EFFECT OF SYSTEM CLOSURE ON RETENTION AND DRAINAGE AID PERFORMANCE IN TMP NEWSPRINT MANUFACTURE - PART II

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INTRODUCTION

The continued performance of retention and drainage aids as a function of increasing system closure levels in newsprint mills is a concern to the newsprint industry. In Part I of this series (1), we investigated the performance of five retention aid systems at three levels of usage of fresh process water. In this paper, we extend the study to include 15 other retention aid systems that are currently available and/or being employed by newsprint mills.

Water soluble polymers used for retention and drainage in newsprint manufacture include polyethylene oxide (PEO) (1-3), charged and non-ionic polyacrylamides (4-18), and highly charged, typically low molecular weight, polymers such as polyethyleneimine (PEI), polyamines, and polydiallyl dimethyl ammonium chloride (12,13,18-20). Highly charged, low molecular weight polymers are usually referred to as coagulants, while lower charged, high molecular weight polymers are usually referred to as flocculants. Recently polymers with intermediate properties have been introduced (21). These new polymers combine the higher charge density of coagulants and the higher molecular weights of flocculants.

The boundary between a coagulant and a flocculant is not distinct. However, in general, a coagulant has a molecular weight between 50,000 and 500,000 Daltons while a flocculant has a molecular weight in excess of 500,000 Daltons. In papermaking, coagulants are solely cationic while flocculants may be anionic, cationic, or neutral. Being cationic, coagulants lower the negative surface charge of colloidal particles, fibers, and fines by adsorbing on their surfaces. As a result, these particles form small aggregates with themselves and with the fibers and fines. These aggregates have been found to have poor stability when subjected to shear but to reform upon cessation of the shear

forces. Usually the action of coagulants on a paper machine is not instantaneous but gradual. Flocculants, on the other hand, often have little effect on the surface charge of colloidal particles and tend to form larger flocs, via a bridging mechanism, which have low stability to shear. Their action on a paper machine is more rapid and visible.

Water soluble polymers can be added as single components (only one polymer is added) or dual components. Dual component systems often use both the fixing ability of coagulants and the flocculating ability of high molecular weight flocculants (13, 22-30). The objective of a dual polymer retention aid program is to combine the small scale coagulation induced by coagulants and the larger scale bridging due to flocculants to achieve good retention and drainage without impairing sheet properties such as formation, porosity, strength, opacity, and brightness.

The use of microparticle systems, in particular those involving bentonite, has gained wider acceptance in mechanical grades (31-34). The advantage of microparticle systems is that higher retentions and drainage rates are often attainable compared to single or dual polymer systems. Other added advantages sometimes include better formation, decreased two-sidedness, and improved sheet properties compared to single or dual polymer systems.

Most Canadian mills have had process fresh water usage levels greater than 30 m^3/t. As a result, the concentration of dissolved and colloidal substances (DCS) in Canadian newsprint mills has traditionally been quite low, of the order of 500-2500 mg/L (35). However, environmental issues, economic considerations, and public perception are forcing mills to reduce discharge. Greater system closure has been shown to be economically feasible; mills can recover and reuse valuable resources such as water, fibre, filler, and heat. Francis *et al.* (36) have evaluated the technical and economic feasibility of system closure for older newsprint mills. They have outlined closure measures and options as mills progressively close their systems from 50 m^3/t to 3 m^3/t. White water management strategies for integrated newsprint mills (37,38) and current technologies and design for closed cycle and zero-effluent implementation have also been reviewed (39-42).

Progressive reduction in fresh water intake by mills has however led to increased concentrations of total DCS on the papermachine (40). Although the DCS typically account for between 2-5% of the weight of wood, their impact in system closure is substantial in terms of reduced machine runnability, poorer sheet properties, and decreased chemical efficiency (43-49). Recent studies have indicated that DCS are mainly carbohydrates, wood extractives, hemicelluloses, polysaccharides, and lignin derivatives (2, 35, 40, 50-53). Further studies on the identification, analysis, characterization, chemical control, and changes during bleaching of DCS have shown that DCS nature and quantity are greatly dependent on wood species, pulping method, bleaching method, and seasonal wood variations (54-69).

TMP pulps are usually poorly, if at all, washed. This practice results in a large amount of DCS being carried over to the paper machine and being allowed to accumulate in the machine white water circuit. Published studies (70-72) have shown that simple material balances can be used to estimate the concentration of DCS as a function of effluent volume. In particular, two separate studies by Anderson *et al.* (71) and Ropponen (72) have predicted large increases in DCS white water concentration as mill closure approaches the 5 to 15 m^3/t level. The upper limit of DCS for an integrated mechanical pulp mill using no additives was estimated to be between 10 and 35 g/L. Wearing *et al.* (37) have disputed these figures. A more complex model, which takes into account sorption of DCS onto the fibre, was proposed. Using this model Wearing *et al.* have predicted that

for a 100% TMP mill using no additives and operating at an effluent volume of 3 m^3/t, the white water would contain ~7 g/L of DCS.

Older studies by Melzer and Kuster (73) have investigated the effects of "opening" the white water circuit of an integrated German mill producing TMP/deinked pulp (DIP) newsprint. The mill was opened for a period of six weeks beginning with a closure level of 7 m^3/t to a final closure level of 17 m^3/t. The opening of the white water circuit led to a marked reduction in the amount of inorganic salts and anionic DCS in the mill. Furthermore the consumption of retention aid was significantly reduced. The effects of the reduced DCS levels on physical and optical properties were, however, difficult to assess.

The impact of DCS on physical and optical properties has also been investigated both on laboratory (35, 51) and pilot plant scales (74). These studies evaluated the impact of pulping liquors and white waters on the properties of handsheets. Drainage and wet web properties were examined to assess paper machine runnability while dry handsheet properties were examined to assess possible problems with product quality. Results showed that wet-web tensile strength and drying strength were impaired. Handsheet drainage time was little affected and optical properties were slightly affected. First pass retention (FPR), first pass ash retention (FPAR), and sizing were slightly changed.

A knowledge of the characteristics and amounts of organic and inorganic matter in the papermaking process that interfere with retention aids is of considerable significance (75-86). In a previous paper a limited number of retention aid systems were investigated for applicability to system closure (1). The objective of the present work was to expand upon the previous study by investigating a greater number of retention and drainage aid systems, many of which are considered to be state-of-the-art by suppliers.

EXPERIMENTAL

The Approach

The performances of fifteen different types of retention and drainage aid systems were measured in the laboratory at three levels of system closure. In this work, we have defined the degree of system closure in terms of fresh process water makeup to the mill. The levels of system closure used were 55, 20, and 3 m^3/t.

We have classified the retention and drainage aid systems studied into three categories: flocculant systems, coagulant plus flocculant systems, and dual component systems. For the flocculant systems a single polymer flocculant was used. Typically the polymer flocculant was a cationic polyacrylamide (CPAM). For the coagulant plus flocculant system a polymer flocculant was used in conjunction with a high charge density, low molecular weight polymer EPI-DMA coagulant (see **Table I**). The polymer coagulant was added prior to the polymer flocculant. For the dual component systems, PEO was used in combination with a cofactor (typically a phenolic resin) or bentonite is used in combination with a polymer flocculant. The bentonite was added either before or after a high molecular weight polymer flocculant or coagulant. For the purpose of this study BENT-1 bentonite clay was used for post polymer addition and BENT-2 bentonite clay was used for addition prior to the polymer flocculant. These two bentonite clays were chosen based on their large current use in the paper industry. All the retention and drainage aid systems are commercially available and currently used polymer systems.

Polymer or Clay	Molecular Weight (kDaltons)	Solids (%)	Net Charge Density by Colloidal Titration (meq./g at pH 5)	Chemistry
CPAM-1	4,000	35.9	0.43	Branched cationic polyacrylamide
CPAM-2	5,500	42.2	1.29	Branched cationic polyacrylamide
CPAM-3	7,000	36.8	0.03	Linear cationic polyacrylamide
CPAM-4	6,000	44.6	3.00	Linear amphoteric polyacrylamide
CPAM-5	900 - 1,100	94.3	1.04	Linear cationic polyacrylamide
NPAM	2,000 - 3,000	42.0	0.00	Linear neutral polyacrylamide
APAM	2,700	87.8	-0.01	Linear anionic polyacrylamide
PEO	6,000 - 9,000	99.8	0	Linear polyethylene oxide
Cofactor-1	low	28.9	0	Polybisphenol resin
Cofactor-2	low	33.3	0	Polysulfone resin
BENT-1	N/A	90.1	0	Modified bentonite clay
BENT-2	N/A	91.1	0	Modified bentonite clay
DADMAC	1,900 - 2,100	18.1	5.40	Linear polyDADMAC, i.e., poly(diallyldimethylammonium chloride)
EPI-DMA	50-100	52.3	5.84	polyquarternary amine chloride (EPI-DMA)

Table I. Material Properties.

Pulps and White Waters

The pulps and white waters used for the experiments were the same as those used in the previous study and were characterized previously (1). The analytical data showed an increase in dissolved substances, such as lignin and carbohydrates, with increasing system closure.

Preparation of Polymer Solutions

The retention and drainage aid systems studied are listed and described in Table I. The polymer solutions were prepared as described previously (1).

Charge Densities of the Polymers

The charge densities of the polymers were determined as described in Part I at pH 5 (1). The chemistries were determined by FTIR (Perkin-Elmer 1725X).

Retention and Drainage Measurements

First pass retention (FPR) with mat formation (nominal basis weight 80 - 120 g/m^2), drainage rate, and consistency after vacuum were obtained using our modified dynamic drainage jar (DDJ) method (1).

The headbox stocks were diluted to ~0.15% consistency with white water previously filtered through a Reeve Angel 202 filter paper to remove fines and fibers. Headbox stock from mill A was diluted with filtered white water from mill A and headbox stock from mill B was diluted with filtered white water from mill B or filtered simulated white water at 3 m^3/t. These were the 20 m^3/t, 55 m^3/t, and 3 m^3/t furnishes, respectively. Diluted headbox stocks were poured into a beaker and heated to 60°C. The pH was adjusted to 5.2, if needed.

Experiments were conducted as shown in **Table II** following the procedure previously outlined (1). For experiments involving dual component systems such as BENT-2 bentonite or PEO, the bentonite or phenolic resin cofactor was added to the beaker and stirred two minutes prior to running the DDJ experiment. The BENT-2 bentonite was added at a constant dosage of 0.2% wt/wt oven dry fibre (ODF) and the phenolic resin cofactor was added at a dosage three times that of the PEO dosage. For experiments involving BENT-1 bentonite, the polymer flocculant being tested was added to the beaker at the desired dosage level after which the BENT-1 bentonite was then added to the DDJ at a constant dosage of 0.2% wt/wt ODF. For coagulant plus flocculant systems, the coagulant was added to the beaker at a constant dosage of 0.2% wt/wt ODF.

