Adsorption and Recovery of Nonionic Polymers by Neutralization of Cellulose Fiber Surface Charge via Cationic Polyamide-Epichlorohydrin Resins

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ABSTRACT: Nonionic copolymers, such as poly(1-vinyl-pyrrolidone)-polystyrene, have been used in the production of filtration membranes, catalysts, and sensors. However, their nonionic character and high solubility in water prevents their efficient recovery from waste streams. Cellulose fibers show potential as recovery agents because they are inexpensive, environmentally friendly, and have a large surface area per unit mass. However, due to the anionic nature of the cellulose fiber surface, their adsorptive behavior is often limited to cationic species. We have shown that low-dosage application of a cationic polyamide-epichlorohydrin resin can alter the fiber surface charge so as to provide more neutral surface area for the nonionic polymer to adsorb; furthermore, the adsorbed polyamide-epichlorohydrin resin does not block the approach of poly(1-vinylpyrrolidone)-polystyrene. Single-component adsorption of poly(1-vinylpyrrolidone)-polystyrene was on the order of 10^{-3} g/g; with polyamide-epichlorohydrin resin adsorbed on the fiber, the adsorption increased one-order of magnitude to 10^{-2} g/g. We believe this significant increase is caused by neutralization of fiber surface charge via polyamide-epichlorohydrin resin, creating a surface more favorable for adsorption and recovery of nonionic species. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1476–1485, 2010

Key words: adsorption; water-soluble polymers; fibers; modification; polyelectrolytes

INTRODUCTION

Cellulose, a polysaccharide of β-glucose, is of particular interest in the field of wastewater treatment and chemical area because they possess good characteristics as an inexpensive alternative to adsorbents such as activated carbon. The cellulose fibers have a large surface area of 200 m^2/g; furthermore, they possess a charge density of $\sim$ 1.4 $\mu C/cm^2$, giving the fibers an affinity for ionic species.[1] In paper production, this affinity of cellulose fibers causes the adsorption of aqueous heavy metal ions on the charged cellulose surfaces, which inhibit the interfiber interaction. Chelating agents must be used in paper production to prevent this interference by removal of aqueous heavy metal ions. This apparent problem can be applied reversely as a solution to remove the heavy metal ions effectively in recovery systems. Several research works have already shown that cellulose fibers could be tailored to remove specific heavy metal ions from wastewater systems. Inukai et al. synthesized an *N*-methylglucamine-type cellulose derivative to maximize boron(III) adsorption as using environmentally conscious technology.[2] Cellulose fibers have been modified using polyethyleneimine to selectively adsorb mercury ions from wastewater as using an inexpensive and biodegradable carrier.[3]

However, the use of cellulose fibers has been limited to ionic species like the aforementioned metals. Recovery of nonionic species using cellulose fibers has not explored because it requires modification to change the nature of the fiber surface, which is not practical or cost-effective. However, a polymer adsorbent capable, in low doses, of altering the fiber surface to make it more favorable for nonionic species adsorption would provide the practical solution of recovery of nonionic species.

Polymer adsorption on to cellulose fibers has been thoroughly studied for over 30 years, primarily due to the use of polymer coatings and wet-strength resins in paper products. Polyelectrolytes have received special attention because of their ability to favorably interact with the negatively charged carboxylic acid groups on the fiber surface. Tanaka and Odberg published a significant volume of work regarding the adsorption of cationic polyacrylamides onto cellulose fibers and its dependence on molecular weight of the chains and charge density of the polymer.[4–7] Polyamide-epichlorohydrin (PAE) resins

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have been used in papermaking as wet-strength additive.[8,9] The PAE-resins generally have 3-hydroxylazetidium groups, which are responsible for the reactivity and the cationic character of this PAE-resin and provide favorable electrostatic interactions with negatively charged hydroxyl adsorption sites on the cellulose fiber surface.[10] The local negative charge of cellulose fibers are effectively neutralized; furthermore, the unexchanged ions on the PAE-resins attract anionic species, both free-floating and on the surface of other fibers, which results in layering of these ions around the polymer and bridging of the chain between fibers.[11] Hwang and Chen did a series of works to use these attractive ability of PAE for the removal of anionic and acidic dyes through the chemical synthesis of PAE-cellulose polymer.[12–14] This cationic characteristic can be also used to neutralize the charged surface of cellulose fibers with low enough doses of PAE-resin such that sufficiently more adsorption sites on cellulose surfaces are available for nonionic species, which makes cellulose fibers become a viable alternative for the recovery of nonionic molecules from wastewater.

Poly(1-vinylpyrrolidone)-polystyrene (PVP-PS) is a nonionic diblock copolymer that is readily soluble in water and has been used for several applications due to its ability to provide both hydrophilic and hydrophobic character. It has been used in the production of hydrophilic ultrafiltration membranes through the miscible blending with hydrophobic polyethersulfone membrane.[15–17] It was applied in the development of optical nanosensor and catalysts.[18,19] The driving force behind PVP-PS adsorption to neutralized cellulose fibers is minimization of the entropic penalty that occurs via the solvation of large PS blocks. However, the charged cellulose fiber prevents the adsorption of the PS blocks; instead, the PS blocks would preferentially order themselves on a neutral or hydrophobic surface (such as the air/water interface) so as to minimize contact with water as maximizing their surface energy.

The purpose of this study is to examine the impact of a readily adsorbing polymer, PAE-resin, on the adsorption behavior of a polymer with relatively little affinity for the substrate. We studied how PVP-PS adsorbed onto both bare cellulose fibers and cellulose fibers treated with PAE-resin, and examined the behavior of the PVP-PS polymer on the fibers, in bulk solution, and at the air/water interface in order to fully quantify PAE-resin-treated fibers as a recovery agent.

