that on CT and DP.

Effect of Molecular Weight of the Polymer

The adsorption isotherms in Figures 3 and 4 show that the effect of the molecular weights of the polymer on the formation and the structure of adsorbed layers differs between the formation of monolayer and multilayer. The monolayer formation on CT suggests that below the saturation point, the number of extended polymer segments (loops or tails) is higher for the higher molecular weight sample of the polymer. In contrast, however, at the point of saturation, almost all the polymer segments lie flat on the surface of the fibers with no extended polymer segments, provided that the same number of the negatively charged adsorption sites are available for adsorption of both Mn: 50,000 and 200,000. This interpretation is illustrated in Figure 11. This trend of the molecular weight dependence of the polymer adsorption is consistent with the results
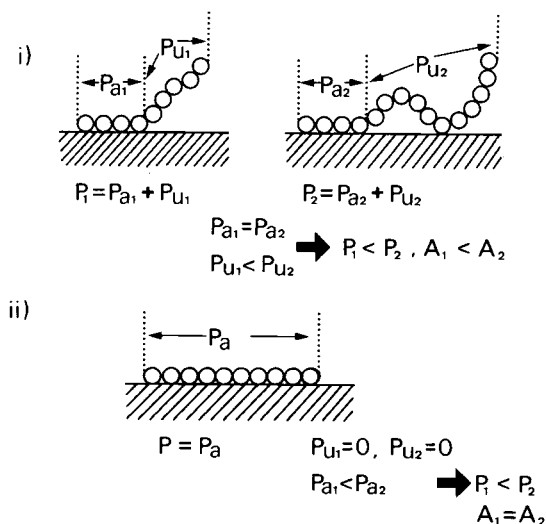

Fig. 11. Schematic representation of molecular weight dependence of polymer adsorption. P_1: the degree of polymerization of the lower molecular weight sample (Mn = 50,000). P_2: the degree of polymerization of the higher molecular weight sample (Mn = 200,000). A_1: the amount of polymer adsorbed with $P = P_1$. A_2: the amount of polymer adsorbed with $P = P_2$. P_a: the number of adsorbed segments per one adsorbed chain. P_u: the number of unadsorbed segments per one adsorbed chain. (i) Before saturated adsorption. The amount of adsorption is molecular weight dependent, i.e., A_1 is not equal to A_2. (ii) At saturated adsorption. The amount of adsorption is independent of molecular weight, i.e., A_1 is equal to A_2.

of the electrokinetic study of monolayer-formed DP fibers (Fig. 8), details of which will be published later in this series.

On the other hand, for the multilayer formation on CMC, no appreciable difference in the amount of adsorption was observed until the residual carboxyls are almost neutralized. However, after all the negative charges are neutralized, the amount of adsorption is slightly higher for the lower molecular weight sample of the polymer. This leads to the suggestion that polymer segments are lying almost flat on the CMC surface in the lower adsorbed layers, and adsorbed with loops or tails in the higher adsorbed layers as discussed in a preceding section (see Fig. 10). In addition to this, adsorbed layers of the lower molecular weight sample appear to have higher content of loops or tails, compared with the higher molecular one.

Stoichiometry of the Adsorbed Layer Formations

When the polymer is adsorbed from solution on cellulose fibers, the freedom of motion of each segment is restricted according to the degree of polymerization of the polymer, and the negatively charged groups of the fibers are also restricted on the two-dimensional plane. Thus, the stoichiometric interactions (1:1 interactions) between the positively charged groups of the polymer and the negatively charged groups of the fibers probably do not take place.

For monolayer formation, the adsorption proceeds with loops and tails as well as trains, and the deviation from the stoichiometric interaction is relatively higher. This deviation in this case results in charge reversal of the fiber surface by cationic polymers.

For multilayer formation, the adsorption proceeds with segments lying almost flat on the surface, and the deviation from stoichiometric interaction is relatively lower. The lower deviation from stoichiometry in this case does not result in charge reversal of the fiber surface by cationic polymers. The results of electrokinetic study of the multilayer-formed CMC supporting this hypothesis will be published later.

In view of the above discussion, it seems reasonable to conclude that deviation from stoichiometry with residual positive charges of the polymers is effective to reverse the charge of fiber surfaces. In the case of monolayer formation, it is suggested that the higher molecular weight polymer deviates more from stoichiometric interaction before saturation. However, the effect of the molecular weight on the deviation is the same for the two different molecular weight samples at the point of saturation adsorption.

In the case of multilayer formation, it is suggested that the molecular weight effect is not significant over the lower polymer concentration region. In contrast, however, a significant effect is observed after all the negative charges are neutralized by the polymer positive charges.

CONCLUDING REMARKS

The formation of adsorbed polymer layers, i.e., monolayer or multilayer, takes place by the combination of the positively charged polymer, poly-DMDAAC, with the negatively charged fibers of different surface charge characteristics. Combined effects of specific surface area of fibers, carboxyl contents of fibers, molecular area of one adsorbed segment, and cationic charge of the polymer

molecule determine whether or not the adsorption proceeds to form multilayer. The presence of excess negative charge due to unneutralized carboxyls at the point of monolayer formation on CMC probably leads to the formation of multilayer.

References

1. B. Alince and A. A. Robertson, *Colloid Polym. Sci.*, **252**, 920 (1974).
2. W. A. Kindler, Jr. and J. W. Swanson, *J. Polym. Sci.*, *A-2*, **9**, 853 (1971).
3. G. G. Allan, K. Akagane, A. N. Neogi, W. M. Reif, and T. Mattila, *Nature*, **225**, 175 (1970).
4. T. Lindström and C. Söremark, *J. Colloid Interface Sci.*, **55**, 305 (1976).
5. L. S. Sandell and P. Luner, *J. Appl. Polym. Sci.*, **18**, 2075 (1974).
6. F. R. Eirich, Transaction of ACS Meeting, Chicago, A7.5, 1968.
7. F. Rowland, R. Bulas, E. Rothstein, and F. R. Eirich, *Ind. Eng. Chem.*, **57**(9), 46 (1965).
8. A. Silberberg, *J. Colloid Interface Sci.*, **38**, 217 (1972).
9. C. A. J. Hoeve, *J. Polym. Sci., Part C*, **34**, 1 (1971).
10. R. G. Anderson and J. G. Penniman, Jr., *Paper Trade J.*, **14**, 56 (1974).
11. M. Y. Chang and A. A. Robertson, *Pulp Pap. Mag. Can.*, **68**, 438 (1967).
12. V. Balodis, A. W. McKenzie, H. G. Harrington, and H. G. Higgins, in *Consolidation of the Paper Web*, F. Bolam, Ed., B. P. & B.M.A., London, 1969, p. 639.
13. D. L. Kenaga, W. A. Kindler, and F. J. Meyer, *Tappi*, **50**, 381 (1967).
14. Whatman's advanced ion-exchange celluloses laboratory manual.
15. K. Wilson, *Svensk Papperstid.*, **69**, 386 (1966).
16. M. Y. Chang and A. A. Robertson, *Can. J. Chem. Eng.*, **45** (4), 66 (1967).
17. A. A. Robertson and S. G. Mason, *Pulp Pap. Mag. Can.*, **50**(13), 103 (1949).
18. E. G. Bobalek, in *Interface Conversion for Polymer Coatings*, Elsevier, New York, 1968, p. 289.