RESULTS

The impact of increased system closure on the parameters studied for flocculant, coagulant plus flocculant, and dual retention and drainage aid systems are shown as follows: Figures 1 to 3, for first pass retention (FPR); Figures 4 to 6, for drainage rate; Figures 7 to 9, for consistency after vacuum; and Figures 10 to 12, for water retention value (WRV).

First Pass Retention

In **Figure 1** the first pass retention (FPR) of fines as a function of polymer dosage for the five single polymer retention aid systems is plotted. The results encompass the three degrees of system closure studied: 55 m^3/t (top), 20 m^3/t (middle), and 3 m^3/t (bottom). Standard deviations are indicated with the error bars; in cases where there are no standard deviations evident, it is because the standard deviation is less than the size of the data point symbol itself.

Time (s)	Single Polymer	Dual Polymer	PEO/ Phenolic Resin	Microparticle		
				DDJ RPM	BENT-1	BENT-2
0	Stir Pulp in Beaker at 60°C*	Stir Pulp in Beaker at 60°C*	Stir Pulp in Beaker at 60°C*		Stir Pulp in Beaker at 60°C*	Stir Pulp in Beaker at 60°C*
10		Add Coagulant	Add Phenolic Resin			Add Bentonite
70					Add Flocculant	
130	Pour into DDJ	Pour into DDJ	Pour into DDJ	500	Pour into DDJ	Pour into DDJ
190	Add Flocculant	Add Flocculant	Add Flocculant	500		Add Flocculant
200				1200		
215				500		
225				500	Add Bentonite	
250	Drain	Drain	Drain		Drain	Drain

(*): with magnetic stirrer at medium speed and low heat settings.

Table II. Experimental Procedures.

The experiments were carried out over a range of retention aid dosages, from zero to concentrations higher than those typically used on paper machines. The high end was explored both for scientific interest and also, especially for the coagulants, to compensate for a lack of polymer recirculation and enrichment which would occur on a paper machine.

At 55 m^3/t, first pass retention in the absence of retention aids was 77%. A high first pass retention blank was obtained because fibre mats were formed in the modified DDJ tester. At 55 m^3/t, increasing dosages of the linear cationic polyacrylamide (CPAM-3) had little influence on retention, showing slight decreases at higher polymer dosages. This polymer possesses a high molecular weight and a low charge density. NPAM, which is neutral and of lower molecular weight, shows a similar trend at higher polymer dosages but a good performance at low polymer dosages, typical of those used commercially. Overall, the best first pass retentions were obtained with the CPAM-1 and CPAM-2 polymers and NPAM at low polymer dosages.

At 20 m^3/t, first pass retention without retention aids was reduced to 74%. At this level of closure, CPAM-1 and the high molecular weight, high charge density CPAM-4 displayed good performances at high dosage levels. NPAM again showed a good performance at low polymer dosages. With the exception of CPAM-1 and CPAM-4, other polymers tested showed an initial improvement at low polymer dosages, going through a maximum, and then a progressive worsening of the FPR at higher dosages. The highest retention gain was approximately 6% with CPAM-1 at a high polymer dosage.

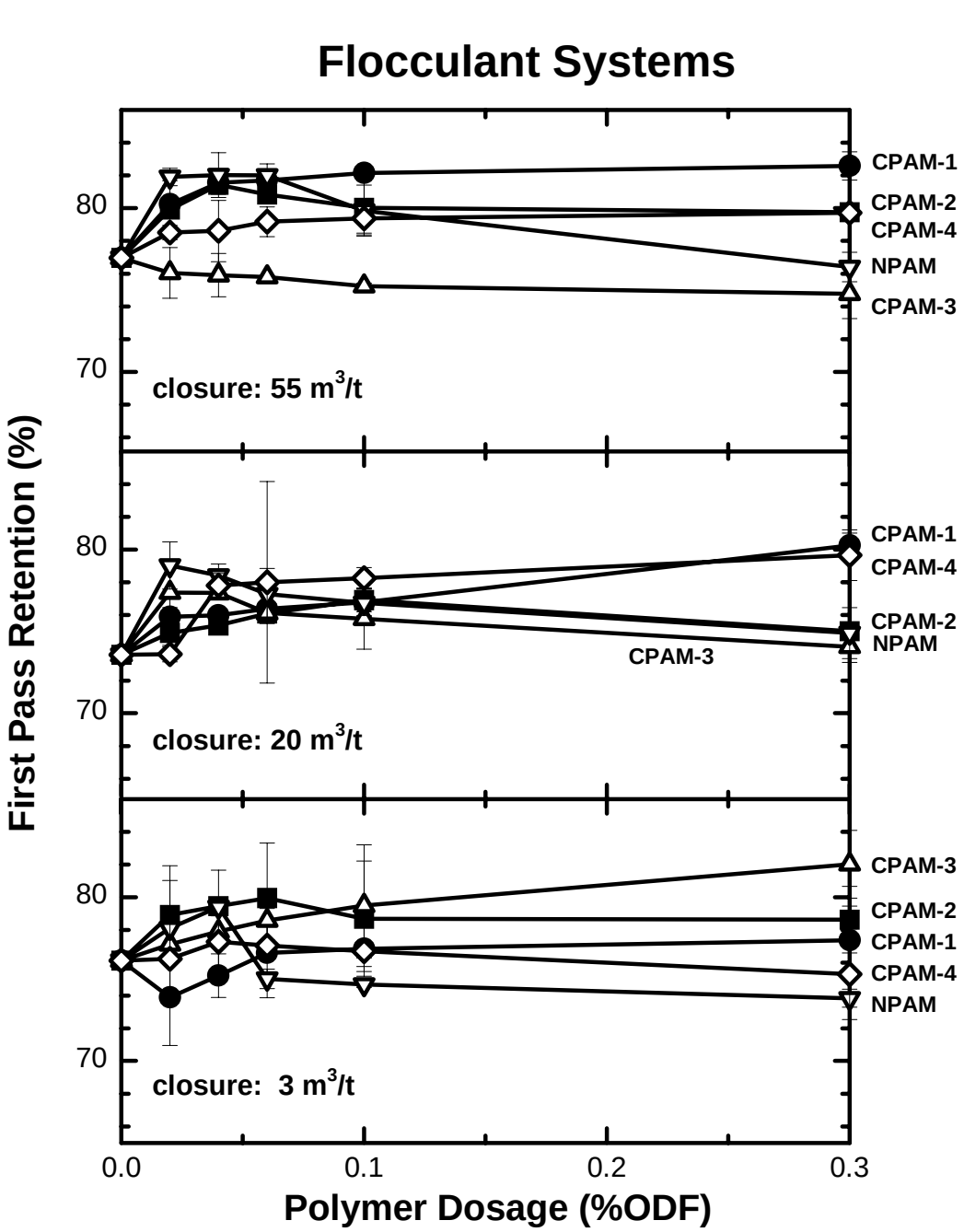

Figure 1. First pass retention for flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (∆) CPAM-3, (∇) NPAM, (◇) CPAM-4.

At a closure level of 3 m^3/t , in the absence of retention aids, the first pass retention was 76%. A possible explanation for the first pass retention being higher than observed at 20 m^3/t is that the headbox stock was the same as was used for 55 m^3/t. CPAM-2 displayed positive results at all dosages. NPAM performed well at low polymer dosages. CPAM-3 exhibited an increasingly improving performance at higher polymer dosages.

In **Figure 2** the first pass retention of fines as a function of polymer dosage for the same five flocculant polymer retention aid systems studied in Figure 1, in the presence of a polymer coagulant,

are graphed. The data show that the addition of the charge neutralizing coagulant improved the retention efficiencies of some flocculants at higher degrees of closure (20 m^3/t and 3 m^3/t) but worsened the first pass retention (FPR) of some flocculants at 55 m^3/t. The best performing polymer flocculants at all degrees of closure were CPAM-4, NPAM and CPAM-2. Both CPAM-4 and CPAM-2 possess a relatively high molecular weight and charge density while NPAM is a neutral polymer. NPAM was found to be the most efficient retention aid at 3 m^3/t, the highest degree of closure. Close analysis of the data also shows that NPAM performed very well at low polymer dosages for 20 m^3/t. An overall improvement in FPR was noted for all the polymers, with the exception of CPAM-3 at 3 m^3/t. The data seem to indicate that high molecular weight and low to intermediate charge density polymers are the most efficient at improving FPR at high degrees of closure.

