Factors influencing the rate of charge decay

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ABSTRACT

Study of mobility decay at measured levels of cationic polymer overdose showed that the rate increased with increasing temperature and stock consistency but decreased with increasing polymer molecular weight. Decay was faster with p- DADMAC than with DMA-epi polymers. Small changes in decay rates occurred with variations in degree of agitation, salt concentration up to 1000 parts per million NaCl, and bleached chemical pulp type.

Application:

Polymer structure, charge density, molecular weight, and some papermaking process variables influence charge decay.

ADDING CATIONIC POLYMERS TO suspensions of cellulose fibers in water moves the electrokinetic charge—mobility, zeta potential—in the positive direction. With time, the charge drifts or decays in the direction of increasing negativity. It becomes less cationic or more anionic *(1–6)*. This effect results from two distinct behaviors of cationic polymers adsorbed onto fiber surfaces. The first, after initial polymer attachment, is reconformation. Continued counter ion release accompanies this process *(7, 8)*. Some polymer may also attach at less accessible "secondary" surfaces resulting in a partial shielding of cationic charge contribution. The second behavior is the migration and diffusion of polymer chains to less accessible areas including pores and internal surfaces *(1, 5, 8, 9)*.

Reconformation occurs with both synthetic cationic polymers and cationic starches. It usually occurs within approximately 30 min. For any individual polymer or starch, the time required for essentially complete reconformation will vary with the charge density and molecular weight *(5, 6)*.

Migration and diffusion of cationic polymers and starches to secondary and internal surfaces proceeds at a slower rate than reconformation. Polymer migration as indicated by charge decay decreases in rate as the cationic charge density, molecular weight, or both increase *(3, 5)*.

The aim of this current work was to define the effects of polymer structure, charge density, molecular weight, and some papermaking process variables on the rate of charge decay.

EXPERIMENTAL

Pulp preparation and characterization

Commercial dry lap pulps were treated by stirring at 1.0% consistency in the following sequence of steps:

1. 0.1*N* HC1 for 16 h
2. Deionized water for 1 hr
3. 1.0% Na_2CO_3 for 4 h
4. Deionized water for 1 h
5. 1.0% $NaHCO_3$ for 4 h
6. Deionized water for 1 h.

Washed pulps in sodium salt form were further rinsed with deionized water in a Dynamic Drainage Jar at approximately 0.5% consistency and 1000–1100 rpm. This reduced the fines content of each pulp to less than 2.0% by weight. The pulps were oven dried at 105°C. When reslurried in deionized water at 0.4% consistency, the pH was 7.6–7.7.

Table I shows the carboxyl number and cationic demand values for the prepared pulps. Carboxyl numbers are also in weight percentage of poly- diallyl dimethyl ammonium chloride (p-DADMAC) on fiber. The 5.20 carboxyl number therefore equates to 0.84% p-DADMAC or 16.8 lb/ton. Cationic demand titrations were done with p-DADMAC and followed with an electrophoretic mobility analyzer. The demands are expressed both in percentage p-DADMAC on fiber and meq/100 g.

Comparison of carboxyl numbers and cationic demands reveals that only 1–2% of the total carboxyl contents are immediately available for titration with p- DADMAC.

Materials

Samples of dimethyl amine-epichlorohydrin (DMA-epi), p-DADMAC, and diallyl dimethyl ammonium chloride-acrylamide copolymer (DADMAC-AMD) and the molecular weight information came from CPS Chemical Co., Inc., West Memphis, AR. Polyamino polyamide-epichlorohydrin (PAE-epi) wet-strength resin was from Georgia-Pacific Paper Chemicals, Atlanta, GA.

Procedures

Stock solutions of cationic polymers were prepared at 0.05% solids and adjusted to pH 7.5–7.8. Activity as meq cationic charge/mL was determined by titration with potassium poly(vinyl sulfate) to the *o*-toluidine blue color change endpoint.

