

**Characteristics of Floc: Interplay between Retention Aid and Hydrodynamic
Forces Effects in Fines Flocculation**

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Abstract

Flocculation of particles with cofactor (CF) and polyethylene oxide (PEO) is widely used to retain particles in sheet and coat surfaces, where floc size selection is quite essential to fulfill sheet and surface specifications. In this work we studied the effects of CF addition with PEO and hydrodynamic forces on floc size and flocculation fastness. In one result, we found that increases in CF addition, with constant PEO and stirring rate, caused an increase in floc size (amplitude) and a decrease in characteristic time of flocculation (fast flocculation). In the second result, stirring rate increase at constant CF-PEO addition caused a decrease in floc size and an increase in characteristic time of flocculation. Plotting stirring rates, CF additions with constant PEO, and characteristic times of flocculation versus floc size on x-axis was proposed as a method enabling operator in mill to fix the wanted floc size and select the values that satisfy less cost.

Key words: fines, polyethylene oxide, cofactor, stirring rate, flocculation.

Introduction

Best retention aid systems of dual or multi components are used in retention processes to flocculate and retain colloids and fines. Higher molecular weight, the water soluble and neutral polyethylene oxide (PEO) is used as an alternative to conventional cationic retention aids due to their interference with charged substances in furnishes [1,2]. PEO was found working efficiently with a cofactor (CF) having phenolic groups [1,2,3]. The most conventionally used cofactors were modified phenolic resin (MPR), sulphonated kraft lignin (SKL), phenol formaldehyde resin (PFR), tannic acid (TA) and sodium naphthalene sulphonate (SNS) [4]. Despite phenolic resins and PEO do not adsorb on some colloids, fines and fiber, the combinative retention aid system was found effective [5]. One hypothesis explained the work of the retention aid was transient the network mechanism; stating that fillers were captured by the polymeric network and smaller ones passed its holes [5]. The second hypothesis was the mechanism of association-induced polymer bridging by van de Ven and Alinec [6], who argued the network mechanism, and showed bridging of fillers in two ways. One, PEO coils are expanded by the negatively charge CF segments adsorbed on the coils, making them capable to bridge surfaces; CF works as a stiffness modifier enlarging the size of PEO coil (δ) to a size greater than the thickness of electrostatic double layer (κ^{-1}); $\delta > \kappa^{-1}$ [7]. In this case, the adsorbed CF segments on PEO coils induce repulsion among the coils causing them to expand, resulting in the CF-PEO complex, which in turn works as a polyelectrolyte (De Witt, et al., 1992 [7]. Second way; the cofactor adsorbs on surfaces facilitating for PEO adsorption, reducing PEO molecule entropy making it more compact. Explanation of induce polymer bridging between similar and dissimilar colloid, fines,

and fiber shown in Fig.1b: added CF made PEO a stiffer complex; Fig.1c: PEO adsorbs on adsorbed CF on surfaces; Fig.1a: PEO alone couldn't adsorb on surfaces and was small not to bridge surfaces [6].

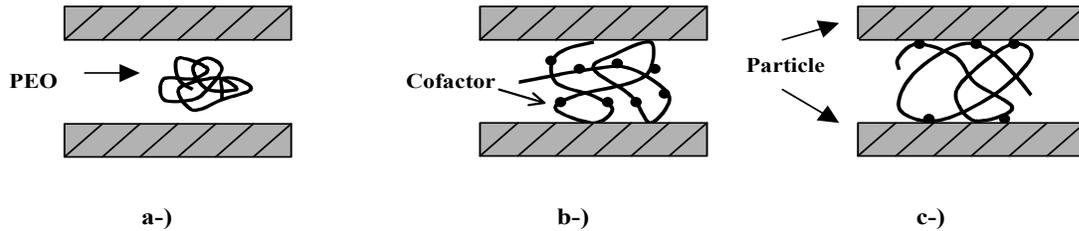


Fig. 1: Schematic of association-induced polymer bridging. Here; a-) no chain adsorption onto surfaces; b-) polymer adsorption and bridging occur when association stiffens the chain; c-) Bridging also occur when cofactor links PEO coils to surfaces.

In retention processes, flocculation takes place when particles are interacted and bridged by CF-PEO, where some interactions are desirable. In papermaking, selection of interactions depends upon required paper sheet properties and quality aim of production. Fiber interactions are undesirable since fiber flocs lead to heterogeneous sheet. Fiber-filler interactions are desirable for incorporation of small particles into sheet, improving sheet property and reducing circulation cost of white water [8]. Similarly are fines-fines and fines-fillers interactions, which improve sheet strength, permeability, opacity, and density. Interaction among fillers, leading to fillers aggregates, can either be desirable or not. When the aim of production is to incorporate large amount of fillers to lower the cost, these interactions are desirable. When the aim is to improve optical and printing properties of sheet, coagulation of fillers is undesirable, since individual particles scatter light better. Polymer interactions with suspended particles can be desirable or not depending on required bridging [8].