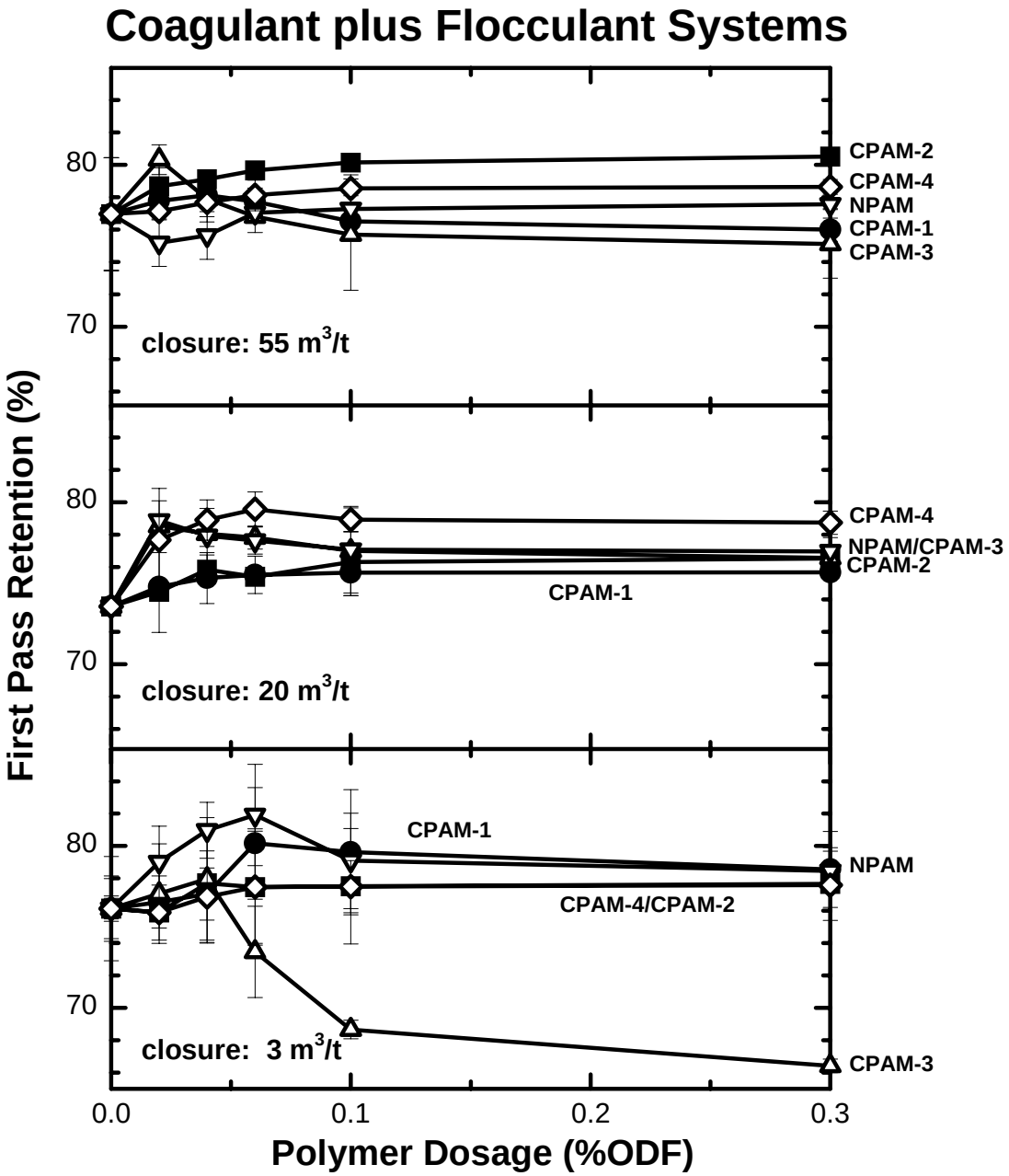

Figure 2. First pass retention for coagulant plus flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (Δ) CPAM-3, (∇) NPAM, (◇) CPAM-4.

In **Figure 3** the results for the dual component PEO and bentonite systems are presented. At all three levels of closure, the overall best performers were the PEO/phenolic resin cofactor systems as in the previous figures. It is noteworthy that the PEO performance was very dependent on the cofactor used. The bentonite systems showed the following trend: BENT-1 systems perform better than the BENT-2/APAM system. This may be explained by the fact that the BENT-2 bentonite surface may be contaminated to a greater extent from detrimental substances present in solution since it is added sooner in the process. Once contaminated it may be difficult for the polymer to adsorb onto the bentonite particle. Comparing the BENT-1 systems, it is clearly evident that the CPAM-5/BENT-1 system showed a better performance than the BENT-1/DADMAC system. Presumably these results are due to the ability of the CPAM to flocculate as compared to the DADMAC polymer, which functions primarily as a charge neutralizer.

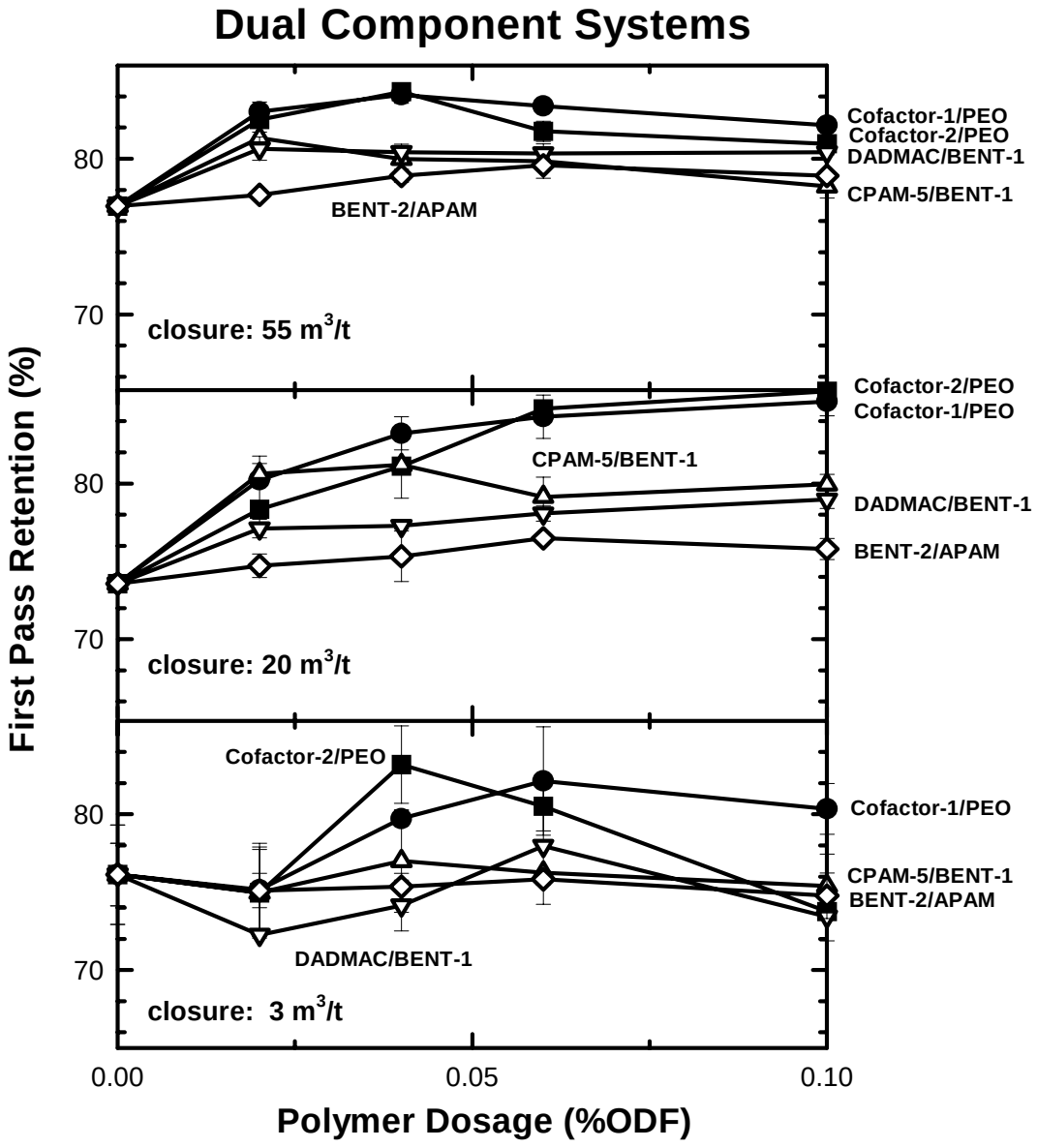

Figure 3. First pass retention for dual component systems as a function of polymer dosage at three levels of water closure. Symbols: (●) Cofactor-1/PEO, (■) Cofactor-2/PEO, (Δ) CPAM-5/BENT-1, (∇) DADMAC/BENT-1, (◇) BENT-2/APAM.

Drainage Rate

In **Figures 4** to **6**, the drainage rates are plotted as a function of polymer dosage for the polymer retention aid systems. The figures clearly show that, in the absence of retention aids, an increase in level of closure resulted in an overall decrease in the drainage rate with the greatest decrease occurring between 20 m^3/t and 3 m^3/t. At low dosages, the best performing flocculant systems were the high molecular weight, high charge density CPAM-2 and CPAM-4 polymers but these had almost no influence at 3 m^3/t. Similar results were found for the dual polymer retention aid system, as seen in Figure 5. The use of the polymer coagulant had a negligible effect on drainage improvement, except in the case of CPAM-3 at 20 m^3/t, which showed a large increase in drainage at low polymer dosage.

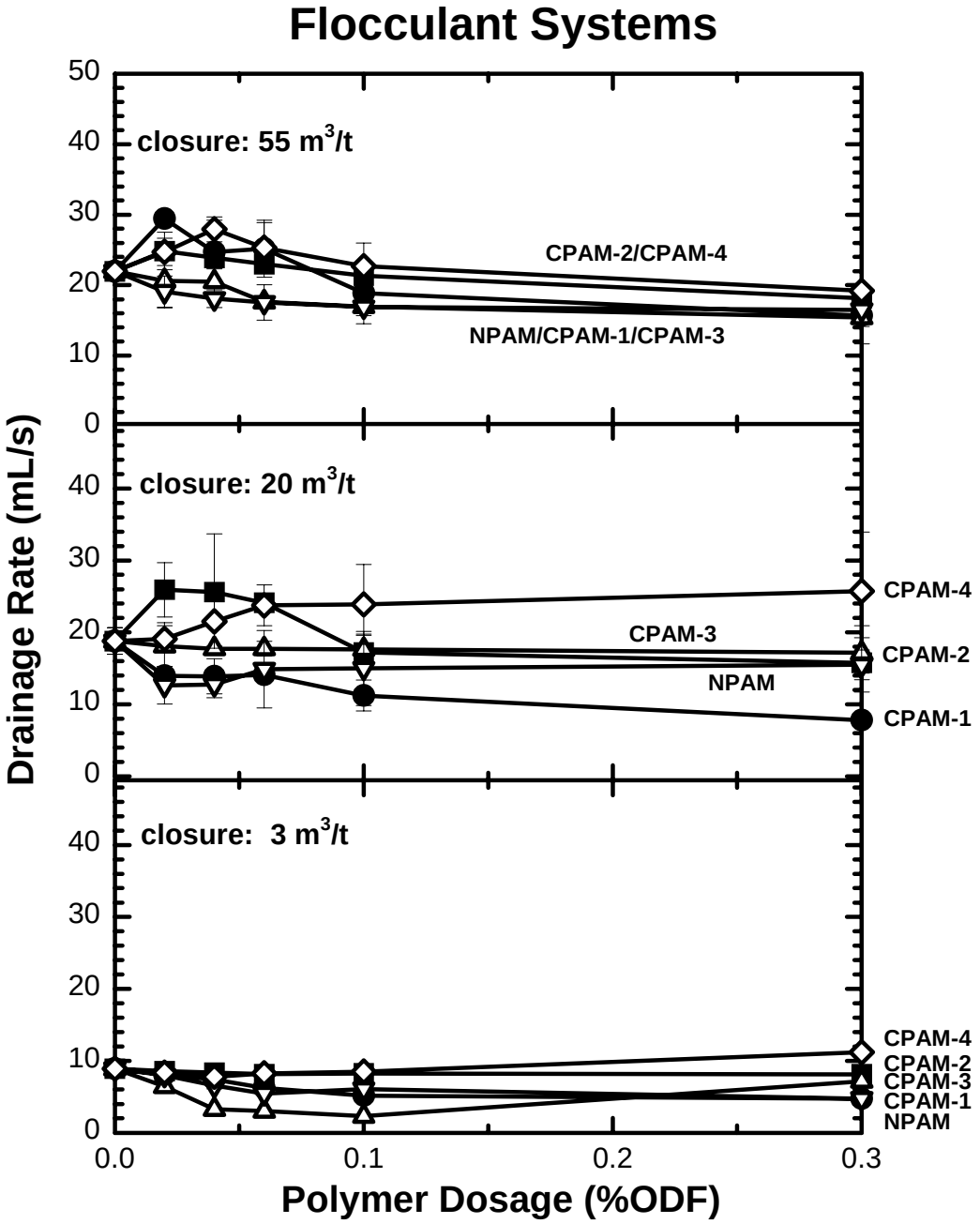

Figure 4. Drainage rate for flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (Δ) CPAM-3, (∇) NPAM, (◇) CPAM-4.