EXPERIMENTAL

Materials

Two different polymers were used in this study: Poly(1-vinylpyrrolidone)-polystyrene (PVP-PS) was obtained from Aldrich and a polyamide-epichlorohydrin (PAE) resin, Kymene 557H, was obtained from Hercules. PVP-PS provided a UV/Vis spectroscopic peak at 224 nm. Using gel permeation chromatography with chloroform as a carrier, the number-average molecular weight and weight-average molecular weight of PVP-PS were determined to be 660,818 Daltons and 1,378,000 Daltons, respectively. The polydispersity index of PVP-PS is 2.086. PAE-resin used has a molecular weight range of 750,000 to 850,000 Daltons. PAE-resin produced a UV/Vis peak at 313 nm, whereas producing a baseline shift in the range of 200–250 nm. The cellulose fiber used in the experiment was fully bleached hardwood Kraft pulp. Before use, the fiber was air-dried for 72 h in ambient conditions. Deionized water was used as a solvent.

Adsorption and desorption experiment

UV/Vis measurements were done by using a Perkin-Elmer Lambda 900 UV/Vis/NIR Spectrophotometer to study adsorption and desorption phenomena of PVP-PS and PAE-resin in a cellulose fiber solution. The wavelengths of 224 nm and 313 nm were used for UV/Visible measurements for PVP-PS and PAE-resin, respectively. For adsorption experiments, a cellulose fibers solution was prepared by dispersing 0.10 g of air-dried pulp in 100 mL of deionized water using a magnetic, Teflon-coated stir bar. Different volumes of polymer were then added to the solution. For the single-component PVP-PS system, the concentration of PVP-PS ranged from $\times 10^{-6}$ 4.0 $\times 10^{-6}$ g/mL to $\times 10^{-5}$ 4.4 $\times 10^{-5}$ g/mL. These concentration ranges were chosen based on the quality and intensity of the signal they produced during UV/Vis spectroscopy. Any additional addition of PVP-PS would have produced an unreadable signal during spectroscopic measurements. The PVP-PS system was allowed to mix for 10 h and then allowed to settle for 1 h. For the single-component PAE-resin system, the concentration of PAE-resin ranged from $\times 10^{-4}$ 1.3 $\times 10^{-4}$ g/mL to $\times 10^{-3}$ 1.3 $\times 10^{-3}$ g/mL. The PAE-resin system was allowed to equilibrate for 4 h. Equilibrium times for both polymers were found using kinetic UV/Vis adsorption studies; however, it should be noted that the times used are significantly longer than the necessary adsorption time, so as to eliminate the possibility of incomplete adsorption. Once the single-component polymer system was at equilibrium, the solution was filtered so as to minimize the amount of cellulose fines in the supernatant, which were found to cause a baseline shift in the region of 200–300 nm. A 2.7 μm Whatman glass fiber filter was supported in a Pyrex 50 mL vial with an ASTM 40–60 ceramic filter. According the Aldrich, the size of the PVP-PS emulsion droplets is <0.5 μm; thus, the filters used

posed very little risk of trapping the polymer. The
filtrate solution was then placed in a quartz cuvette
and analyzed using a Perkin-Elmer Lambda 900
UV/Vis/NIR Spectrophotometer.

Because of the rather significant baseline shift in
the range of 200–250 nm produced by PAE-resin, the
dual component adsorption system was performed
both simultaneously and sequentially so as to pro-
vide the most accurate adsorption values. Figure 1
shows the calibration curve for UV/Vis measure-
ment of PVP-PS in dual component system at 27°C,
with a constant dosage of 0.013 g PAE-resin. When
compared with a calibration curve for UV/Vis mea-
surement of single-component PVP-PS in water (Fig.
4), the absorbance values for PVP-PS in the dual
component system were reduced. However, the high
degree of linearity seen in Figure 1 demonstrated
that the adsorption values determined for PVP-PS in
the presence of PAE-resin are also accurate.

The sequential adsorption study was done by add-
ing either PVP-PS or PAE-resin to different solutions
of 0.10 g cellulose dispersed in 100 mL deionized
water, and allowed to mix for 10 h. After allowing time
for the fiber to settle, the solution was filtered through
a 200-mesh metal sieve. Fiber was collected and lightly
rinsed with deionized water to allowing any
entrapped polymer solution to drain. The fiber was
then resuspended in a clean beaker in 100 mL of deion-
ized water. The other polymer was then added and
allowed to mix for 10 h. Once the system was equili-
brated, the same filtration procedure was followed.

To study polymer desorption from the fibers, the
adsorption of polymer on the fibers was done first by
using the same methods described earlier. A single
polymer was added to different solutions of 0.10 g cel-
lulose dispersed in 100 mL deionized water, and
allowed to mix for 10 h. After allowing time for the
fiber to settle, the solution was filtered through a
metal sieve of 200 mesh size. Fiber was collected and
lightly rinsed with deionized water to allowing any
entrapped polymer solution to drain. The fiber was
then resuspended in a clean beaker in 100 mL of
deionized water. The fiber was allowed to settle, so as
to minimize cellulose fibers and fines in the samples,
and samples were taken at time intervals to estimate
the rate of desorption. Initial measurements were
taken in order to provide a baseline. Samples were
then taken every one-half hour up until a time of 8 h.
After 1 week, the fiber solution was filtered and the
filtrate was analyzed using UV/Vis spectroscopy to
measure desorbed polymer at a very large timescale.

