

Water-Soluble/Dispersible Cationic Pressure-Sensitive Adhesives. I. Adhesives from Solution Polymerization

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ABSTRACT: Pressure-sensitive adhesives (PSAs) have long been a problem as sticky contaminants for paper recycling mills. The main problem associated with such stickies is that the PSAs in the waste papers deposit on the felts, press rolls, and drying cylinders of paper machines, and this creates problems with paper formation, reducing the paper quality and paper machine runnability. The annual cost of stickies to the U.S. paper industry is estimated to be about \$600,000,000–650,000,000. To solve this problem, a series of cationic water-soluble/dispersible PSAs have been synthesized by the free-radical solution polymerization of butyl acrylate and [3-(methacryloylamino)propyl]trimethylammonium chloride in ethanol. The PSA end-use properties, repulpability

in paper recycling, and the effects on the properties of recycled paper products have been studied. The cationic PSAs can be dissolved or dispersed in water if the cationic charge density in the PSA backbone is controlled, and so they do not deposit as stickies during recycling and papermaking processes. Because the PSAs are cationically charged, they can easily be removed from the papermaking system by adsorption onto the negatively charged fibers and fine surfaces. Furthermore, the adsorbed colloidal or dissolved PSAs have little effect on the final paper properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1624–1630, 2003

Key words: adhesives; recycling; solution properties; fibers

INTRODUCTION

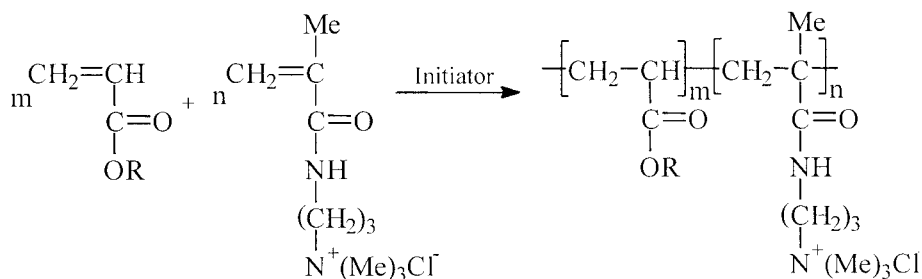
Pressure-sensitive adhesives (PSAs) are widely used for self-adhesive stamps, tapes, labels, and paper coatings. PSAs have long been a problem as sticky contaminants for paper recycling mills.^{1–4} The main problems associated with such stickies include deposition on the felts, press rolls, and drying cylinders, which creates problems with paper formation, reducing the paper quality and paper machine runnability. The annual cost of stickies to the U.S. paper industry is estimated to be about \$600,000,000–650,000,000.^{5,6}

Many researchers have focused on understanding and resolving the problem of stickies in waste-paper recycling and papermaking. Two approaches have been made to solve these problems: sticky control and new adhesive development. The technologies that have been developed or studied for sticky control include: (1) treating machine surfaces with surface-active agents to protect the deposition of sticky particles; (2) using talc, clay, or precipitated calcium carbonate (PCC) to stabilize the sticky particles and protect against their deposition; (3) using detackification agents to reduce the tackiness of stick particles; (4) using dispersion agents such as surfactants or polymers to stabilize stickies; (5) adding chelating agents

to reduce the concentration of some metal ions to reduce the precipitation of stickies; (6) enzymatic treatment; (7) using washing, cleaning, screening, and flotation techniques to remove stickies; and (8) modifying or washing paper-machine forming fabrics and felts to reduce their affinity for stickies. Although problems with stickies can be reduced by one or another of the techniques listed, the techniques that work well in one paper mill may not work for others because of the differences in the adhesives, pulps, and papermaking conditions. To fully solve the problems of stickies for the paper recycling industry, new adhesives that are repulpable and easily removable must be developed. For this reason, the development of repulpable PSAs is of great interest to the paper industry.^{6–8}