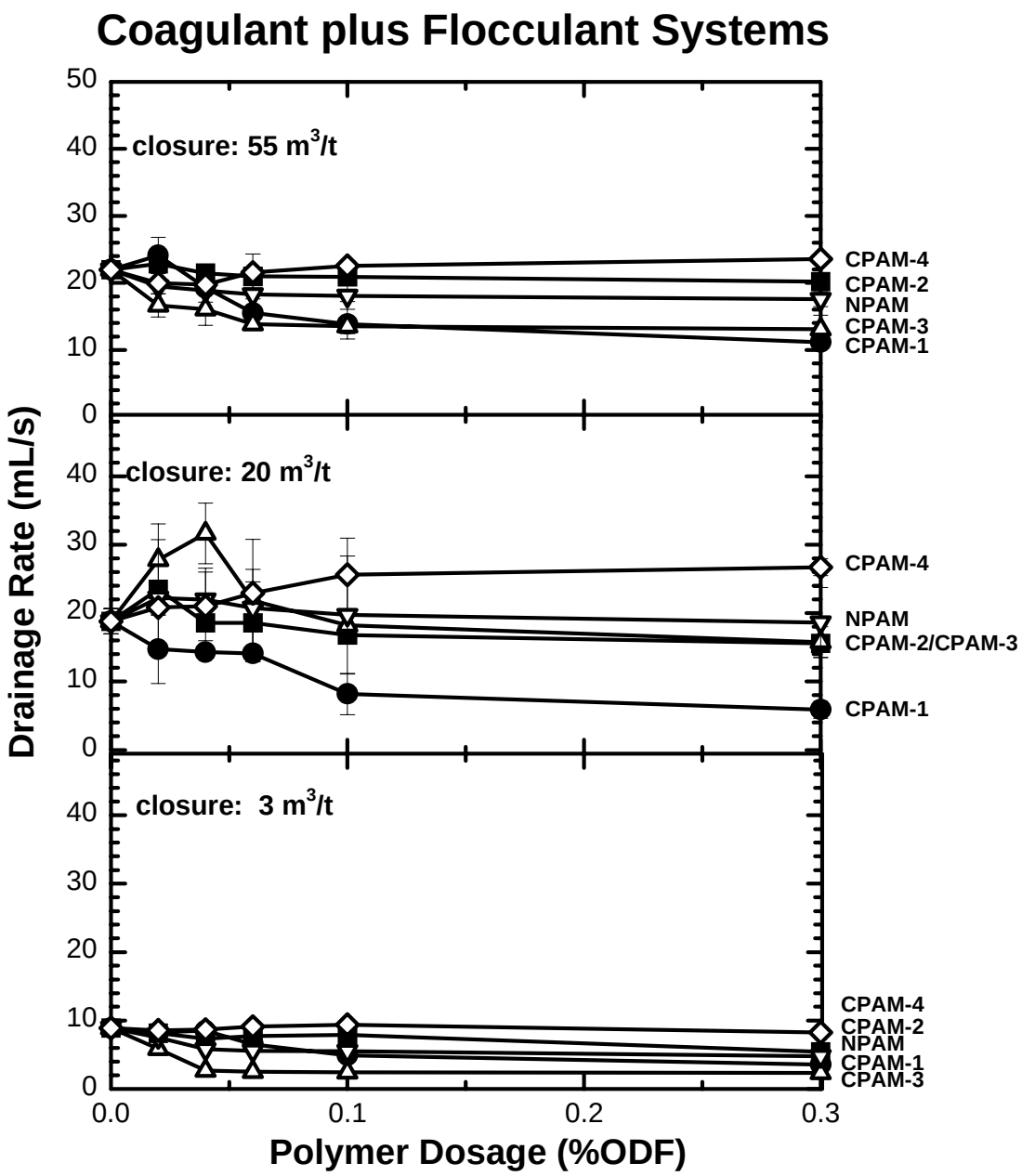

Figure 5. Drainage rate for coagulant plus flocculant systems as a function polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (Δ) CPAM-3, (∇) NPAM, (◇) CPAM-4.

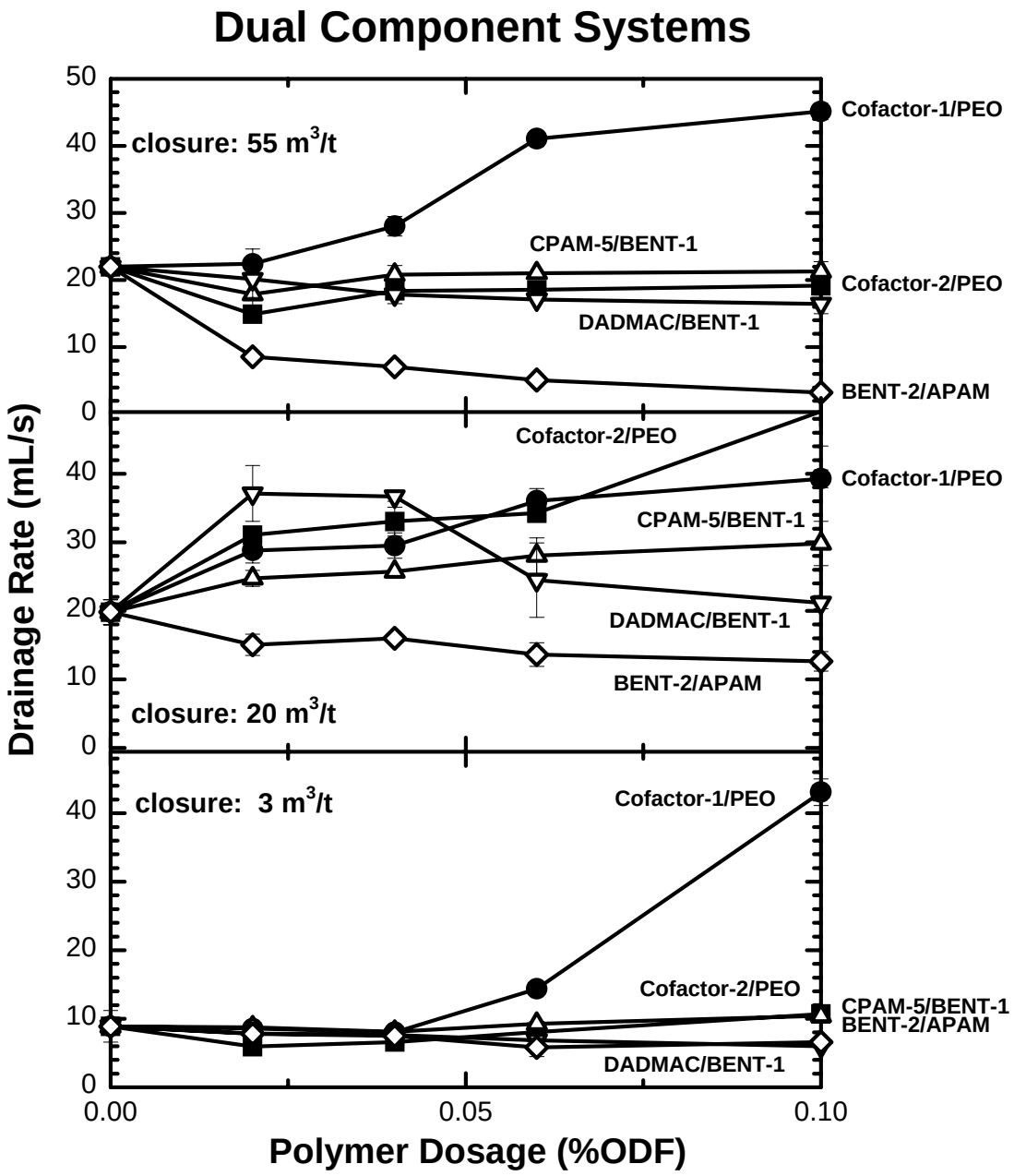

Figure 6. Drainage rate for dual component systems as a function of polymer dosage at three levels of water closure. Symbols: (●) Cofactor-1/PEO, (■) Cofactor-2/PEO, (Δ) CPAM-5/BENT-1, (∇) DADMAC/BENT-1, (◇) BENT-2/APAM.

In Figure 6 the drainage rate is presented as a function of polymer dosage for the dual component PEO and bentonite polymer retention aid systems. The results, encompassing the three degrees of system closure, show that the PEO chemistries again performed well at low degrees of closure and extremely well at higher degrees of closure. The results also indicate that the use of the correct type of resin was very important when using PEO. Cofactor-1 was again found to perform very well especially at a high degree of closure. In addition, the results show that the bentonite retention and drainage aids often had a negative effect on drainage. This is particularly true of the BENT-2 system. Of these, BENT-1 with CPAM-5 was the least detrimental.

Consistency after Vacuum

In **Figures 7** to **9** the consistency after vacuum is given as a function of polymer dosage for the polymer retention aid systems. The results in Figure 7 are similar to those obtained for the drainage rate data: for flocculant systems the best performing polymers were the high molecular weight CPAM-2, CPAM-4, and CPAM-3 polymers. For the flocculant systems at 3 m^3/t, NPAM was found to be the most efficient at lower dosage levels.