Calculation of adsorbed polymer

Because we had access to no direct method of poly-
mer adsorption, the amount of polymer adsorbed on
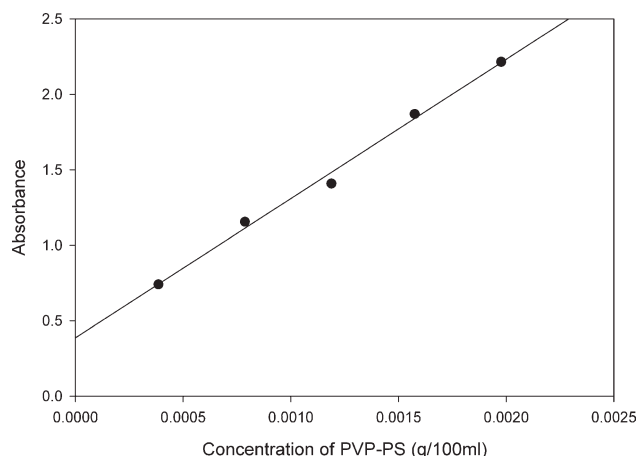to the fibers was calculated via mass balance.

Figure 1 Calibration curve for UV/Vis measurement of
PVP-PS in dual component system at 27°C, with a con-
stant dosage of 0.013 g PAE-resin.

$$m_{\text{fiber}} = m_{\text{in}} - m_{\text{air/water}} - m_{\text{bulk}} \qquad (1)$$

Essentially, any polymer that is not detected in the
bulk or at the air/water interface must be adsorbed
on to the fiber. Determination of the polymer con-
centration in the bulk phase was done by developing
a calibration curve based on the known amounts of
polymer.

PAE-resin, being cationic, displays no surface
active behavior, and thus we can neglect adsorption
of this polymer at the air/water interface. However,
the amphipathic PVP-PS presents a difficulty in two
regards. First, PVP-PS will readily adsorb to the
hydrophobic air interface so as to orient the PS
blocks out of solvent; thus, a method is needed to
estimate the amount of PVP-PS at the interface prior
to saturation. Second, this correction must retroac-
tively be introduced into the bulk calibration curves,
as PVP-PS will partition itself between the bulk and
interface; therefore, the amount of polymer added is
larger than the amount of polymer actually in the
bulk at equilibrium.

Using Gibbs' equation[20] to examine the surface
excess Γ,

$$\Gamma \frac{\text{mol}}{m^2} = -\frac{1}{RT}\frac{\partial \gamma}{\partial \ln c} \qquad (2)$$

where γ is the surface tension in N/m, we can esti-
mate how much polymer exists in a given volume at
the interface compared with the same given volume
in the bulk. The surface tension of PVP-PS solution
was measured by a Fisher Surface Tensionmeter
Model 20. The value $\frac{\partial \gamma}{\partial \ln c}$ was determined using the
linear region of the surface tension plot (Fig. 2). The
surface excess, Γ, was estimated to be on the order
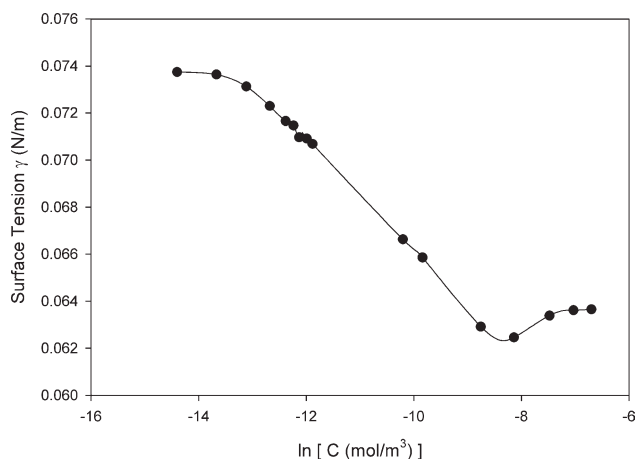of 10^{-3} mol/m² (1 g/m²). Technically, the air/water

Figure 2 Surface tension versus ln [Concentration of PVP-PS (mol/m^3)].

interface does contain more polymer than that bulk; however, the amount of polymer in a given interfacial volume compared with the same volume in the bulk is approximately same. The interfacial area, we are dealing with, is in the order of 10^{-3} m^2, making the total excess mass at the interface around 10^{-3} g. This is lower than the total polymer mass added, which further supports that the composition of the air/water interface is very similar to that of the bulk. Because we are dealing with only a few points before the saturation of the air/water interface, the similarity of the bulk and interface compositions make any corrections via the Gibbs' equation negligible.

The surface tension (Fig. 3) decreases at a constant rate until it reaches a critical point at which an approximately constant surface tension is observed. For our system, this point, the critical micelle concentration, occurs between $\times 10^{-4}$ 2.0 $\times 10^{-4}$ g/mL and $\times 10^{-4}$ 7.0 $\times 10^{-4}$ g/mL. The exact critical micelle concentration (CMC) is obscured by a "dip"
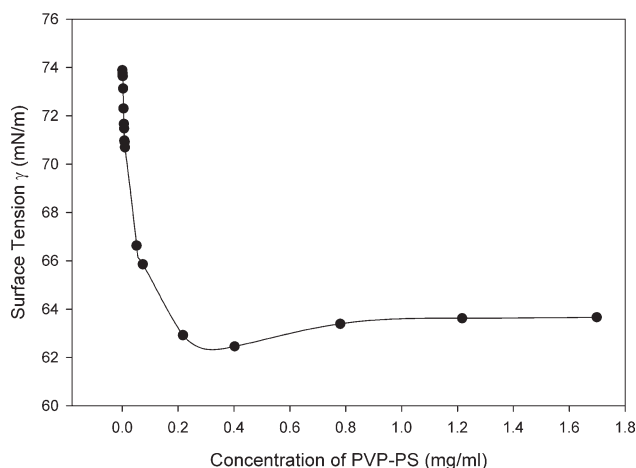
observed at $\times 10^{-4}$ 4.0 $\times 10^{-4}$ g/mL, which is due to impurities in the polymer and would be eliminated if the polymer solution were sufficiently filtered.[21] Regardless of the exact location of the CMC point, it occurs at a very early point on the adsorption isotherm shown below. This point around $\times 10^{-4}$ 4.0 $\times 10^{-4}$ g/mL exists in the plateau region before the increased adsorption regime, which occurs due to apparent multilayering at high concentrations. The air–liquid surface becomes saturated with PVP-PS at low concentrations. Consequently, any additional polymer added must either form micelles in the bulk solution or adsorb to the fiber. A calibration curve for UV/Vis measurement of single-component PVP-PS in water (Fig. 4) shows that micellization does not produce a discontinuity in UV/Vis absorbance signal. Therefore, we can conclude that the significant change in UV/Vis signal at concentrations beyond the CMC is a consequence of PVP-PS adsorbing to the cellulose fiber.