Charge decay procedure

Dried pulp was gently slurried in deionized water in a blender at reduced speed. The slurry was transferred to a 1000 mL beaker and dilute NaCl and $NaHCO_3$ added. Deionized water was added to a total of 1000 g less the weight of polymer solution to

Pulp	Carboxyl number, meq/100g	Carboxyl number, as % p-DADMAC	Cationic demand, % p-DADMAC	Cationic demand, meq/100g	CD/COOH no., %	Mobility, u/s/volt/cm
Hardwood kraft (mixed So.hwd)	5.20	0.840	0.0102	0.0629	1.21	-2.01
Softwood kraft (So. pine)	2.73	0.443	0.0074	0.0489	1.79	-1.64
Softwood sulfite (west coast)	2.71	0.439	0.0045	0.0274	1.01	-1.80

Mobility measured in 50 ppm NaC1, 10 ppm NaHCO3.
CD = cationic demand

I. Properties of washed pulps

Pulp:	**Bleached hardwood kraft**
Consistency:	**0.4%**
Polymer:	**Low molecular weight (20K) DMA-epi**
Polymer dose:	**10% on carboxyl number**
Sodium chloride:	**50 ppm**
Sodium bicarbonate:	**10 ppm**
Temperature:	**22°C**
Agitation:	**Rapid magnetic mixing**
pH:	**7.6–7.8**

II. Experimental conditions

be added. The mixture was stirred magnetically. After 20–30 min, polymer was added. Samples were withdrawn at intervals and screened through a 100-mesh screen. The mobility of the fines was measured using a commercial electrophoretic mobility analyzer. **Table II** shows the conditions used throughout this work unless otherwise specified.

RESULTS AND DISCUSSION

Before discussing the results, developing an easily visualized concept of polymer migration is necessary. One need only consider that electrostatic bonding of a cationic polymer to anionic cellulose is an equilibrium process. This means that any single bonding site on the polymer spends certain time in a "bonded" state and the remaining time unbonded. Each cationic group is then continually adsorbing, desorbing, readsorbing, etc. The key to polymer migration is the readsorption at a different fiber site from which desorption occurred. This behavior is analogous to a walking caterpillar whose location changes although most feet may be in fixed contact with the ground at a single time. With polymers of sufficient molecular weight, there are at any single time sufficient bonded sites to prevent the molecule from desorbing totally and reentering solution.

Using this model, one can visualize cationic polymers migrating preferentially to surfaces of lower potential—to less cationic or to more anionic surfaces. These alternate surfaces can be on other fibers or on fines or pigment particles. In that case, polymer transfer occurs presumably until reaching equilibrium. Examples from recent literature are the transfer of cationic polyacrylamide from fibers and fines to polystyrene latex *(10)* and of alum from fibers to clay *(11)*. In the extreme degree, high concentrations of polyvalent metal ions can cause the desorption of significant amounts of cationic polymer *(12)*.

In the current work, the alternate surfaces are "secondary" or internal. This process results in reduced influence of polymer on measured mobility with time.

Mobility was by necessity measured on the fines. The mobility of the "whole furnish" decays more rapidly than the mobility of the fines alone *(3)*. As fiber charge diminishes, the system will seek equilibrium by a transfer of polymer from fines to fiber *(13)*. The fines present at very low levels therefore act as a convenient mobility indicator. They are only a minor "reservoir" of cationic polymer. In calculating rates of decay, we assumed that the charge or mobility of the fibers and fines are identical at or very near the isoelectric point.

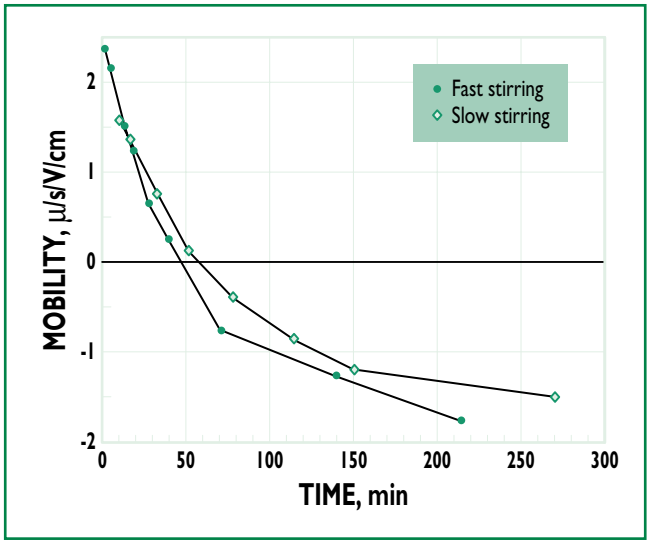
Agitation rate

DMA-epi of 20K molecular weight was added to bleached hardwood kraft at a level equivalent to 10% on the carboxyl number. Two rates of magnetic stirring were evaluated—slow (slight vortex) and fast (full vortex). **Figure 1** shows that mobility decayed from initially highly cationic to zero (isoelectric) more rapidly with the higher rate of stirring. Strazdins reported a similar result with polyethylene imine and attributed it to increased transient exposure of additional fiber surface at the higher agitation rate *(1)*. This effect was modest compared with those subsequently observed with other variables.