The technologies currently being evaluated by adhesive manufacturers in an effort to make repulpable adhesives can be divided into two categories: recoverable (or screenable) and dispersible/soluble adhesives.⁹ Two different approaches have been employed in recoverable adhesive development: (1) adhesives that have a high glass-transition or melting temperature and will not soften and break down under repulping conditions and (2) adhesives that have a density significantly lower or higher than that of water and fibers. Unfortunately, polymers with high glass-transition or melting temperatures can only be used for hot melts but not for PSAs. Although some high- or low-density polymers have been used for PSA, only a limited number of polymers can meet this unique requirement. In contrast to recoverable PSAs, water-

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Scheme 1 Polymer synthesis.

soluble/dispersible PSAs have been developed.¹⁰⁻¹⁴ These adhesives include acrylic or acrylate copolymers modified with hydrophilic components such as starch, sugar, carboxylic acids, polyglycols, and maleic acid. Although these water-soluble adhesives will not form stickies during recycling, the accumulation of water-soluble adhesives in paper process water is still an unsolved problem. Therefore, a water-soluble PSA that can easily be removed from process water is needed. In this paper, the development of cationically charged water-soluble/dispersible PSA, which can easily adsorb onto fiber and fine surfaces in a colloid or molecule form and be removed from the papermaking process water, is reported and discussed.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) Butyl acrylate (BA; >99%) and ethylene glycol dimethylacrylate (EGDM) were washed with a 5% sodium hydroxide aqueous solution three times and then with deionized water three times for the removal of inhibitors. [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC; 50 wt % in water) was extracted with ethyl ether five times for the removal of inhibitors, and the residual ethyl ether was removed by a rotary evaporator at room temperature under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN), methanol, and ethanol were used as received. The solvents were all high-performance-liquid-chromatography grades.

Polymer synthesis and characterization

Copolymers of BA and MAPTAC were synthesized by free-radical polymerization in ethanol. The chemical reaction is shown in Scheme 1.

Because acrylates are water-insoluble and the cationic monomer is water-soluble, they are difficult to react in water to form uniform random copolymers. Therefore, a polar solvent that can dissolve both monomers and copolymers should be used for preparing this type of copolymer. The effects of solvents on

the reaction kinetics and polymer structures were reported previously.¹⁵ For the polymers used in this study, ethanol was used as a solvent. A typical example for the PSA synthesis is as follows. A 250-mL, three-necked, round flask equipped with a thermometer, a nitrogen inlet, a condenser, and a mechanical stirrer was charged with 25.6 g of BA (0.20 mol), 7.8 g of MAPTAC (0.035 mol), and 42.9 g of ethanol. The mixture was purged with nitrogen for 30 min and heated to 65°C. After the temperature reached equilibrium, 0.193 g of AIBN (1.18 mmol) in about 5 mL of ethanol was injected. The mixture was kept at 65°C for 4 h. The solution was used as a PSA without further purification. The solubility of the PSA in water was measured according to the following procedure. The dried PSA (0.4 g) was added to 100 mL of water at pH 8.0. The mixture was stirred at 50°C for half an hour. The solubility was identified from the visual appearance of the solution. With the water-dispersible sample, the particle size of the dispersed particle was measured with a Malvern Zetasizer (Worcestershire, UK).

PSA properties

The 180° peel strength was measured according to Pressure Sensitive Tape Council standard method PSTC-1 (1994). The shear strength was measured according to standard method PSTC-7 (1994).

Repulpability of the PSA

A 50- μm thickness of the PSA was applied on a silicon release liner, dried at 90°C for 3 min, and then transferred to commercial copy paper. The final PSA content was adjusted to 1% of the copy paper. The paper was torn into small pieces and soaked in water (pH 8.0) with a 1% consistency for 16 h. The mixture was heated to 50°C and disintegrated for 20,000 revolutions in a standard disintegrator with the propeller operating at 3000 rpm in the stock. A hand sheet was made according to Technical Association of Pulp and Paper Industry (TAPPI) standard method T 261 and dyed. The sticky particles on the hand sheet were

TABLE I
Characteristics of PSA Copolymers

Sample	Cationic unit fraction (mol %)		EGDM (mol %)	$M_w/10^5$ (g/mol)	M_w/M_n	Solubility (H ₂ O, 50°C)
	In feed	In polymer				
PSA1	5.0	5.7	0	2.3	1.5	No
PSA2	8.0	8.6	0	2.0	1.3	Swollen
PSA3	10.0	10.6	0	1.8	1.3	< 1.5 μm
PSA4	15.0	15.2	0	1.4	1.3	Soluble
PSA5	20.0	20.9	0	2.3	1.6	Soluble
PSA6	15.0	17.6	0.2	8.6	1.6	Soluble
PSA7	15.0	17.3	0.5	13	2.0	Soluble
PSA8	15.0	—	0.8	Gel formed in polymerization		

M_n = number-average molecular weight.

identified by image analysis (Microteck Scan Maker 4 scanner with Image Pro-Plus 4.0 software, Carson, CA).