Electrokinetic charge analysis (ECA)

The net charge of the cationic polymer solution containing PAE-resin was measured using an ECA obtained from ChemTrac Systems (Norcross, GA). The solutions used contained 0.1 wt % cellulose fibers. With varying doses of PAE-resin, the resulting effect on the solution was measured. A solution initially containing only water and fiber has a net negative charge, due to anionic molecules from the fiber dispersed in the water. Upon addition of the PEA resin, the net charge of the solution moves toward positive. Adsorption of additional doses of cationic polymer can be detected by decreases in the solution charge. A strong upswing in net positive charge indicates saturation of the adsorbent.
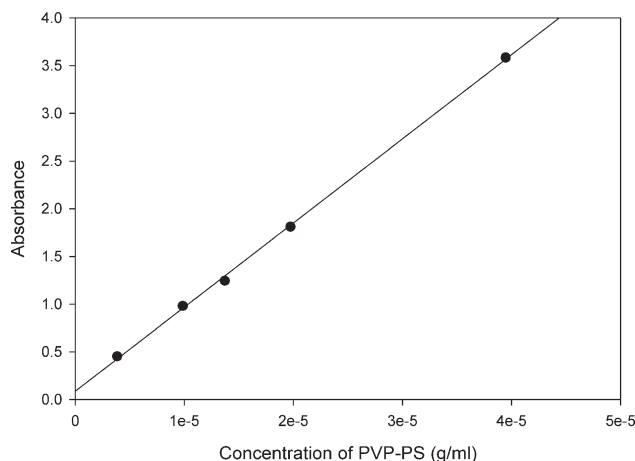

Figure 3 Surface tension versus concentration of PVP-PS.

Figure 4 Calibration curve for UV/Vis measurement of single-component PVP-PS in water.
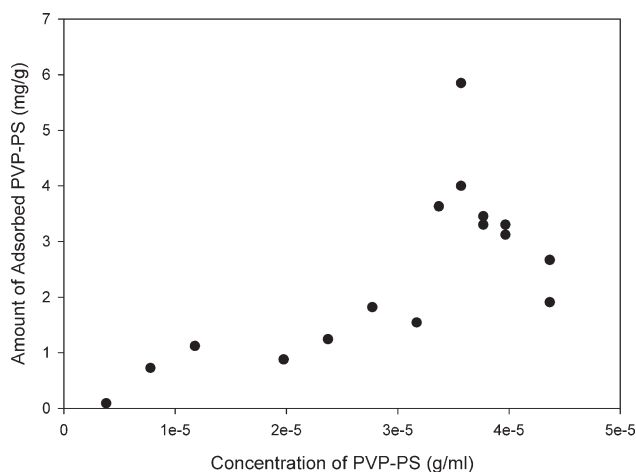
Figure 5 Adsorption isotherm of PVP-PS single component system.

RESULTS AND DISCUSSION

Adsorption of PVP-PS single component system

Figure 5 shows the adsorption isotherm of PVP-PS single component on cellulose fiber at 27°C. The adsorption isotherm shows the distinct curvature of multilayer adsorption on a porous solid.[22] One idiosyncrasy of this isotherm is that, instead of reaching an asymptotic value, the adsorption decreases sharply at high concentrations. To the best of our knowledge, no system in the literature has shown this sort of thermodynamic behavior. However, because of the amphipathic nature of the copolymer, we believe that the rate of micellization may become significantly faster than the rate of adsorption on to the fiber, with the polystyrene blocks favoring self-contact. PVP-PS adsorption was on the order 1 mg/g, ranging from 0.1 mg/g to as much as 4.0 mg/g. The total amount of PVP-PS adsorbed was quite small, ranging from ∼ 3% to 16% of total polymer mass. As expected, PVP-PS does not readily adsorb; however, experiments have shown that the copolymer will adsorb in small amounts, and relatively large amounts under conditions of higher concentration. Initially, we hypothesized that the adsorption mechanism for PVP-PS would involve orientation of the polystyrene coil around neutral segments of the fiber in order to minimize contact with the polar solvent, creating a monolayer. The multilayer adsorption indicated by the isotherm refutes this idea, instead suggesting that the pores in the fibers may play a crucial role in adsorption.