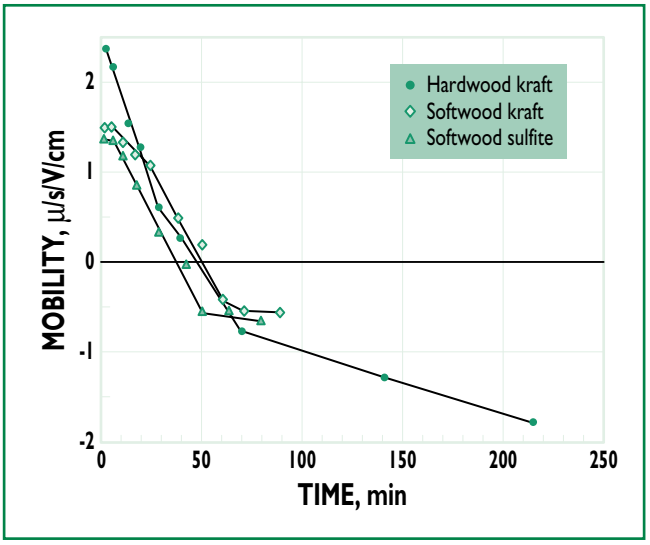
All subsequent work used fast stirring since it was more reproducible mechanically and would be more suitable over a range of fiber consistencies.

Effect of pulp type

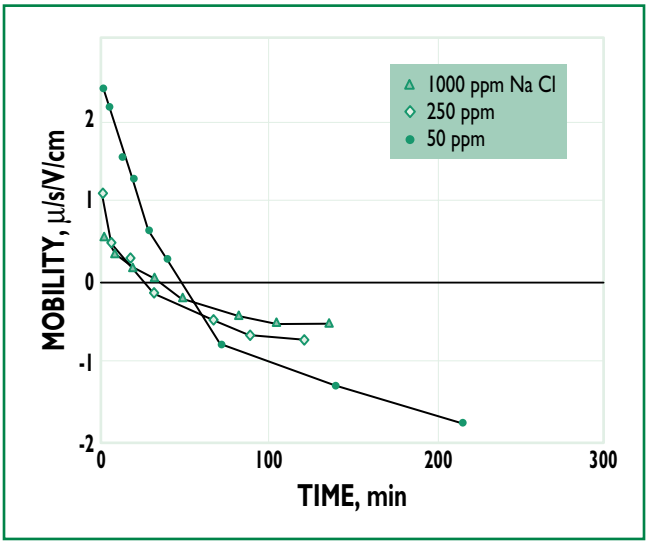
Bleached hardwood kraft, softwood kraft, and softwood sulfite pulps were compared for mobility decay behavior. Each pulp was treated with DMA-epi at 10% based on carboxyl number. **Figure 2** shows that time to decay to zero mobility varied only moderately, 46 ± 9 min, among the three pulps.



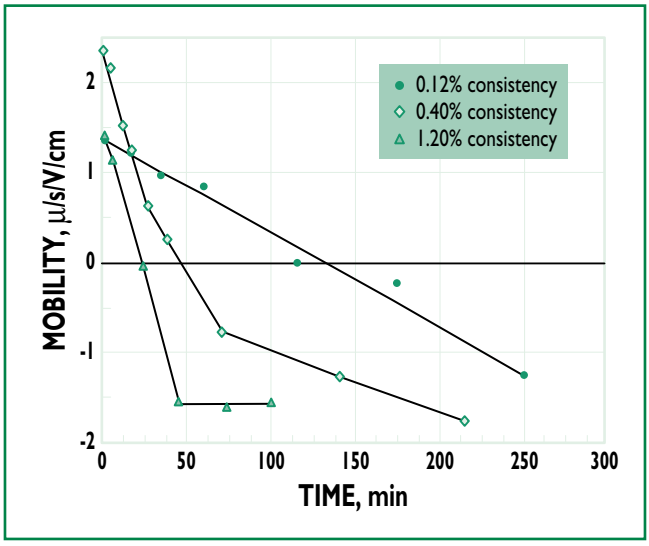
1. Effect of stirring rate on mobility decay for hardwood treated with 20K molecular weight DMA-epi at 10% on carboxyl number with consistency 0.4%, 50 ppm NaCl, and 10 ppm $NaHCO_3$ at 22°C