PSA adsorption on wood fibers and accumulation in process water

The adsorption isotherm of the cationic PSA on wood fibers was measured as follows. Copy paper with various PSA contents (0.5–8% based on oven-dried paper) was repulped at pH 8. After standing for 4 h, the pulp stock was centrifuged at 3000 rpm for half an hour. The content of PSA in the supernatant clear solution was measured by colloidal titration or UV spectroscopy.

For the determination of the PSA accumulation in the papermaking process water, a pulp stock of 1% consistency with 0.25% PSA based on oven-dried paper was made. After standing for 1 h, the stock was filtered through a 200-mesh screen; 50 mL of the filtrate was collected for analysis, and the rest of the filtrate was used for the next pulping experiment. In every step, about 20% fresh water was needed to compensate for the water lost in the last step. The pH was kept at 8. Water from another pulping process without the PSA was collected as a reference. Then, the PSA content in the filtrate was measured.

Effect of the PSA on the paper properties

Hand-sheet paper was made according to TAPPI method T 261. The tensile strength of the paper was measured with an Instron 1122 (Canton, MA). The sizing effect (paper hydrophobicity) was evaluated by the Hercules sizing test (HST) method. For the sizing test, the hand-sheet paper was dried on a drum drier at 115–120°C for 4 min. The HST test was conducted with a 1% formic acid ink solution (80% reflectance).

RESULTS AND DISCUSSION

PSA polymer characteristics

It has been demonstrated that the glass-transition temperature, molecular weight and molecular weight distribution, and surface energy are important properties for PSAs.^{16,17} A commercial solvent-based acrylic PSA normally has a weight-average molecular weight (M_w) of 100,000,¹⁸ and an M_w distribution between 1.4 and 1.8. Sometimes, a small amount of a crosslinker is introduced to the PSA polymer to increase the polymer internal strength, and so the M_w value of the polymer will be significantly increased.

Table I shows the characteristics of the cationic PSA polymers prepared in this study. The molar fractions of BA and the cationic comonomer in the PSA copolymer are all close to the feed ratios. The molecular weight of the polymer is slightly higher than that of the commercial PSA. In the polymerization, ethanol as the solvent also acts as a chain-transfer agent. No other transfer agent has been added to optimize the molecular weight in this study. Introducing a small

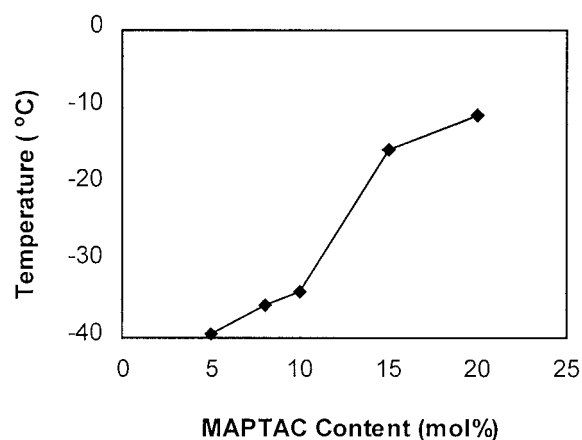


Figure 1 Glass-transition temperature of the BA/MAPTAC copolymer as a function of the MAPTAC content in the copolymer.