Adsorption of PAE-resin single component system

The adsorption of PAE-resin single component was studied at various concentrations in order to understand how the modification of cellulose fiber surfa-

ces by PAE-resin effects the adsorption environment for PVP-PS, compared with bare fibers. The adsorption isotherm of PAE-resin in Figure 6 noted that PAE-resin also displays adsorption behavior consistent with multilayer adsorption onto a porous solid. The observed multilayer adsorption is reasonable in the case of PAE-resin because of its cationic nature. The PAE-resin has a charge density significantly larger than the fiber; thus, PAE-resin becomes a favorable gathering place for anionic charge such as cellulose fragments and solvated ions. Other PAE-resins in the bulk solution migrate toward the electrostatic potential gradient around the already adsorbed PAE-resin.[23,24] Significantly large amounts of PAE-resin (relative to PVP-PS) were necessary in order to produce a usable UV/Vis signal; as such, more insight is gained by examining the relative adsorption compared to PVP-PS. The total amount of PAE-resin adsorbed is in the range of 7–18%; approximately the same percentage range as PVP-PS. It is surprising that a PAE-resin with such favorable electrostatic interactions with the substrate does not adsorb in greater amounts. However, the adsorption behavior of PAE-resin is indicative of the relatively sparse amount of possible adsorption sites on the fiber compared to its large surface area.

Simultaneous adsorption of PVP-PS/PAE-resin dual component system

PVP-PS and PAE-resin were added both simultaneously and sequentially for two REASONS: To determine if PAE-resin can alter the fiber surface so as to improve adsorption, and, if so, gain an understanding into the adsorption mechanism. PVP-PS and PAE-resin were added simultaneously to determine if the adsorption of PAE-resin acts synergistically to improve PVP-PS adsorption. In UV/Vis measurement of dual component system, there is some
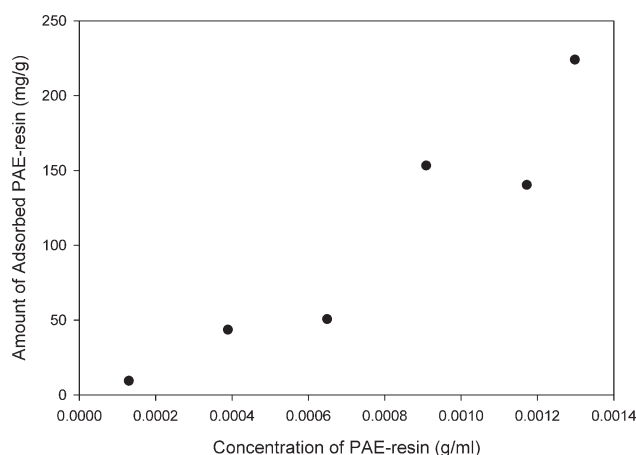

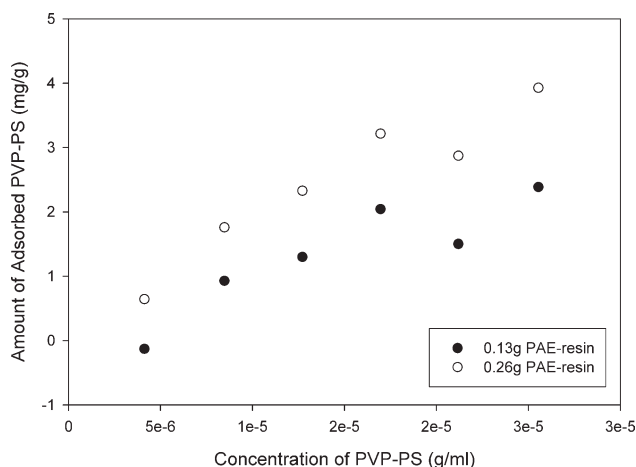**Figure 6** Adsorption isotherm of PAE-resin single component system.

Figure 7 Simultaneous adsorption of PVP-PS/PAE-resin dual component system.
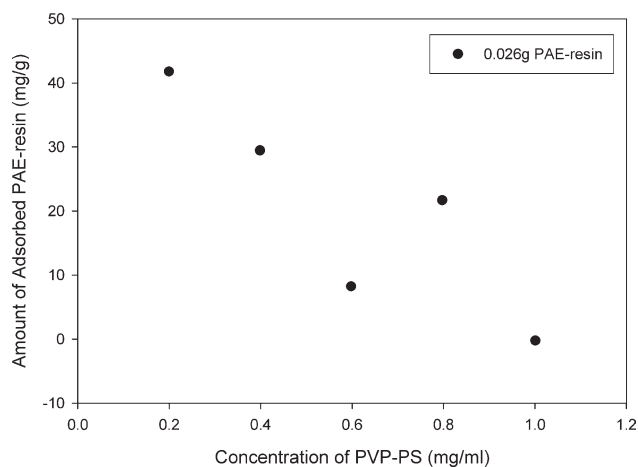

Figure 8 Sequential adsorption: PVP-PS added in the initial adsorption step, followed by a constant amount of PAE-resin after PVP-PS equilibration.

interference at 224 nm due to a baseline shift caused by PAE-resin. However, as noted in the Experimental section (Fig. 1), the high degree of linearity during calibration supports the validity of the data. Allowing the competitive polymer adsorption to equilibrate for $\sim$ 4 h, the fibers showed similar PVP-PS adsorption values as the single-component PVP-PS system. Figure 7 shows that the simultaneous adsorption of dual component system brings a very slight improvement in PVP-PS adsorption, with adsorption ranging from 0.1 to 4.0 mg/g. Although the increase is not significant, it is evident that the presence of PAE-resin does positively influence the adsorption of PVP-PS.

Sequential adsorption: PAE-resin adsorption after PVP-PS attachment on cellulose fiber

The sequential adsorption study was done by adding PVP-PS to the fiber solution first and allowing the adsorption of PAE-resin after equilibration of PVP-PS adsorption. As shown in Figure 8, the amount of PAE-resin adsorbed depends heavily on the presence of PVP-PS on the fiber, despite the fact that PVP-PS is not competing for the same adsorption sites as the cationic PAE-resin. It should also be noted that no PVP-PS was detected in any of these samples, indicating that there was negligible PVP-PS desorption due to the presence of PAE-resin. Although PAE-resin will migrate to the fiber surface more quickly due to favorable electrostatic interactions, it cannot dislodge adsorbed PVP-PS. Furthermore, if a PVP-PS chain is located near a carboxylic acid binding site, PAE-resin will not adsorb to the site due to the entropic penalty incurred by interacting with the PVP-PS chains. Entropy instead favors that the PAE-resin chains remain solvated.