2. Mobility decay with three bleached pulp types using same conditions as Fig. 1 except pulp type



3. Effect of electrolyte on rate of mobility decay with same conditions as Fig. 1 but NaCl varied

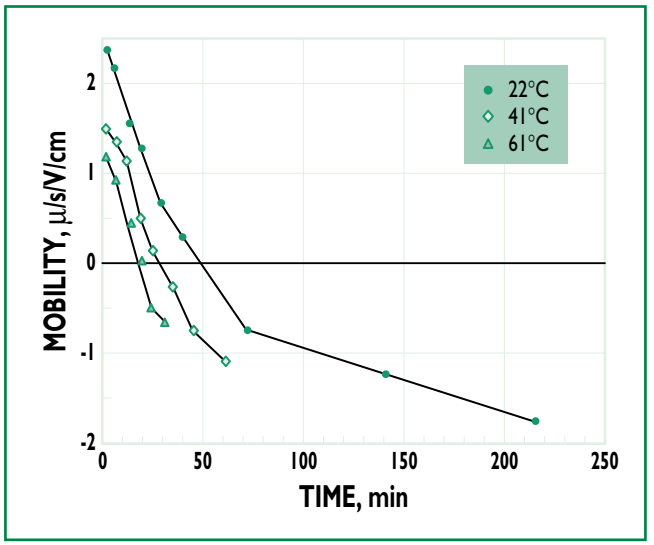


4. Effect of consistency on rate of mobility decay using same conditions as Fig. 1 but consistency varied

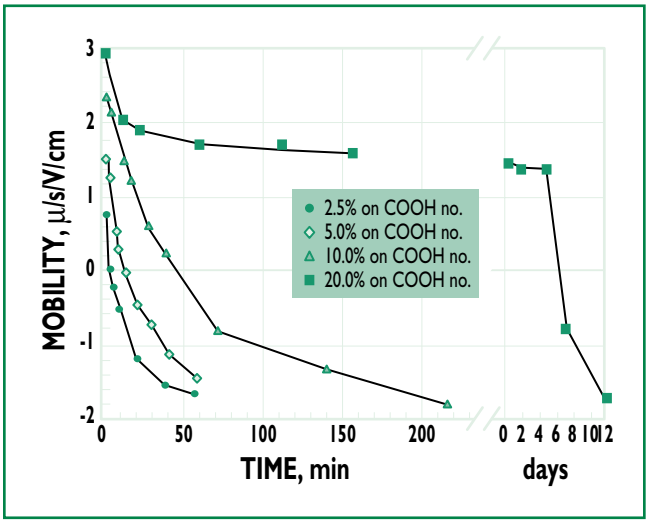
The lower carboxyl number softwood pulps showed lower cationic mobility immediately after polymer addition than did the higher carboxyl number hardwood. This follows from the lower weight percentage of polymer doses required and should result in a lower driving force for polymer migration and mobility decay. Also contributing to a lower rate of polymer migration is the reduced number of alternate (carboxyl) bonding sites. These factors offset the fact that less polymer needs to migrate to reach the zero mobility state. This argument assumes only minor differences in polymer migration rates due to differences in fiber morphology.

Electrolyte level

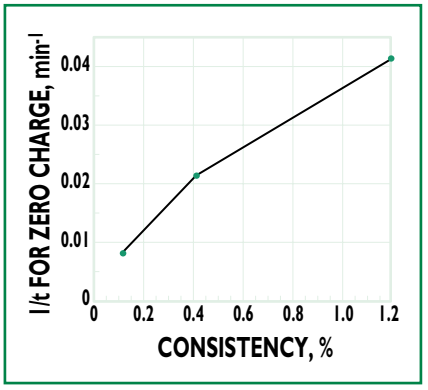
Electrolyte was added as 50, 250, and 1000 ppm sodium chloride. **Figure 3** shows that the time to decay to zero mobility—the only valid point of comparison—decreased with increasing salt level. Decay was more rapid as salt level increased. Increasing electrolyte concentration suppresses all charges toward zero. This is obvious in the starting and finishing points of the three curves in Fig. 3. One can rationalize that the suppressed charges can slow migration by reducing polymer to polymer repulsions while simultaneously favoring migration by reducing the tenacity of the polymer to fiber electrostatic bond. The results show that these driving force and barrier reductions are not exactly equivalent. The differences observed were small