TABLE II
Adhesive Properties of Cationic PSAs
and Commercial PSAs

Sample	180° peel adhesion (10-min Dwell time; PSTC-1)		Shear strength (PTSC-7)	
	g in. ⁻¹	Failure type	h	Failure type
PSA1	653.7	C	0.2	C
PSA2	586.3	C	0.3	C
PSA3	532.0	C	0.4	C
PSA4	155.6	A	1.0	A
PSA5	70.8	A	2.8	A
PSA6	249.0	A	5.7	A
PSA7	110.4	A	>40	No failure
Com1 ^a	266.0	C	3.9	C
Com2 ^b	509.4	A	>40	No failure
Com3 ^c	7.9	A	Instant failure	A
Com4 ^d	939.6	A	3.7	A

A = adhesion failure; C = cohesion failure.

^a Polyacrylic-based PSA from Company 1.

^b Polyacrylic-based PSA from Company 2.

^c Peelable note.

^d Nonpeelable general postal label.

amount of the crosslinker EGDM significantly increases the molecular weight of the copolymer, but gelation occurs when the crosslinker content is high. The molecular weight distribution of the cationic PSAs is in the optimized range. The glass-transition temperatures of the PSA samples are shown in Figure 1. It is obvious that with increased cationic content, the glass-transition temperature of the copolymer increases. With a cationic content of less than 20%, the glass-transition temperature of the PSA polymer is in a reasonable range for normal PSA applications. Because the polymerization kinetics and polymer characterization of these cationic polymers have been reported previously, only the adhesive properties and recycling ability of these new cationic PSAs will be the focus of this article.

As indicated before, this study involved synthesizing cationically charged and water-soluble/dispersible PSA to solve the problem of stickies in paper recycling. Therefore, the solubility or dispersibility of these cationic PSAs must be studied. Table I shows the relationship between the cationic content and PSA solubility in water at pH 8. A PSA with a cationic monomer content of about 5% is not soluble in water. With increased cationic monomer in the polymer, the polymer becomes water-dispersible, forming micro-particles.¹⁹ The PSA polymer becomes water-soluble when the cationic monomer content is greater than or equal to 15%. The cationic monomer MAPTAC is hydrophilic, whereas BA is hydrophobic. When the cationic monomer content in the polymer increases, the polymer becomes more hydrophilic. Therefore, the water solubility increases.

Adhesive properties

The function of PSAs is to ensure instantaneous adhesion upon the application of light pressure. PSAs must possess viscous properties to flow and to be able to dissipate energy during the adhesive bonding process and must also be elastic and be able to store bond rupture energy to provide strong bonding. The end-use properties, which are essential in characterizing the nature of PSAs, include tack, peel adhesion, and shear strength. Tack measures an adhesive's ability to adhere quickly, peel adhesion measures its ability to resist removal through peeling, and shear strength measures its ability to hold in position when a shear force is applied. These PSA end-use properties depend on the nature and composition of the PSA polymer. The adhesive properties of cationic PSAs on polyester films have been measured in this study and compared with those of commercial products. The results are shown in Table II. The different commercial products show significantly different adhesive properties. The peel and shear strengths vary widely, depending on the PSA applications. Generally, peelable PSAs have weak shear and peel strengths, whereas nonpeelable PSAs have very strong peel strengths. Cationic PSAs have different PSA properties depending on the PSA composition.

Figure 2 shows the effect of the cationic monomer (MAPTAC) on the PSA properties. When the cationic monomer content increases, the 180° peel strength decreases, and the shear strength generally increases. Peel adhesion is the force required to remove a PSA-coated film from a specific test surface under standard conditions (a specific angle and rate). The measurement of peel adhesion involves a bonding step and a debonding or peeling step. The efficiency of the bonding process is related to an adhesive's ability to exhibit viscous flow. To achieve peel adhesion, the bonding stage requires some dwell time. The debonding pro-

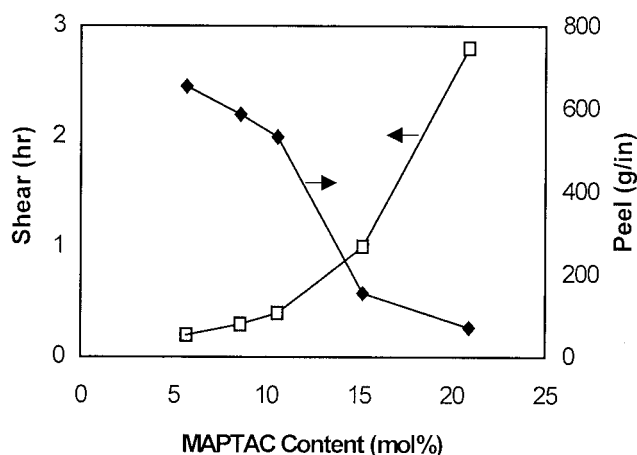


Figure 2 Effect of the MAPTAC content in the PSA copolymer on the PSA properties.