Sequential adsorption: PVP-PS adsorption After PAE-resin attachment on cellulose fiber

When the adsorption sequence is reversed (PAE-resin being added first), further insight is gained into the adsorption mechanism. Figure 9 shows the adsorption isotherm of PVP-PS after the attachment of PAE-resin on cellulose fibers. The most noticeable characteristic of this sequential adsorption is that the adsorption of PVP-PS increases by approximately an order of magnitude, from 0.1–4.0 mg/g to 0.5–35.0 mg/g. The isotherm also appears to have a curvature more similar to traditional Langmuir adsorption; however, because the neutralization of the negatively charged carboxylic acid groups through the PAE-resin adsorption is considered to enable the favorable adsorption of nonionic PVP-PS adsorption, multi-layering may not occur until significantly higher concentrations of PVP-PS is applied than concentration used in this study. Based on UV/Vis
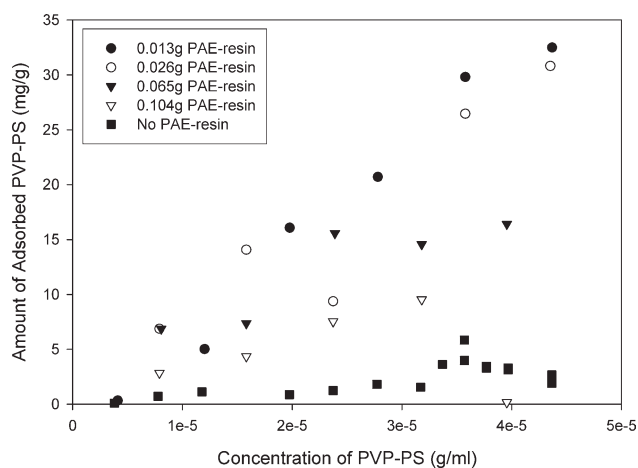

Figure 9 Sequential adsorption of PVP-PS after adding PAE-resin before PVP-PS.
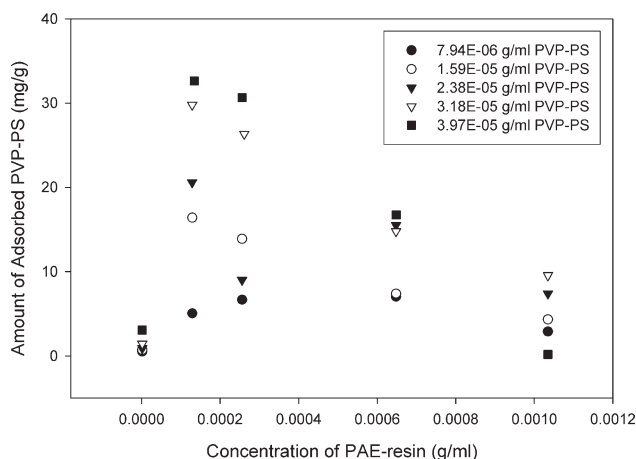
Figure 10 Adsorption of PVP-PS as a function of PAE-resin concentration.

spectroscopy limitations at higher concentrations, we are unable to expound upon this. The adsorptive behavior of PVP-PS as a function of PAE-resin becomes clearer when plotted against PAE-resin concentration (Fig. 10). It is easily seen that a well-defined maximum exists for each set of data, with the peak occurring around $\times 10^{-4}$ 1.3×10^{-4} g/mL PAE-resin dosage. The amount of PVP-PS adsorbed, beyond this point, varies inversely with the amount of PAE-resin added to the fiber. As PAE-resin dosage becomes excessively high, the amount of adsorbed PVP-PS decreases to a level near that of PVP-PS adsorption on to bare fiber. This indicates that there is an optimum point of PAE-resin dosage to achieve the effective adsorption of nonionic polymer such as PVP-PS. We believe this optimum coincides with a net charge on the fiber surface of approximately zero, an environment where the adsorbing PS blocks experience little-to-no electrostatic repulsion from the fiber. Bare cellulose fibers and fibers saturated with PAE-resin are both equally unfavorable for promoting adsorption of non-ionic polymers, as each carries a significant net charge.

Electrokinetic charge analysis (ECA)

By using ECA, we are able to measure the change in the solution charge. When the cationic PAE-resin polymer is added and adsorbed on to the fiber, the net charge of the solution will shift to the positive side. This analysis informs us what PAE-resin addition point corresponds to a nearly neutral fiber, and if this point can be correlated to the maximum adsorption observed in Figures 8–10. Figure 11 shows the change of the fiber solution charge with increase of concentration of PAE-resin added. We can observe that a significant decrease in solution charge occurs between $\times 10^{-4}$ 1.5×10^{-4} and $\times 10^{-4}$ 2.4×10^{-4} g/mL in PAE-resin concentration. The so-

lution charge reaches a constant value around $\times 10^{-4}$ 1.0×10^{-4} g/mL, indicating that the PAE-resin adsorption is roughly constant as a function of its concentration. The noticeable drop in solution charge indicates that the cationic PAE-resin is much more readily adsorbing on the fiber; which is not seen at lower concentrations of PAE-resin. It is important to note that this apparent transition from one steady state to another occurs around the PAE-resin concentration that corresponds to maximum PVP-PS adsorption (Fig. 10). Although we cannot directly measure the fiber charge, we believe that the transition point at $\times 10^{-4}$ 1.5×10^{-4} g/mL represents a change in the adsorptive nature of PAE-resin which manifests itself in blocking PVP-PS adsorption at higher PAE-resin concentrations.