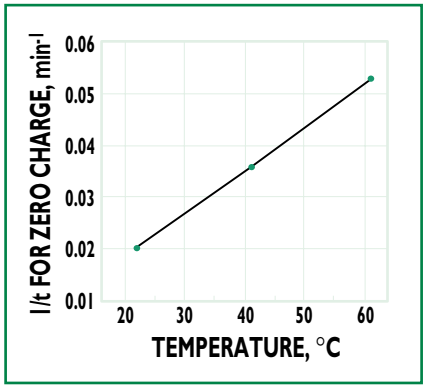
6. Effect of temperature on mobility decay rate with same conditions as Fig. 1 but temperature varied



8. Effect of DMA-epi dose on mobility decay rate with same conditions as Fig. 1 except for polymer dose



5. Average rate of decay to zero mobility as a function of consistency derived from same data as Fig. 3



7. Decay rate vs. temperature from same data as Fig. 5

and may be attributable to electrolyte induced changes in polymer chain spatial configuration.

Consistency

Figure 4 shows that mobility decay rate increased markedly with increasing consistency. In comparing decay rates, using the isoelectric point as the "finish line" is most convenient. At zero charge, the process has proceeded to a known extent—the cationicity added per unit of fiber minus the cationic demand. The following equation shows the rate of the process:

$$R = \Delta C/\Delta t \qquad (1)$$

where

R = rate
C = microequivalents of cationicity/g fiber
t = time.

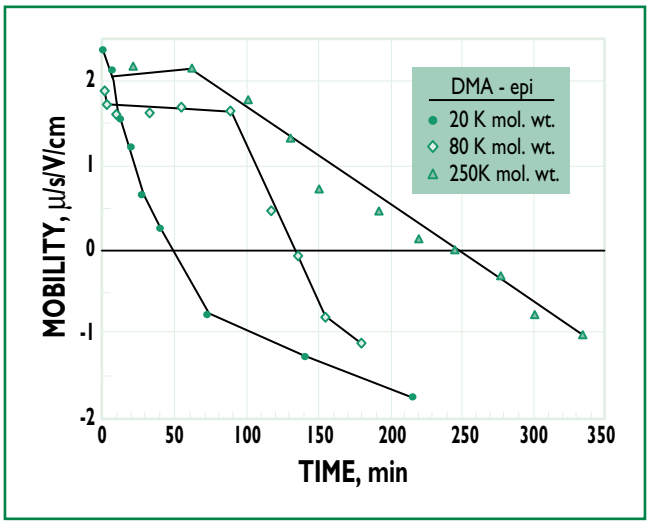
When the total cationicity added is constant, the average rate of decay is proportional to 1/t where t is the time to decay to zero charge. **Figure 5** shows that a plot of 1/t—minutes to zero mobility—vs. consistency is approximately linear. In a kinetics sense, increasing consistency results in increasing the concentration of fiber and unadsorbed polymer in solution. This magnifies the influence of the cationic surfaces on each other by proximity and collisions. Resultant polymer to polymer repulsions apparently can drive migration and charge decay. In addition, increasing concentration of unadsorbed polymer in solution—not measured in this work—may also drive migration. Since the process observed was at most first order in consistency only, it would appear that essentially all polymer (0.084% on fiber) was initially adsorbed. The absence of a stable initial mobility supports this. Mobility decrease began immediately after polymer addition.

Effect of temperature

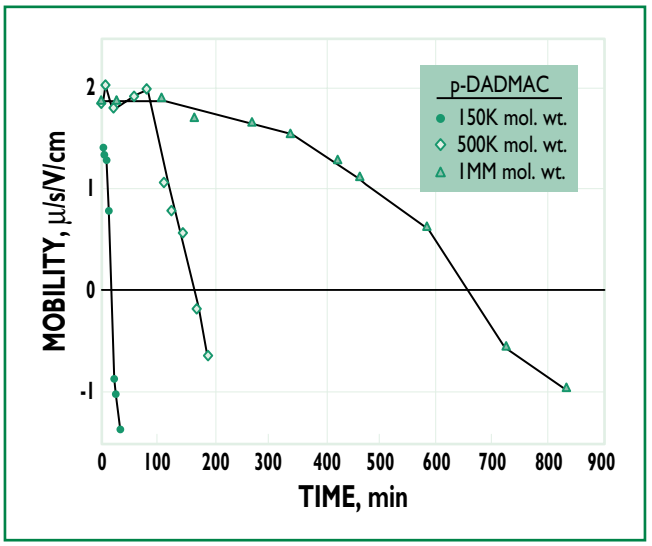
Mobility decay was followed at 22, 41, and 61°C. The 41° and 61°C samples were rapidly cooled to room temperature before mobility was measured. **Figure 6** shows that the rate of decay increased steadily with increasing temperature. Note that a significant degree of decay occurred in the first minute at 41°C and 61°C compared with the room temperature run. A plot of 1/time to zero mobility (rate) vs. temperature gave the straight line of **Fig. 7**. The slope of this line is the decay rate dependency on temperature for this system. One can use it to calculate the relative decay rate change at any temperature in the range covered. For example, this work calculated that the mobility decay rate increases by 2.0%/°C temperature increase at 50°C.