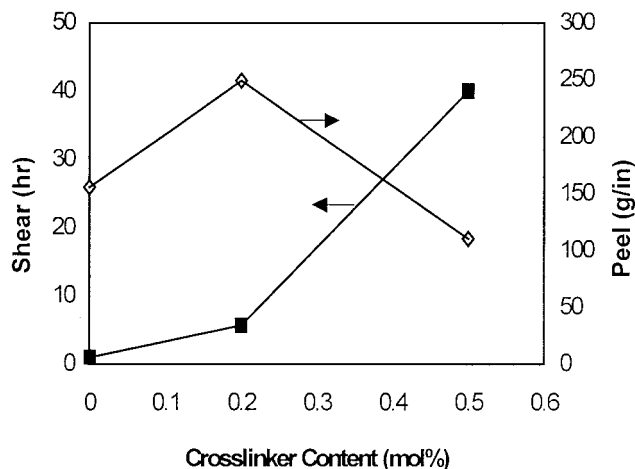


Figure 3 Effect of the crosslinker content in the PSA copolymer on the PSA properties (PSA contains 15 mol % MAP-TAC).

cess involves a rapid deformation of the adhesive mass. Therefore, the higher the peel strength is, the higher the PSA's ability is to resist bond deformation at high strain rates. The peel strength gives a measure of adhesive or cohesive strength, depending on the mode of failure.²⁰ The shear resistance is measured as a force to pull a PSA material parallel to the surface to which it is affixed with a definite pressure.²¹ It measures the cohesion strength of a PSA. For a PSA with a low cationic monomer content, the glass-transition temperature is low; therefore, it is more viscous and more easily forms a continuous layer on a substrate for strong bonding. However, when the adhesive has a higher viscous flow ability, the cohesive bonding between adhesive molecules will be weaker. PSA1–PSA3 all have cohesion failures in peel and shear. The results indicate that they have stronger bonding strength on substrates than cohesion strength. With increased cationic monomer content, the cohesion strength increases, but the molecule flow ability decreases. Therefore, the shear strength increases, and the peel strength decreases.

Introducing a small amount of a crosslinker into a polymer can increase the polymer cohesion strength. Figure 3 shows the effect of a crosslinker on the PSA properties. With increased crosslinker content, the shear strength increases. The effect of the crosslinker on the peel strength is not significant. Too much crosslinker can significantly limit polymer diffusion on a substrate and, therefore, may reduce the peel strength.

Summarizing the data in Figures 1–3 and Tables I and II, we can conclude that cationically charged PSAs with different peel and shear strengths can be prepared according to the requirements of the end-use properties. By the introduction of cationic components into the polyacrylate backbone, the PSAs can be water-soluble or dispersible, depending on the cationic comonomer content, molecular weight, and crosslinking degree. High humidity may affect the adhesive properties of these cationic water-soluble/dispersible PSAs as they affect anionic water-soluble PSAs.^{11,14}

PSA repulpability

Figure 4 shows the repulpability of the cationic PSAs during the paper recycling process. The dark spots indicate the PSA stickies. PSAs form large sticky particles when the cationic content is low. When the cationic content is high, no sticky particles are observed. The repulpability of PSA is obviously dependent on the PSA water solubility/dispersibility. PSA1 is not water-soluble. PSA3 could disperse in water and form colloidal particles. PSA4–PSA7 are water-soluble. Although PSA2 as a bulky polymer can only swell in water, when it forms a very thin PSA layer (<25 μm) on paper and then is recycled, the shear at repulping breaks the PSA film into invisible microparticles.