Proposed mechanism of adsorption of nonionic polymer on neutralized cellulose fiber

The mechanism of adsorption must be understood in order to optimize this behavior. Cellulose fiber, although not homogeneous, carries a net negative charge due to the presence of carboxylic acid functional groups on the surface. Consequently, bare cellulose fibers are not suited for the adsorption of non-ionic polymers, due to the substantial entropy penalty incurred in a polar solvent; the amount of fiber surface not influenced by this negative charge, and thus suitable for adsorption, is limited. The limited number of adsorption sites is reflected in the small amount of PVP-PS adsorbed on the bare cellulose fibers, on the order of 0.1 mg PVP-PS/ g fiber. PAE-resin, as a cationic polymer, is capable of adsorbing based on electrostatic attraction to the negatively charged carboxylic acid groups of cellulose fibers. Adsorption of cationic polymer neutralizes the surrounding region of fiber, increasing the effective surface area available for the nonionic
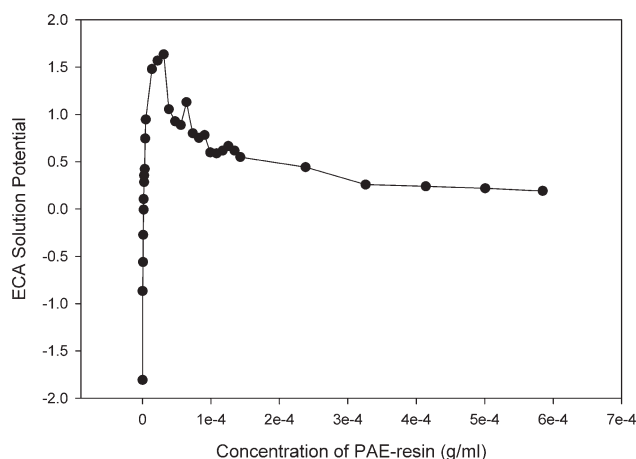

Figure 11 ECA analysis of the fiber solution charge as a function of PAE-resin concentration.

PVP-PS to adsorb. However, as shown by Figure 10, the overall charge of the fiber is crucial to PVP-PS adsorption. Maximal adsorption occurs when the net charge of the fiber is approximately zero; further, PAE-resin adsorption results in a net positive charge for the fiber and a less favorable environment for nonionic polymer adsorption. Thus, there exists a maximum in the amount of PVP-PS adsorbed at the optimum concentration of PAE-resin treatment, where shows a nearly 10-fold increase in PVP-PS adsorption compared with the bare fibers. Beyond this maximum point, the now positively charged fiber surface repulses any nonionic polymer that approaches. Proposing that PAE-resin creates more available and thermodynamically stable adsorption sites for PVP-PS makes intuitive sense when reconciled with data. That notwithstanding, there is one intricacy of the mechanism, which is how the presence of the adsorbed PAE-resin chains, at low concentrations, does not provide steric inhibition to PVP-PS adsorption. When PAE-resin adsorbs to a carboxylic acid group, the local negative charge is neutralized; however, PVP-PS adsorption onto these neutral sites is dependent on the configuration of the PAE-resin chain following adsorption. If the PAE-resin chain adsorbs only at one location, the unattached chain segments will sweep out a considerable volume in the solution (we assume that because PAE-resin is cationic, water is at least a θ-solvent at this temperature). This then introduces the possibility of anionic molecules aggregating around the remaining cationic charge, creating layers of molecules with a charge gradient. The presence of these additional molecules would provide significant resistance to the diffusion of PVP-PS near the fiber surface and inhibit adsorption. However, if the PAE-resin chain adsorbs at more than one point on the fiber surface by bridging[21,25] or in a loop or train configuration, the volume occupied by the unattached chain segments becomes considerably smaller and thus the surface area affected by the gathering of charged moieties decreases. We believe that both adsorption scenarios occur and are concentration dependent. At very low PAE-resin concentrations, bridging of adsorbed chains is more apt to occur because the probability of a free polymer chain finding an adsorption site on the fiber is much lower, simply because there are significantly less chains in the solution. Any chain that is already adsorbed has access to binding sites on its own fiber and neighboring fiber; given sufficient time, the chain should encounter these sites. At the other end of the spectrum, when the PAE-resin concentration is very high, the probability of a free chain finding an adsorption site is much higher; therefore, the likelihood of a chain being adsorbed at only one location is much greater than at low concentrations. We
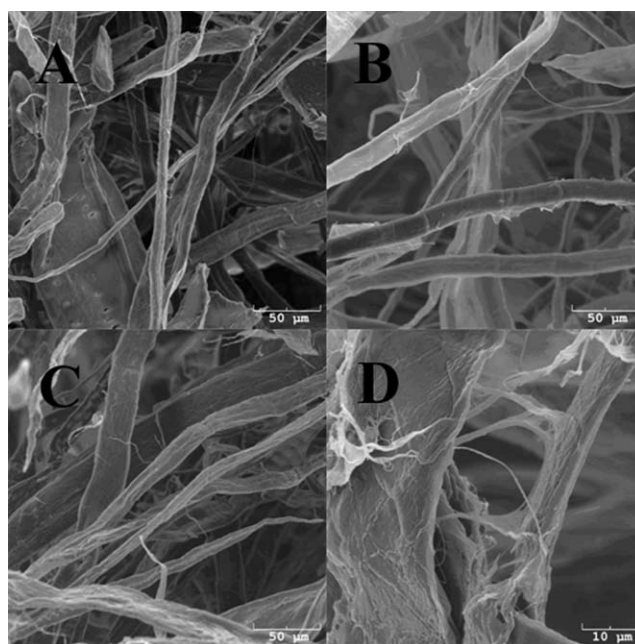

Figure 12 Scanning electron microscopy analysis: (A) Bare kraft cellulose fibers at ×400 magnification, (B) PVP-PS adsorbed on to kraft cellulose fibers at ×400 magnification, (C) PAE-resin 557H adsorbed on to kraft cellulose fibers at ×400 magnification, (D) PVP-PS + PAE-resin 557H adsorbed on to kraft cellulose fibers at ×1700 magnification.

believe this difference in adsorptive behavior to be partially responsible for the severe drop-off in PVP-PS adsorption at high PAE-resin concentrations.