Effect of DMA-epi dose

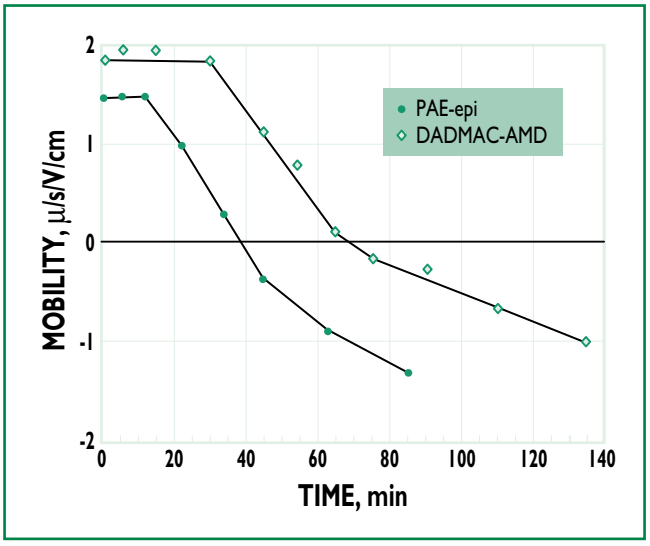
DMA-epi was added at levels equivalent to 2.5, 5.0, 10.0, and 20.0% on carboxyl number. **Figure 8** shows that



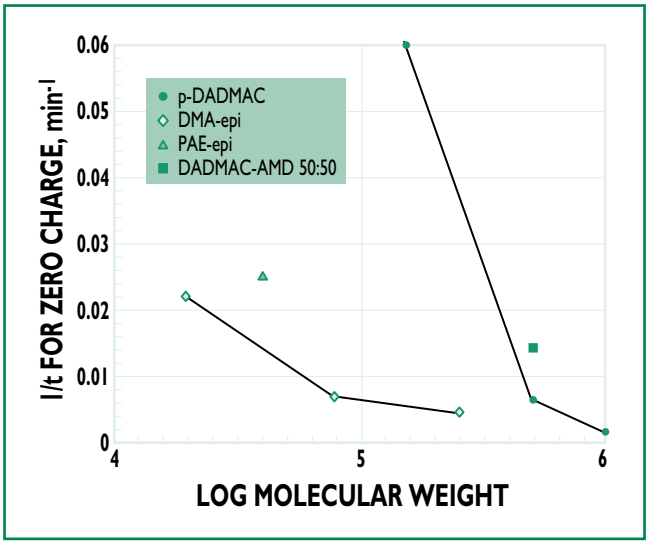
9. Effect of DMA-epi molecular weight on mobility decay rate using same conditions as Fig. 1 except for polymer dose



10. Effect of molecular weight on mobility decay with p-DADMAC with same conditions as Fig. 1 except for polymer used



11. Mobility decay with a 50:50 DADMAC-AMD copolymer and with a PAE-epi resin using same conditions as Fig. 1 except for polymers used