PSA adsorption isotherm on wood fibers

When a cationic PSA on recycled paper dissolves or disperses during repulping, it becomes cationically

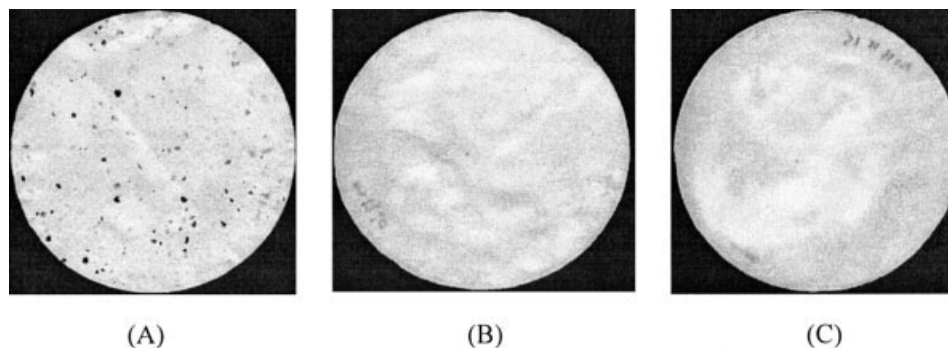


Figure 4 Repulpability of cationic PSAs with cationic monomer contents of (A) 5.7, (B) 10.6, and (C) 15.2 mol %.

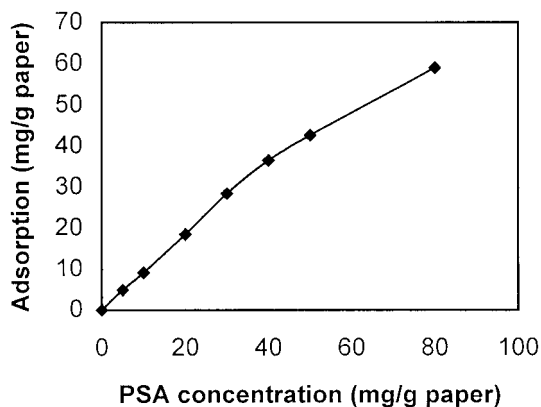


Figure 5 Adsorption isotherms of PSA4 on the wood fiber of office copy paper.

charged molecules or microparticles. Because fibers are negatively charged, cationically charged materials will be able to adsorb on fibers. The adsorption capability is dependent on both the cationic PSA and the fiber. Figure 5 shows the adsorption isotherm of PSA4 on the pulp of copy paper. When the total amount of cationic PSA in the copy paper is less than 4%, more than 90% of the PSA will be adsorbed on the fiber. The adsorption equilibrium cannot be reached even when the PSA content in the copy paper reaches 8%. In the paper recycling plant, recycled paper normally contains more anionic materials than pure copy paper. Therefore, more cationic PSA should be able to be removed from the papermaking system.

Accumulation of PSA in pulping water

Because of environmental concerns and the desire to save costs, papermaking mills are totally or significantly closing the water loops to reduce wastewater discharge. When water loops are closed and the papermaking process water is reused, the contaminants in the water increase. Currently, commercial water-soluble/dispersible PSAs are all negatively charged. They cannot adsorb on negatively charged fibers and be removed from the water system. Therefore, they will accumulate in the papermaking water system. When there are sudden changes in the temperature, pH, or electrolytes in the water, soluble PSAs at high concentrations may precipitate and cause problems with stickies. For these problems to be avoided, the process water would have to be treated frequently to remove the PSAs.

It is known that cationic PSAs can adsorb on fibers. However, it is worthwhile to determine if cationic water-soluble PSAs will accumulate in a closed papermaking system. The accumulation of cationic PSAs in a closed pulping water system has been studied, and the results are shown in Figure 6. In the study, copy paper with 0.25% of cationic PSA4 was repulped at a

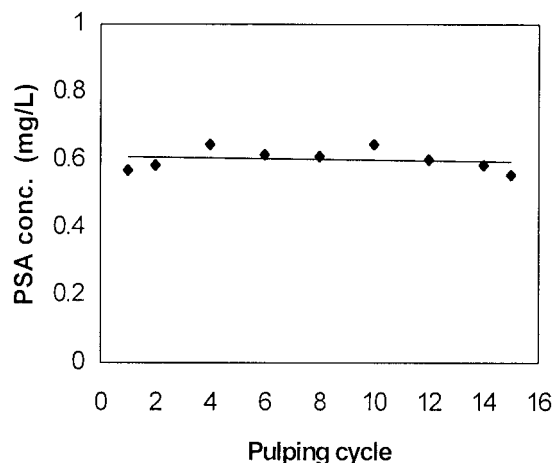


Figure 6 Accumulation of PSA4 in the closed pulping water system.