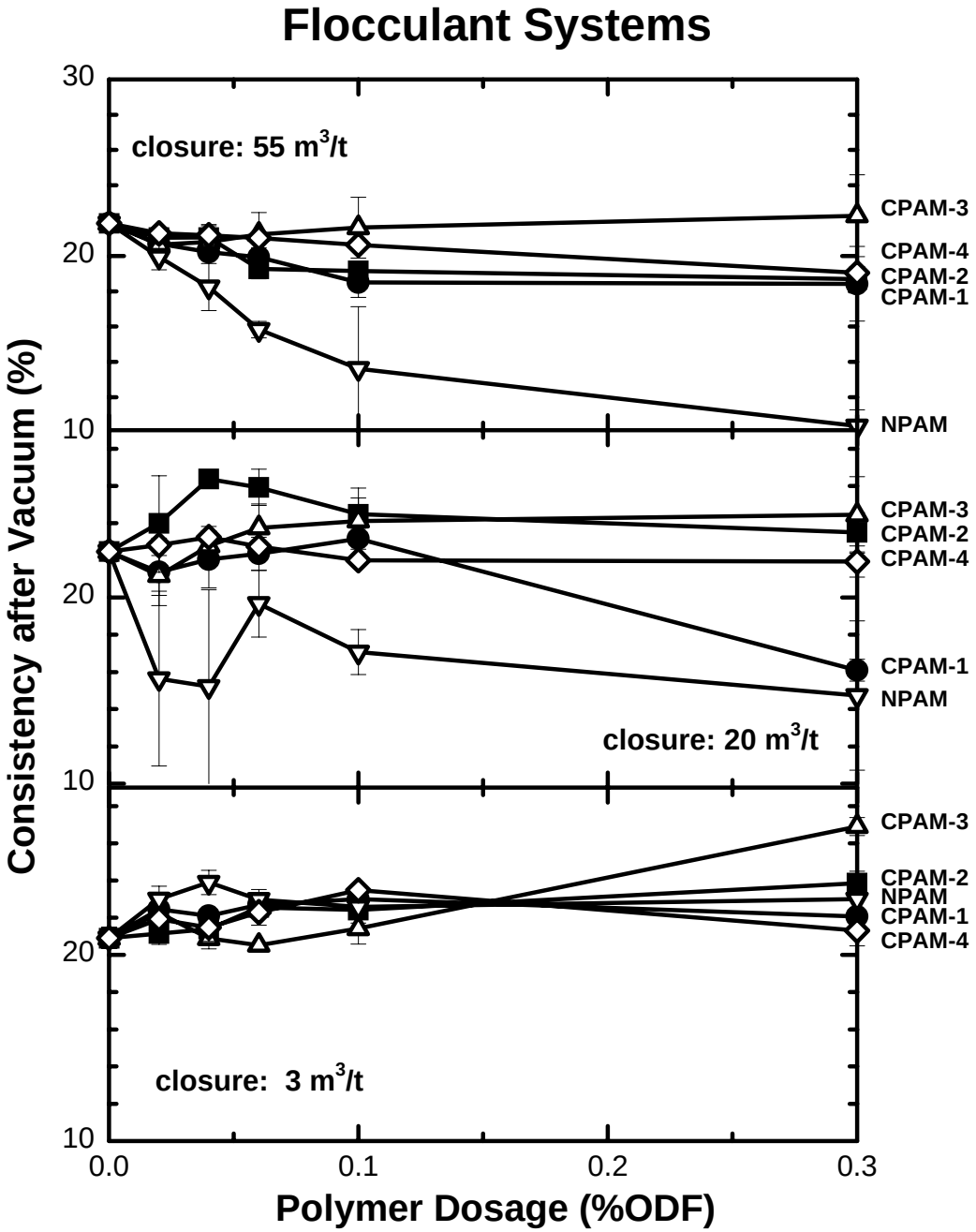

Figure 7. Consistency after vacuum for flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (Δ) CPAM-3, (∇) NPAM, (◇) CPAM-4.

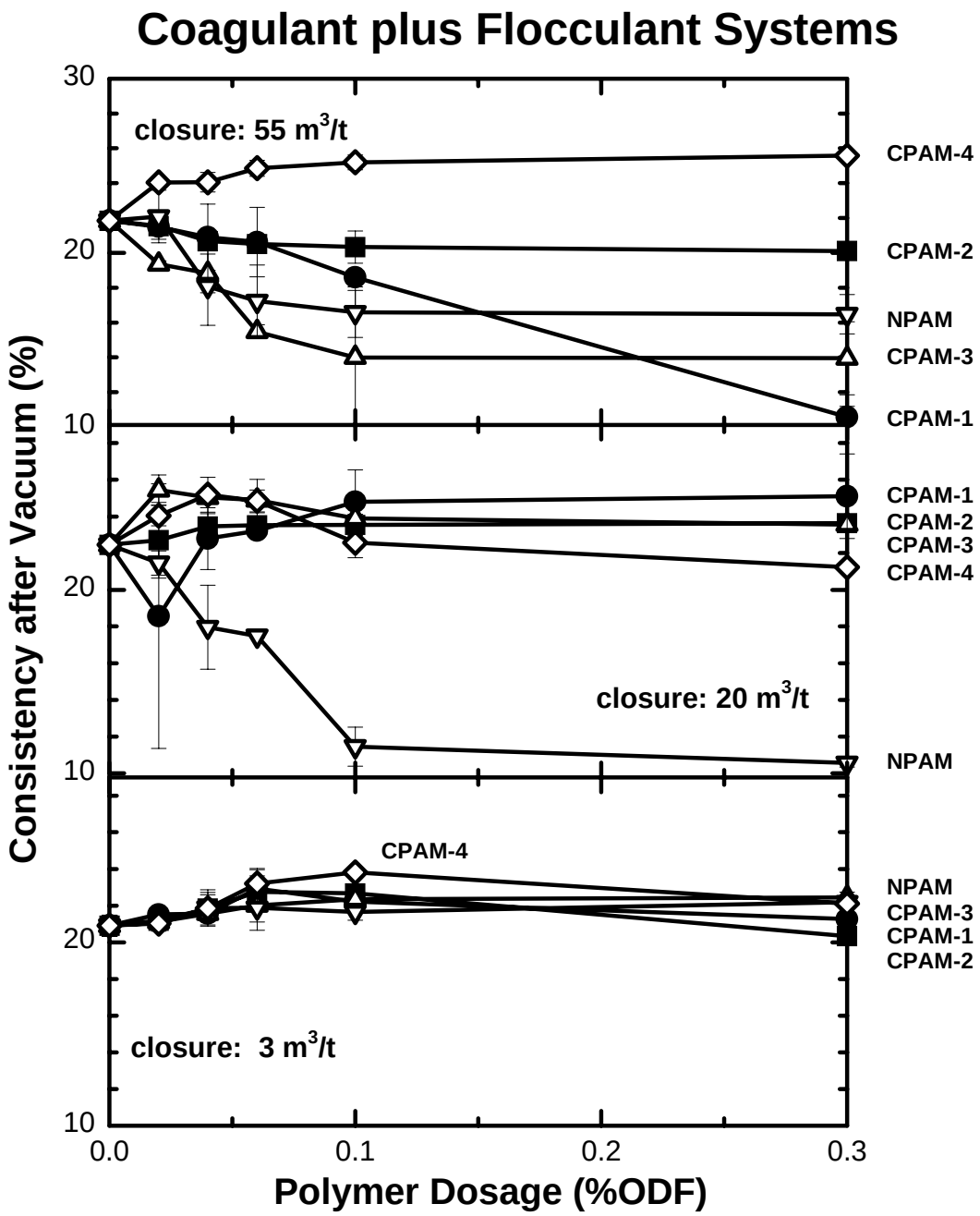

Figure 8. Consistency after vacuum for coagulant plus flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (∆) CPAM-3, (∇) NPAM, (◇) CPAM-4.

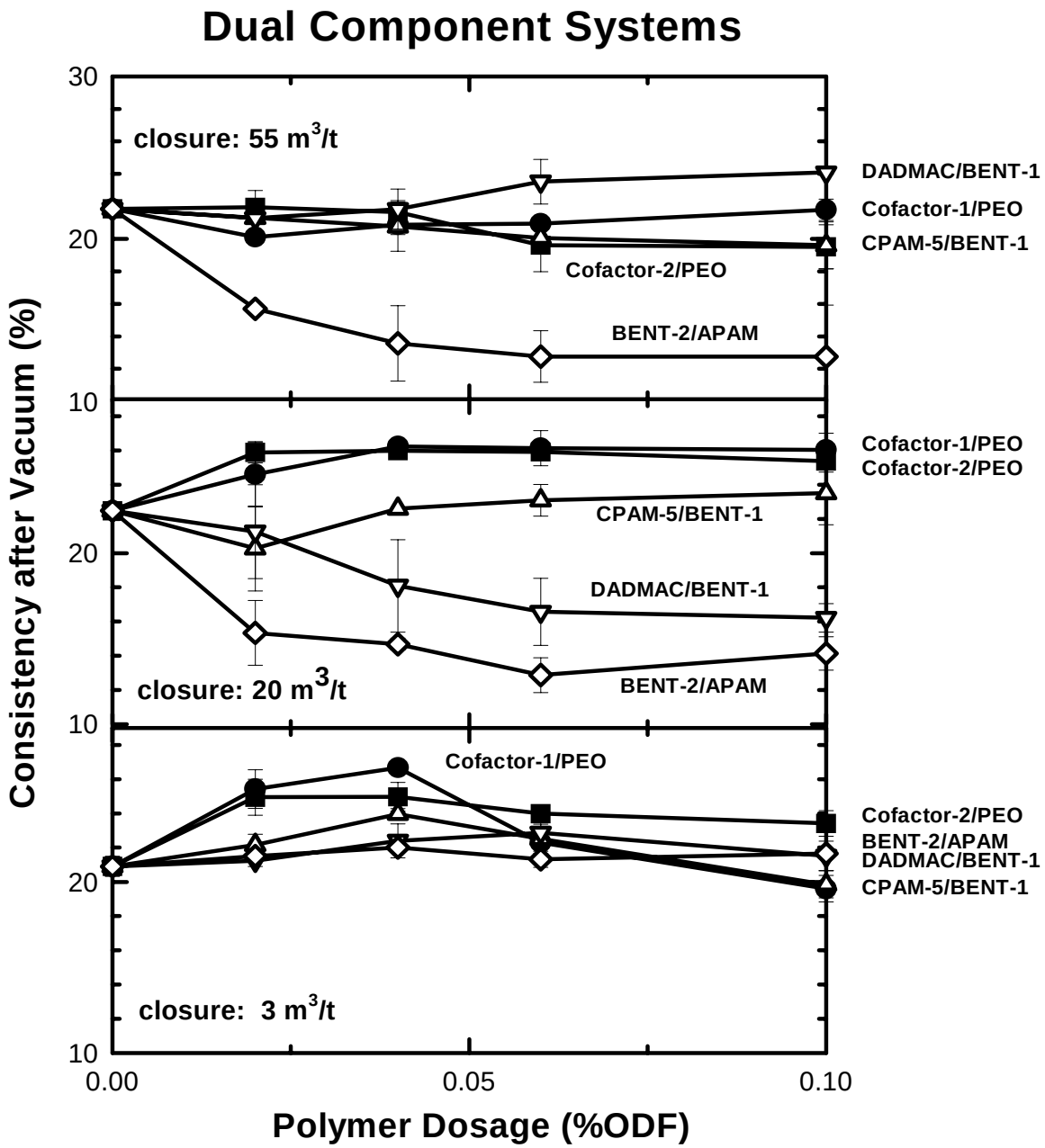

Figure 9. Consistency after vacuum for dual component systems as a function of polymer dosage at three levels of water closure. Symbols: (●) Cofactor-1/PEO, (■) Cofactor-2/PEO, (∆) CPAM-5/BENT-1, (∇) DADMAC/BENT-1, (◇) BENT-2/APAM.