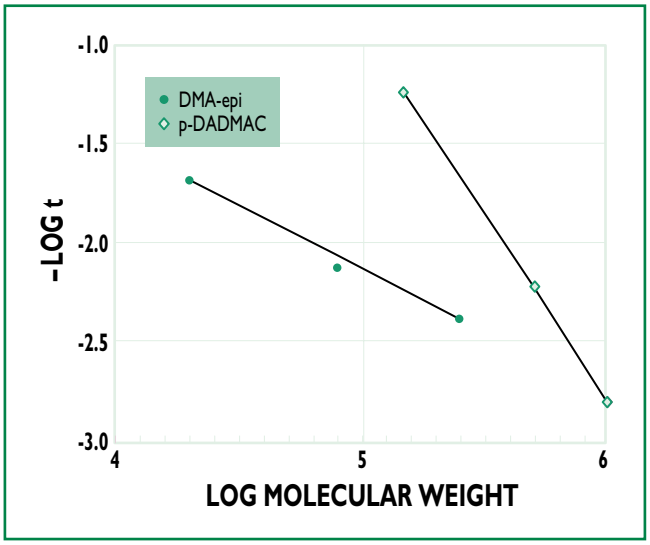


12. Relationship between mobility decay rate and molecular weight for different polymers

time to decay to zero mobility increased exponentially as polymer dose increased. With higher dosages, more polymer must migrate from the primary surfaces while the availability of alternate adsorption sites continually diminishes. At the 20% on carboxyl level, the extended period of stable cationic charge suggests a significant level of unadsorbed polymer in solution. This near-plateau persisted for 5 days before the mobility rapidly declined to zero. In this experiment, the fiber had adsorbed 16.5 times its conventionally defined cationic demand while ultimately reverting to an anionic mobility. It is interesting that decay still may be continuing after the mobility had decayed to –1.65 vs. –2.01 before polymer addition.

Effect of DMA-epi molecular weight

Figure 9 shows that time to decay to zero mobility increased with increasing DMA-epi molecular weight. Earlier workers reported similar results with this and other synthetic polymers *(5)*. It is important to note that crosslinking agents—typically ethylene diamine—find common use in the preparation of "high molecular weight" DMA-epi polymers. In the current work, the low molecular weight (20K) polymer contains no crosslinker. The higher molecular weight (80K and 250k) polymers do contain crosslinker. Besides molecular weight, the polymers differ in a critical structural feature. Expecting a crosslinked or more rigid structure to migrate slower than a linear structure of similar "molecular weight" under the same



13. Mobility decay with DMA-epi and p-DADMAC polymers showing plot of - log t vs. log molecular weight

conditions is reasonable. With the limited data available, distinguishing between pure molecular weight and crosslinking effects with DMA-epi is not possible.

Comparison of DMA-epi, p-DADMAC, and other polymers

P-DADMAC

Three homopolymers of p-DADMAC of varying molecular weight were evaluated. **Figure 10** shows that decay rate decreased with increasing molecular weight. Koethe and Scott previously reported this *(5)*. The decay rate change with molecular weight was far greater than with the DMA-epi polymers in Fig. 9. P-DADMAC differs from the DMA-epi polymers being without branching and crosslinking. With p-DADMAC, the decay rate dependence on molecular weight must relate strictly to chain length. By inference, with DMA-epi it relates more to crosslinking.

KEYWORDS

Cationic compounds, chemical properties, consistency, electric charge, electrical properties, molecular weight, polymers, process variables, solids content, synthetic polymers, temperature, variables, weight, zeta potential.

DADMAC-AMD and PAE-epi

Figure 11 shows decay results with a 50:50 DADMAC-AMD copolymer (ca. 500K molecular weight) and with a PAE-epi resin (estimated 40K molecular weight). Decay rates were of the same order as those with the low to medium molecular weight DMA-epi polymers.

Comparison of these different classes of polymers must be without any molecular weight bias. This is accomplished by plotting decay rates (1/t to zero mobility) vs. molecular weight. For convenience, 1/t was plotted against log molecular weight in **Fig. 12**. The plot reveals that the DADMAC-AMD copolymer does not differ significantly in its mobility decay behavior from the p-DADMAC homopolymers. One might have expected that hydrogen bonding of the amide groups to cellulose hydroxyl would act as a "brake" to reduce the rate of polymer migration. This may not be the case to any significant degree. It is therefore likely that hydrogen bonding via the hydroxyl groups of DMA-epi also plays little to no role in determining mobility decay rates.

Mobility decay rate with the PAE-epi resin is most similar to the DMA-epi polymers. It is faster when making allowance for molecular weight. The PAE-epi resin is probably more extensively crosslinked than the DMA-epi. One would therefore expect a slower decay rate. No explanation of this result is possible now.

Figure 12 shows that mobility decay rates when allowing for molecular weight are far greater with p-DADMAC than with DMA-epi. Previous work suggested that crosslinking retards migration of the DMA-epi polymers. This does not explain the observation that the uncrosslinked 20K molecular weight DMA- epi polymer exhibited a much lower rate of mobility decay than the higher molecular weight (150K) p-DADMAC.

Studying the mobility decay rates with the various DMA-epi and DADMAC polymers showed that they fit the form of the following equation:

$$1/t = a(\text{molecular weight})^b \quad (2)$$

where

a and b = constants.