1% consistency. In 15 pulping cycles, the PSA concentration in the pulping water was almost constant at about 0.6 mg/L. The PSA concentration in the pulping water would be 25 mg/L if there were no PSA adsorption on the fibers. This suggests that over 97% of the PSA was adsorbed on the fibers, and the accumulation of the cationic PSA in the pulping water was negligible.

Effect of the PSAs on the paper properties

Cationic PSAs can adsorb on fibers and be removed with the fibers during papermaking. Because the fiber surface would partially be modified by adsorbed cationic PSAs, it is necessary to know if the adsorbed PSAs have any effect on the final paper properties. Figure 7 shows the effects of PSA2, which forms water-dispersible microparticles during repulping, on the paper tensile strength. Figure 8 shows the effect of PSA4, which forms water-soluble molecules, on the paper tensile strength. Neither the water-dispersible

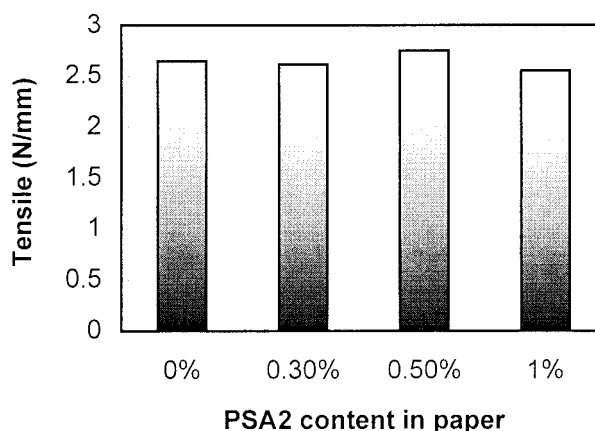


Figure 7 Effect of the PSA2 content on the paper tensile strength.

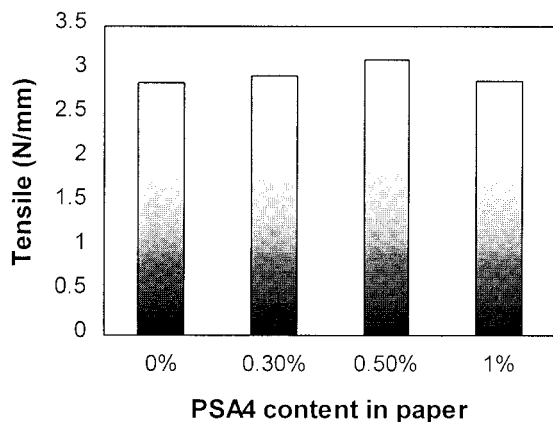


Figure 8 Effect of the PSA4 content on the paper tensile strength.

nor water-soluble PSAs have obvious effects on the paper tensile strength. Because the cationic PSAs contain hydrophobic units, they may affect the hydrophobicity of the paper after adsorbing on the fiber surface. In the paper industry, the effect of a material on the paper hydrophobicity is called the sizing effect. Therefore, the effect of cationic PSAs on paper sizing has been studied. With 1% PSAs in paper, the HST value of the paper increases from 0 s to a few seconds for PSA2 and PSA4. This slight increase in HST should be negligible.

CONCLUSIONS

Cationically charged PSAs with various end-use properties have been developed. These PSAs can be water-dispersible or soluble in paper recycling accord-

ing to the charge densities of the PSAs and will not cause problems with stickies in pulping and papermaking processes. The dispersed/dissolved PSAs can adsorb on negatively charged fibers and be removed from the papermaking system. They will not accumulate in the process water. Adsorbed PSAs on fibers do not have obvious effects on the final paper properties. The results indicate that new cationic PSAs are a possible solution for the problems with stickies in paper recycling.

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