With the exception of CPAM-4, which showed an improvement with the use of a coagulant at 55 m^3/t, the use of a coagulant reduced the consistency after vacuum (Figure 8). For the dual component systems shown in Figure 9, the PEO chemistries, were found to be the best performers at higher degrees of closure while at 55 m^3/t, the DADMAC/BENT-1 system proved to be the most efficient. The BENT-2 bentonite chemistry again performed poorly in closed systems.

Water Retention Value

In **Figures 10** to **12** the water retention value (WRV), expressed as percent consistency, is given as a function of polymer dosage for the polymer retention aid systems. WRV is the consistency of the sheet after centrifugation and is an indication of the water retained by the fibers and fines after pressing, as described in a previous paper (1).

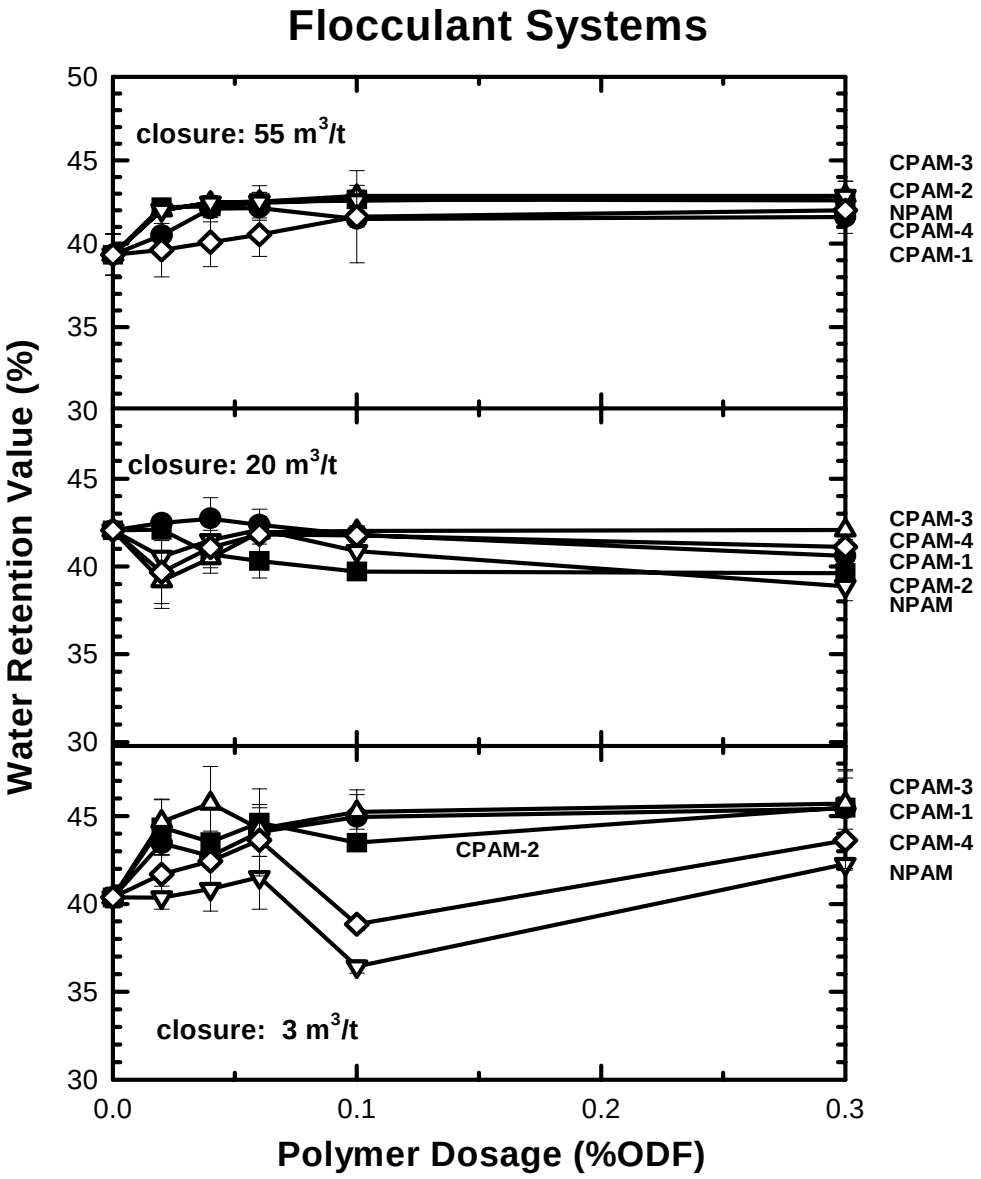

Figure 10. Water retention value for flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (Δ) CPAM-3, (∇) NPAM, (◇) CPAM-4.

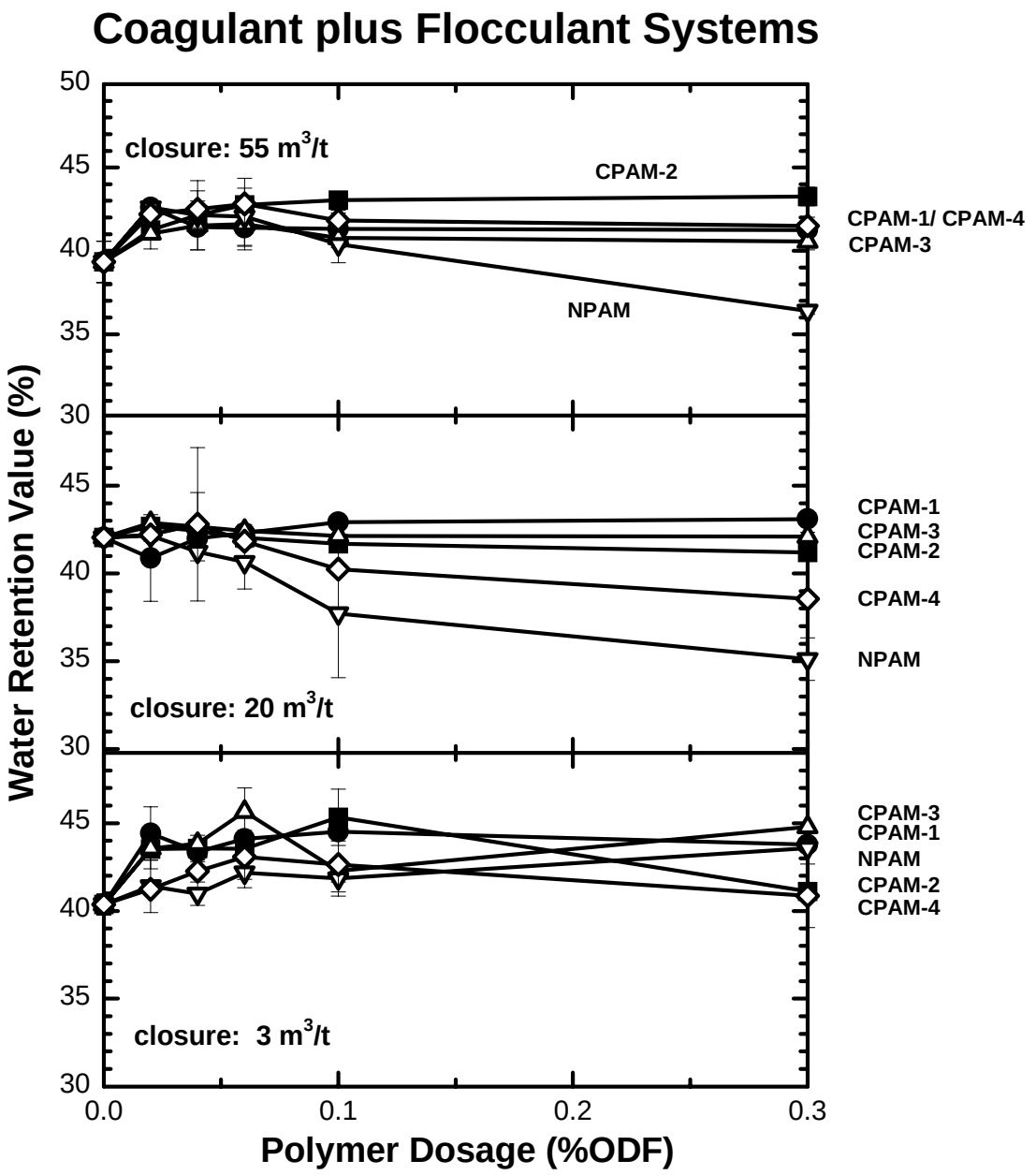

Figure 11. Water retention value for coagulant plus flocculant systems as a function of polymer dosage at three levels of water closure. Symbols: (●) CPAM-1, (■) CPAM-2, (∆) CPAM-3, (∇) NPAM, (◇) CPAM-4.