A plot of -log t vs. log molecular weight gave the essentially straight lines in with slopes of b. Calculations showed b equal to –2/3 for DMA-epi and –1.9 for p-DADMAC.

For p-DADMAC, the following equation expresses the relationship:

$$D = a/\text{Molecular weight}^{1.9} \quad (3)$$

where

D = mobility decay rate.

Stated simply, the mobility decay rate with p-DADMAC is inversely proportional to the square of the molecular weight. Saying now whether this relationship has any utility or validity in systems other than those studied is not possible.

CONCLUSIONS

Mobility decay rates increased modestly with increased stock agitation and conductivity. At a constant ratio of

added cationicity to carboxyl number, decay rates were approximately the same with hardwood kraft, softwood kraft, and softwood sulfite pulps.

Increased temperature and consistency significantly increased mobility decay rates. The consistency effect suggests that mutual repulsion of cationic polymer chains on neighboring fibers are a part of the driving force in mobility decay. This effect merely magnifies the repulsion of neighboring polymer chains in an over-cationized system.

Mobility decay rates were greatly reduced as polymer molecular weight increased. The effect was true for DMA-epi and for p-DADMAC polymers. Decay rates were higher with p-DADMAC than with DMA-epi despite the higher molecular weight of the p-DADMAC. A partial explanation may lie in the crosslinked nature of the higher molecular weight DMA-epi polymers. This alone does not permit a rationalization of the results.

At equal added cationicity, a 50:50 DADMAC-AMD copolymer gave approximately the same decay rate as a similar molecular weight p-DADMAC. This result shows that any effect of amide to cellulose hydrogen bonding on the migration rate is negligible compared with normal electrostatic bonding. Similarly, the hydroxyl groups in DMA-epi polymers probably play no significant role in retarding polymer migration.

All observed results are consistent with the generally accepted three-step process of mobility decay: adsorption, reconformation, and migration. Migration obviously accompanied by rapid mobility decay begins immediately upon polymer addition when using lower molecular weight polymers.

The best explanations of the current findings are an equilibrium in polymer to fiber bonding and individual polymer bonding sites constantly desorbing, readsorbing, etc. In this way, polymers can migrate or diffuse through pores or transfer to other fiber or particle surfaces. Introduction of simple polyvalent cations such as Ca^{+2} or La^{+3} would probably create competition for fiber bonding sites. This would limit polymer readsorption and cause some total chain polymer desorption. Some polymer exchange might also occur with mixing of differently treated fibers.

Mobility decay can be a potential problem when adding low molecular weight cationic polymers to thick stock with a substantial dwell time. The problem becomes greater if the stock temperature is very high. Addition points may need changing to obtain the maximum benefit where cationic mobility contribution is important.

Note that the highest rate of mobility decay observed in the current work was with the 150K molecular weight p-DADMAC. This polymer is similar to the one most commonly used in the industry to measure cationic demands. These titrations should obviously occur as rapidly as possible. The time between sampling and testing for mobility and ionic demand should also be at a minimum. **TJ**

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LITERATURE CITED

1. Strazdins, E., *Tappi* 55(12): 1691(1972).
2. Strazdins, E., *Tappi* 57(12): 76(1974).
3. Davison, R.W., *Tappi* 57(12): 85(1974).
4. Strazdins, E., *Tappi* 60(7): 113(1977).
5. Koethe, J. L. and Scott, W. E., *Tappi J.* 76(12): 123(1993).
6. Gupta, B. and Scott, W. E., *TAPPI 1995 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 85.
7. Winter, L., Wågberg, L., Ödberg, L., Lindström, T. , *J.Coll. Interface Sci.* 111(2): 537(1986).
8. Ödberg, L., Tanaka, H., Swerin, A., *Nordic Pulp and Paper Res. J. (1): 6(1993).*
9. Wågberg, L., Ödberg, L., Lindström, T., *J.Coll. Interface Sci.* 123(1): 287(1988).
10. Tanaka, H., Swerin, A. and Ödberg, L., *Tappi J.* 76(5): 157(1993).
11. Ödberg, L., Barla, P., and Glad-Nordmark, G., *J. Pulp and Paper Sci.* 21(7): J250(1995).
12. Pelton, R. H., *J.Coll. Interface Sci.* 111(2): 475(1986).
13. Lindström, T. and Söremark, C., *J.Coll. and Interface Sci.* 55(2): 305(1976).