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) images (Fig. 12) allow us to view the fiber surface at high resolution and qualitatively compare fibers from different adsorption systems. SEM images do not show any observable difference among untreated, PVP-PS treated, and PAE-resin treated fibers and cannot provide the concrete confirmation of the adsorption of a specific polymer molecule. It was shown that the bare fiber samples have more visible pores with larger diameters than any of the other samples. This also indicates that the PVP-PS chains prefer to diffuse into the fiber pores in order to adsorb.

Desorption

By measuring the desorption of PVP-PS in both the single and dual component systems, we can verify the thermodynamic stability of the adsorption of PVP-PS and gain the further understanding about the reversibility of adsorption mechanism. Fibers showed practically no desorption of PVP-PS during samples taken up to 8 h. Although PVP-PS will not readily adsorb on the fibers, it will not readily

desorb either. It should be noted that desorption did occur, but only under conditions where the maximum chemical potential existed between the fiber surface and the solution with significant amount of time required for this to occur ($\sim$ 1 week) and agitated mixing. The extreme conditions required for desorption tell us that adsorbed PVP-PS is thermodynamically stable, such that even a large chemical potential gradient is insufficient to induce a large degree of mass transfer. Although PVP-PS adsorption occurs in very small amounts, the sites at which it adsorbs must allow for an favorable thermodynamic consideration such the large chemical potential gradient when the fibers are placed in pure water is unable to cause desorption. On the basis of preliminary kinetic studies we have done,[26] and noting the long equilibration time in conjunction with apparent irreversible desorption, we believe that the adsorption mechanism for PVP-PS on untreated fibers requires that polymer chain diffuse into pores. A situation where the polymer has diffused into the fiber presents an environment that is not only thermodynamically favorable (sufficiently larger neutral surface area than available on the outside of the fiber) but also introduces the possible of chains becomes kinetically trapped and entangled. Vitrification of the PS block has been observed in styrenic block copolymers, leading to "kinetically trapped nonequilibrium structures."[27] Furthermore, the decreased visibility of fiber pores shown in the SEM images (Fig. 12) warrants further investigation into this mechanism. Consequently, we believe this is further evidence that PVP-PS is adsorbing into fiber pores. The large amount of surface area available to exclude the PS blocks from water, in conjunction with the possibility of chain entanglements, presents an ideal environment for PVP-PS.

Thermodynamics of PVP-PS

The adsorption mechanism for PVP-PS onto cellulose fiber is an attempt to minimize the significant local entropy loss caused by solvation of a large hydrocarbon by water.[28] In the absence of a substrate, this occurs via adsorption of the PS chains at the air/water interface and micelle formation. Adsorption to the cellulose fibers is analogous to micelle formation, with the PS block of the copolymer using the neutral areas of the fiber as a nucleation point. The hydrophilic PVP block can then layer on top of the adsorbed PS block, essentially removing it from the solvent. The low adsorption value for PVP-PS in a single component system ($q^* = 10^{-3}$ g/g) is a consequence of the copolymer design. On average, the polymer chains are 64% PS by weight. Applying this to the number average MW, there are approximately twice as many monomer units in the PS

block as the PVP block, 4000–2100, respectively. For the majority of copolymer chains in the system, there is a paucity of PVP units needed to successfully encase the adsorbed PS block. Only chains that are capable of minimizing exposure of the adsorbed PS blocks could remain on the fiber. This again raises the question of whether the PVP-PS chains must diffuse into pores of the fiber in order to adsorb.

We can gain insight into the behavior of PVP-PS by estimating the free energy gained by forming micelles. Using the equation[28]

$$\Delta_{mic}G^0 = RT \ln(CMC) \qquad (3)$$

where CMC is the critical micelle concentration in mol/dm^3, the value of $\Delta_{mic}G^0$ is given to be -20.3 kJ/mol. As a comparison, the free energy gained through micellization of Pluronic block copolymers (such as PEO-b-PBO-b-PEO) ranges from -24.5 to -28.8 kJ/mol. Thus, we can conclude that the driving force for any adsorption is entropy-driven.

CONCLUSIONS

In this study, we have successfully that small doses of cationic PAE-resin polymer can improve the recovery of the nonionic copolymer PVP-PS by modifying the surface charge so as to produce an order of magnitude increase in adsorption. Consequently, cellulose fibers show tremendous potential as an inexpensive and biodegradable tool for the recovery of both ionic and nonionic species in wastewater streams. We have also shown the mechanism for improved PVP-PS adsorption on to PAE-resin-treated fibers is neutralization of the carboxylic acid groups on the fiber surface such that the net charge of the fiber approaches zero. Any additional PAE-resin adsorption beyond this region introduces steric and electrostatic inhibition to PVP-PS adsorption, which results in significantly less PVP-PS adsorption at high PAE-resin concentrations. To further understand the capabilities of the fibers, it is necessary to explore the adsorption of other nonionic copolymer species to observe the role that specific polymer functional groups play in the adsorption process.

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