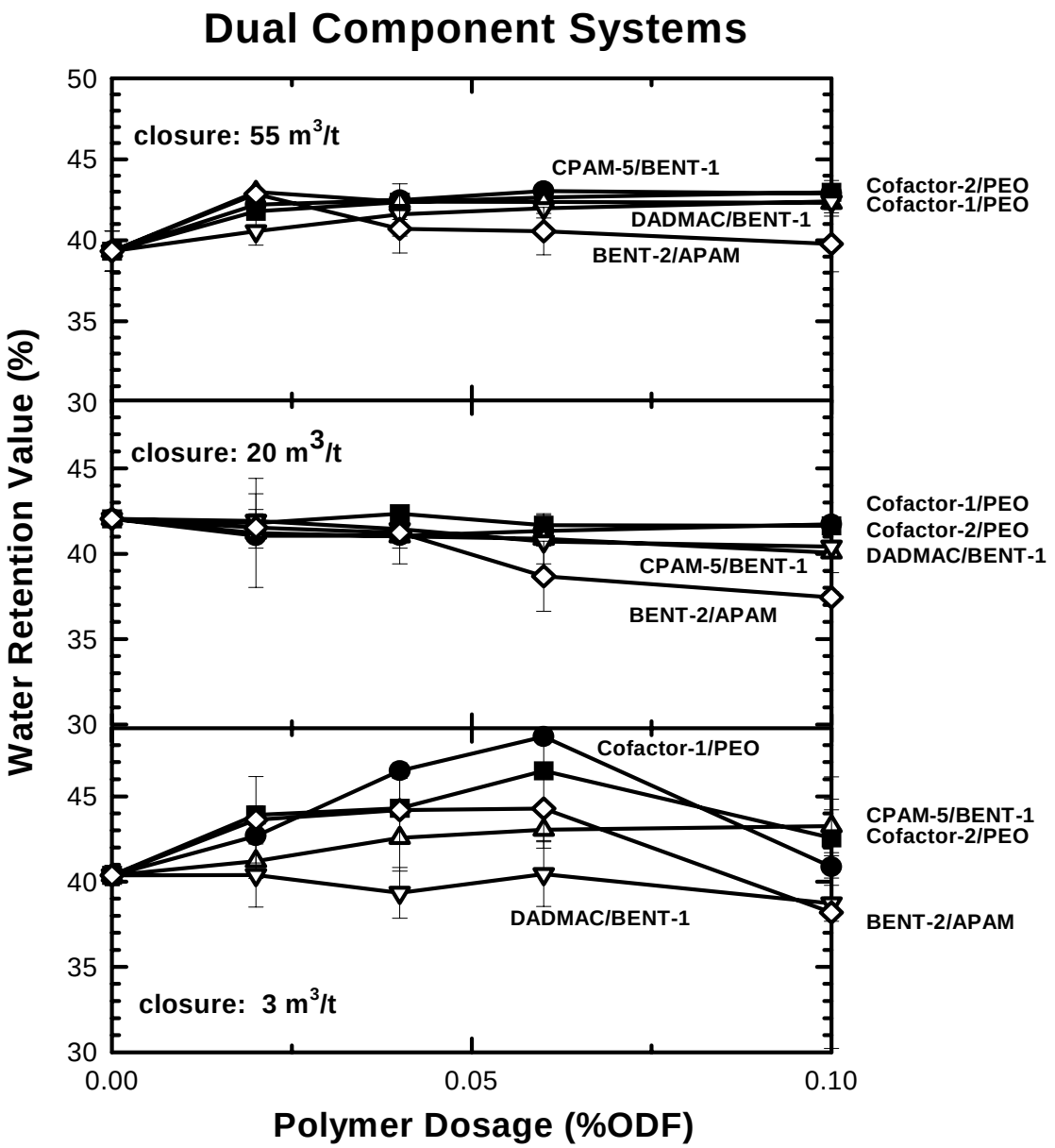

Figure 12. Water retention value for dual component systems as a function of polymer dosage at three levels of water closure. Symbols: (●) Cofactor-1/PEO, (■) Cofactor-2/PEO, (Δ) CPAM-5/BENT-1, (∇) DADMAC/BENT-1, (◇) BENT-2/APAM.

The higher molecular weight CPAM-2, CPAM-3, and CPAM-4 polymers were again found to perform very well as single and dual polymer retention aids (Figure 10). The use of a coagulant for the dual polymer retention aid systems worsened the WRV for certain polymers at lower degrees of closure but improved the WRV slightly at 3 m^3/t (Figure 11). The PEO retention and drainage aids were found to be the overall best performers at the highest degree of closure, as can be seen in Figure 12. The BENT-2 and BENT-1 bentonite chemistries were found to perform well at low degrees of closure and polymer dosage but begin to perform progressively worse at higher degrees of closure and polymer dosage.

DISCUSSION

The results presented in this study are in agreement with those obtained in the previous study (1):

1) At a high degree of closure, such as 3 m^3/t, the PEO/resin enhancer system proved to be very efficient, as it improved first pass retention of fines, drainage rate, consistency after vacuum, and the water retention value. The choice of the correct cofactor is very important for PEO performance and will depend on the furnish used.

2) At progressively higher degrees of closure, the BENT-1 polymer system becomes increasingly inactive. However, the BENT-1 system functions well at degrees of closure greater than 20 m^3/t. The BENT-2 bentonite chemistries were found to be relatively inefficient and detrimental to both drainage and water retention value.

3) With increasing system closure, increased concentrations of dissolved and colloidal substances result in an increasingly poorer performance of cationic polymers, such as cationic polyacrylamide (CPAM).

4) For cationic polyacrylamides, polymer chain length (degree of polymerization) and charge density (degree of substitution) are important parameters in the choice of a retention aid for system closure. Close inspection of Table I indicates that the most efficient CPAMs in closed systems are those possessing high chain lengths and moderate to high cationic charge densities.

PEO in combination with resin enhancer results in the best overall efficiency for system closure. In support of this, Rahman and Tay (2) have shown that increased specific conductivity and poorer washing of the headbox pulp stocks resulted in poorer performance of bentonite polyacrylamide chemistries and an improved performance of the PEO-cofactor chemistries. Although the mechanism is not well understood it is believed that certain soluble substances in mechanical pulps, which increase in concentration as a function of closure level, improve the performance of PEO. PEO has recently been shown to operate by a complexing (association-induced polymer bridging) mechanism with phenolic resins. The phenolic resin is thought to stiffen the PEO polymer chain by hydrogen bonding (87) and thus aid PEO in flocculation efficiency. Some of the DCS found in mechanical pulps and closed systems may also aid in this reinforcement (2). These same substances, on the other hand, were shown to have a negative effect on bentonite clays.

Notwithstanding the ability of PEO to complex with certain soluble substances found in solution or added to solution as cofactors (e.g. phenolic resins), another explanation for the superior flocculation efficiency of PEO in closed systems is the high polymer chain length of PEO compared to those of the polyacrylamides with similar molecular weight.

Let us first consider the high polymer chain length of PEO by comparing two polymer chains of equal molecular weught; the first polymer chain is that of a homopolymer of PEO while the second is that of a polyacrylamide homopolymer. Calculations based on monomer molecular weights and polymer chian dimensions will indicate that the chain length of PEO is approximately 1.6 times that of the polyacrylamide polymer chain. This ratio would significantly increase if a co-monomer such as acrylic acid is copolymerized onto the polyacrylamide backbone. A higher polymer chain length

implies a higher radius of gyration (R_g) of the polymer chain in solution and, thus, improved flocculation efficiency.

A possible explanation for the decreased drainage brought about by certain retention aid systems can be correlated to the floc size formed by the polymers. Weak flocculants, typically those of low molecular weight, form small flocs due to their higher shear sensitivity. Small flocs form tighter sheets upon drainage. Tighter sheet have a decreased average pore size which causes an increase in filtration resistance. Conversely PEO systems form larger flocs due to the high molecular weight of PEO. Larger flocs result in more open sheets with larger pore sizes and a subsequent decrease in filtration resistance. At first the large flocs formed by PEO may seem a disadvantage since sheet formation may be adversely affected. However, the PEO system is very efficient when applied to high shear paper machines. The higher molecular weight of the PEO will initially form large flocs, which are subsequently broken-up into small flocs by the high shear forces. Thus both higher drainage and retention as well as good formation are attained. Lower molecular weight polymers form smaller flocs which are not resistant to the high shear forces. Thus the choice of the correct retention aid is also a function of machine used. From the data in Figures 4 and 6 we note that drainage rate is a function of flocculant molecular weight; the higher the molecular weight, the higher the drainage rate.

It has been shown that an increase in R_g correlates well with increased flocculation efficiency (85, 88, 89). In separate studies, Yu *et al.* (88) and Tjipangandjara *et al.* (89) have shown that stretched polymers (i.e., those with a higher R_g) provide better flocculation than coiled ones. A third study by Kitamura *et al.* (30) has also shown that randomly coiled and/or branched cationic polymers can form more bonding sites than rigid and/or linear polymers. Branching can be imagined as being a steric hindrance to the collapse of the polymer coil, thereby allowing a greater radius of gyration. Since pendant branching groups occupy space, the polymer coil would increase in size and extend the radius of gyration. Extension of the polymer coil would increase the ability of the polymer to form bridges between the cellulosic surfaces in the fibre-fines contacts. A more compact coiled polymer would have, by this reasoning, a lower bridge-forming ability than an extended polymer.

Another important factor which affects flocculation efficiency is polymer charge density. Wagberg and Lindstrom (90) have shown that if the polymer charge is increased above a certain critical level, typically 20 to 40 mole percent cationic charge, the forces associated with polymer-surface interactions tend to give the polymer a flatter configuration on the fibre surface and hence a decreased bridge-forming ability for CPAMs. This finding is in part supported by a recent study by Juntai (91) who found that the drainage rate did not improve significantly above a degree of substitution of 24 mole percent, although an optimum dosage level existed.

Thus two factors can be seen to affect flocculation efficiency of polymers: polymer chain length and polymer charge density. These factors help explain the effectiveness of the CPAM-2, CPAM-4, CPAM-3, and PEO retention aids.

Bentonite microparticle chemistries were found to become increasingly ineffective with increasing system closure. The BENT-2 bentonite exhibited the poorest qualities at 3 m^3/t. Presumably the large surface area of bentonite clay is capable of sorbing large quantities of detrimental substances. The bentonite clay, being covered with negative detrimental substances, may then be less able to properly form a complex with the retention aids. In turn, it becomes more difficult for the retention aid system to form a porous sheet thereby impeding drainage and causing much water to be held up by the fines.

It is believed that when the bentonite is saturated with adsorbed detrimental substances it is unable to form either a stable micro- (BENT-1) or macro-flocculated (BENT-2) structure with the polyacrylamide (92) or other retention aids. The fact that BENT-2 is more ineffective than BENT-1 can be a direct consequence of the bentonite addition sequence: BENT-2 is typically added prior to the PAM and further back in the system. BENT-1, on the other hand, is added after the retention aids have been added and typically very close to the headbox. At this point much of the detrimental substances may already have been neutralized or aggregated by the retention aids, allowing the bentonite clay to be flocculated more effectively. However, many of these mechanisms are still speculation and more study is evidently required.

CONCLUSIONS

At high degrees of closure, the PEO-cofactor chemistries proved to be the most efficient. The choice of the correct cofactor was found to be important. The results also confirmed that, with increased system closure, the increase in dissolved substances concentration tends to result in a poorer performance of cationic polyacrylamide polymers. It was generally found that the best performing CPAMs were those with high molecular weight and medium to high charge density. Coagulants used in conjunction with flocculants tended to have, in general, a neutral to slightly negative effect on the variables studied. Bentonite retention systems performed less well with increasing system closure.

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REFERENCES

1. Allen, L. H., Polverari, M., Levesque, B., and Francis, D. W., Tappi J., 82(4): 188-195 (1990).
2. Rahman, L., and Tay, C. H., Tappi J. 69(4): 100-105 (1986).
3. Lueng, P. S., and Goddard, E.D., Tappi J. 70(7): 115-118 (1987).
4. Lindström, T., and Söremark, C., J. Coll. Int. Sci. 55(2): 305-312 (1976).
5. Dobbins, R .J., Paper Trade J. 162(21): 42-46 (1978).
6. Didato, D. T., and Balliett, F., *in preprints,* 1991 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 445-448.
7. Baron, J. J., and Montani, R. C., *in preprints,* 1986 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 79-87.
8. Muller, F., and Beck, U., Paper 33(10A): 89-95 (1979).
9. Moore, E. E., Tappi J. 58(1): 99-100 (1975).
10. Lindström, T., Söremark, C., and Eklund, L., Pulp Pap. Can. 78(12): TR114-118 (1977).
11. Scalfarotto, R .E., and Tarvin, R. F., *in preprints,* 1984 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 65-75.

12. Farley, C.E., *in preprints,* 1987 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 295-299.
13. Fowler, A., Paper 187(3): 122 (1977).
14. Howard, G. J., Hudson, F. L., and West, J., J.Appl. Poly. Sci. 21: 1-16 (1977).
15. Howard, G. J., Hudson, F. L., and West, J., J.Appl. Poly. Sci. 21: 17-27 (1977).
16. Howard, G. J., Hudson, F. L., and West, J., J.Appl. Poly. Sci. 21: 29-43 (1977).
17. Howard, G. J., Hudson, F. L., and West, J., J.Appl. Poly. Sci. 21: 45-54 (1977).
18. Petäjä, T., Kemia-Kerni 7(3): 110-112 (1980).
19. Das, B. S., and Lomas, H., Pulp Pap. Mag. Can. 74(8): 95-100 (1973).
20. LeRoux, R., Armstrong, J. R., Lin, J. F., Polverari, M., Pruszynski, P., and Angelac, A. P., Pulp Pap. Can. 98(9): 54-61 (1997).
21. Doiron, B. E., *in preprints,* 1994 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 603-607.
22. Hagedorn, R. A., Tappi J. 71(8): 131-134 (1988).
23. Dykstra, G. M., and Wenzl, D. J. H., *in preprints*, 1987 Advanced Topics in Wet End Chemistry: TAPPI Press, Atlanta, pp. 21-34.
24. Adamsky, F. A., Gibbon, D.L., Simon, G. C., and Williams, R. H., *in preprints,* 1991 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 469-480.
25. Petäjä, T., Kemia-Kerni 7(3): 129-130 (1980).
26. Wilharm, M. T., *in preprints,* 1984 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 7-12.
27. Rahman, L., Tappi J. 70(10): 105-112 (1987).
28. Wagberg, L., and Lindström, T., Nordic Pulp Pap. Res. J. 2(2): 49-55 (1987).
29. Kitamura, M., Tanaka, H., and Sumimoto, M., *in preprints,* 1983 International Symposium on Wood and Pulping Chemistry, vol. 3: TAPPI Press, Atlanta, pp. 124-128.
30. Ford, P. A., *in preprints,* 1987 Advanced Topics in Wet End Chemistry: TAPPI Press, Atlanta, pp. 35-37.
31. Lowry, P. M., *in preprints,* 1988 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 231-234.
32. Langley, J. G., and Litchfield, E., *in preprints,*1986 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 89-92.
33. Smith, J. H., *in preprints,*1991 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 481-499.
34. Wearing, J. T., Barbe, M. C., and Ouchi, M. D., J. Pulp Pap. Sci. 11(4): J113-120 (1985).
35. Francis, D. W., Reside, D. A., and Wearing, J. T., Pulp Pap. Can. 99(12): 134-139 (1998).
36. Wearing, J. T., Huang, S., Piggott, A., Ouchi, M. D., and Wong, A., Pulp Pap. Can. 86(5): TR139-145 (1985).
37. Paris, J., International Environmental Conference and Exhibit, TAPPI Press, Atlanta, Book 1, pp. 267-279 (1998).
38. Towers, M., Richardson, B., Uloth, V., Singbeil, D., Hogikyan, R., Turner, P., Forget, C., Lownertz, P., Gleadow, P., Swaney, J., Wasik, L., Yu, J., Hastings, C., Constantin, E., and Yuen, T., private communication.
39. Dorica, J., Ramamurthy, P., Elliott, A., Crotogino, R., Vrooman, W., and Chatterjee, A. (to be published).
40. Herschmiller, D., Uloth, V.C., Gleadow, P., Wearing, J. T., and Galloway, L., private communication.
41. Towers, M. T., and Wearing, J. T., Technology and Environmental Enhancement in Pulp and Paper Mills Workshop Proceedings #3, Ottawa, pp. 61-74 (March 1994).
42. Williams, D. G., Tappi J. 56(12): 144-147 (1973).

43. Webb, L., Pulp Pap. Int. 37(1): 44-47 (1995).
44. Young, J., Pulp Pap., March 1994: 73-75 (1994).
45. Young, J., Pulp Pap., March 1994: 56-61 (1994).
46. Patel, J. C., Am. Papermaker 58(1): 36-39 (1995).
47. Jantunen, E., Pap., July 1993: 34-35 (1993).
48. Scott, W. E., Tappi J. 69(11): 30-34 (1986).
49. Linhart, F., Auhorn, W. J., Degen, H. J., and Lorz, R., Tappi J. 70(10): 79-85 (1987).
50. Springer, A., Dullforce, J. P., and Wegner, T. H., Tappi J. 69(4): 106-110 (1986).
51. Mutton, D. B., *in* Wood Extractives and Their Significance to the Pulp and Paper Industries, W. E. Hillis ed., Chap. 10, Academic Press, New York (1962), p. 333.
52. Allen, L. H., Tappi J. 71(1): 61-64 (1988).
53. Kleen, M., and Lindström, K., Nordic Pulp Pap. Res. J. 9(2): 111-119 (1994).
54. Thorton, J., Eckerman, C., and Ekman, R., *in preprints,* Appita 6th Int. Symp. on Wood and Pulping Chem. Proc. Vol. 1: 571-577 (1991).
55. Thorton, J., Ekman, R., Holmbom, B., and Eckerman, C., Pap. Puu 75(6): 426-431 (1993).
56. Thorton, J., Ekman, R., Holmbom, B., and Örså, F., J. Wood Chem. Tech. 14(2): 159-175 (1994).
57. Thorton, J., Ekman, R., Holmbom, B., and Pettersson, C., J. Wood Chem. Tech. 14(2): 177-194 (1994).
58. Thorton, J., Tenkanen, M., Ekman, R., Holmbom, B., and Viikari, L., Holzforschung 48(5): 436-440 (1994).
59. Roick, T., Schmitt, G., Schempp, W., Wochenbl. Papierfabr. 122(12): 506-509 (1994).
60. Örså, F., and Holmbom, B., J. Pulp Pap. Sci. 20(12): J361-366 (1994).
61. Sundberg, K., Thornton, J., Holmbom, B., and Ekman, R., J. Pulp Pap. Sci. 22(7): J226-230 (1996).
62. Sjöström, J., Nordic Pulp Pap. Res. J. 5(1): 9-15 (1990).
63. Sjöström, L. and Ödberg, L., Wochenbl. Papierfabr. 122(8): 302-309 (1994).
64. Ekman, R. and Holmbom, B., Nordic Pulp Pap. Res. J. 4(1): 16-24 (1989).
65. Ekman, R. and Holmbom, B., Nordic Pulp Pap. Res. J. 4(1): 188-191 (1989).
66. Alvarado, F., Lindström, K., Nordin, J., and Österberg, F., Nordic Pulp Pap. Res. J. 7(1): 37-41 (1992).
67. Gill, R. I. S., Pap. Technol. 37(6): 23-31 (1996).
68. Nylund, J., Byman-Fagerholm, H., and Rosenholm, J. B., Nordic Pulp Pap. Res. J. 8(2): 280-283 (1993).
69. Stenberg, E., and Norberg, G., Pap. Puu 59(10): 652 (1977).
70. Anderson, R., Stenberg, E., and Sjögren, B., Tappi J. 63(4): 111-115 (1980).
71. Roppenen, M., Paperi Puu 82(4a): 233-243 (1979).
72. Melzer, J., and Küster, U., Papier 10A(10): v32-40 (1982).
73. Heller, P., Scott, W. E., and Springer, A. M., Tappi J. 62(12): 79-84 (1979).
74. Sjöström, J., Holmbom, B., and Wiklund, L., Nordic Pulp Pap. Res. J. 2(4): 123-131 (1987).
75. Wågberg, L. and Åsell, I., Coll. Surf. A: Physicochem. Eng. Aspects 104: 169-184 (1995).
76. Springer, A., McMahen, W. W., and Boylan, J., *in preprints,* 1984 Tappi Papermakers Conference: TAPPI Press, Atlanta, pp. 13-22.
77. Alince, B., *in preprints,* 1987 Tappi Papermakers Conference: TAPPI Press, Atlanta, pp. 165-168.
78. Linhart, F., Auhorn, W. J., Degen, H. J., and Lorz, R., Tappi J. 70(10): 79-85 (1987).
79. Hoel, H., and Aarsand, R., Nordic Pulp Pap. Res. J. 10(2): 98-103 (1995).
80. Wågberg, L., and Ödberg, L., Nordic Pulp Pap. Res. J. 6(3): 127-135 (1991).

81. Ström, G., and Kunnas, A., Nordic Pulp Pap. Res. J. 6(1): 12-19 (1991).
82. Sundberg, A., Ekman, R., Holmbom, B., and Thornton, K., Nordic Pulp Pap. Res. J. 8(1): 226-231 (1993).
83. Meersman, T., *in preprints,* 1991 Tappi Papermakers Conference: TAPPI Press, Atlanta, pp. 559-567.
84. Springer, A., Nabors, L. A., and Bhatia, O., Tappi J. 74(4): 221-228 (1991).
85. Shastri, S., *in preprints,* 1983 Tappi Papermakers Conf.: TAPPI Press, Atlanta, pp. 205-210.
86. van de Ven, T. G. M., and Alince, B., J. Pulp Pap. Sci. 22(7): J257-263 (1996).
87. Yu, X. and Somasundaran, P., J. Coll. Inter. Sci. 178: 770-774 (1996).
88. Tjipangandjara, K. F. and Somasundaran, P., Coll. Surf. 44: 420 (1989).
89. Wagberg, L. and Lindstrom, T., Nord. Pulp Pap. Res. J. 2(4): 152-160 (1987).
90. Juntai, L., Tappi J. 78(4): 149-154 (1995).
91. Rousseau, S. and Doiron, B., in preprints, 82nd Annual CPPA Meeting Technical Section: B87-89 (1996).

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