Flocculation processes bridging dissimilar particles (heteroflocculation) or similar ones (homoflocculation) apply langmuir isotherm [8,9] with flocculation rate (r_f); the net of attaching and detaching rates. The factors affecting process are leading either to flocculate or disperse the particles in suspension. When polymeric retention aid is used, flocculation rate is enhanced by factors enhancing flocculation efficiency (η), which becomes when a polymer used the capture efficiency (α) of the polymer; $\eta = \alpha$ [10]. When the polymer used is PEO with CF, flocculation efficiency η will be a function of factors in PEO and CF. One factor is PEO quantity (Γ) added, usually related to PEO quantity needed to maintain full coverage on surfaces (Γ_m) and expressed in term of fractional coverage $\theta(=\Gamma/\Gamma_m)$. Here, flocculation efficiency was found to apply $\eta = 2\theta(1-\theta)$ [8,11]. The second factor is CF quantity added to suspension or CF to PEO ratio (ϕ), which was found acting to determine the CF-PEO complex size and to its bridging bond strength [12]. The third factor is the shear rate (G) subjected to flocculation process in state of flow or stirring rate N (rpm) in a vessel. The forth factor are ones, existing in units prior to addition to flocculation process and affecting PEO coil microstates, were found to dissociate the PEO entanglements into free coils and smaller entanglements, lowering the PEO efficiency to bridge and flocculate particles [8,13]. The PEO entanglements were initiated in early dissolution in a clear solution when PEO granules were dissolved in water [14]. The entanglement needs at least two interacted coils to form a size larger than a single coil, and gets larger with more interacted coils. Addition of PEO entangled coils with CF produced the CF-PEO complex having a larger size and stronger bridging bonds with surfaces that enhance

flocculation efficiency [8]. In previous work, effects of the process factors, shear rate G and ratio ϕ , on flocculation performance were investigated with their effects on floc size and flocculation fastness. When ϕ at low values was increased, faster flocculation was performed producing larger flocs. When stirring rate N (shear rate G) was increased in flocculation vessel at constant ϕ , faster flocculation was performed producing smaller flocs. In high turbulent flow, having the effective shear rate (G_{eff}) approaching mill conditions, flocs production were also recorded in a flow loop [8].

Taking into consideration, the process factor effects on flocculation mechanism and efficiency studied in previous work and literature, the aim of a mill to produce a specific floc size in less flocculation time and low cost, the objective of this work was to study the process factors (ϕ and G) effects on floc size and flocculation fastness in a wider scale of G and ϕ values that would show clearer effects, guiding mills to their aim. To fulfill these objectives, flocculation experiments at different values of G and ϕ were performed to measure floc size and flocculation fastness. A characterization method was also proposed as a second objective: the resulted floc size and flocculation fastness can be related to the corresponding G and ϕ values. This method when applied in mills, at operation conditions, will serve mills to adjust their CF and G settings at values maintaining the required floc size and the minimum process time. In this work; flocculation amplitude (A_m) was taken as a measure floc size; initial rate (r_f) and characteristic time of flocculation (τ) were taken as measures of flocculation fastness; the particles used were fines, the fiber fragments passing the holes of 76 μm screen [15].

Experimentation

Materials

Fines: the material to be flocculated in experimentation was fines, separated by filtration of a mixture of different pulps taking the particles passing a filter of 200 mesh (76 μm opening).

Retention aids: two components; one was PEO polymer known as (flocc 999) of about 7 million molecular weight used as a flocculent, and the second was Interac 1323 (a phenolic material) used as a cofactor. Pulps were provided by Masson Maclaren Mill (Canada) and retention aids were provided by I.Q.U.I.P Inc (Canada).

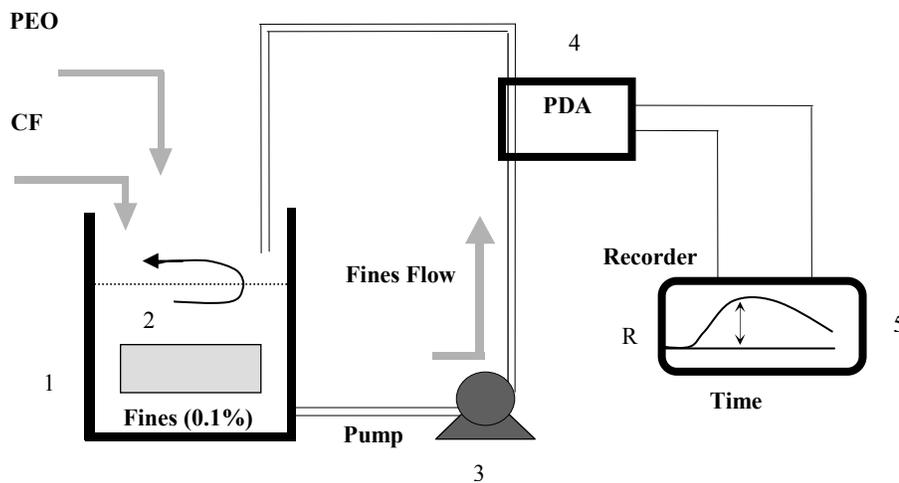


Fig.2: Experimental set up of flocculation vessel: 1 = flocculation vessel (Beaker), 2 = mixer, 3 = peristaltic pump, 4 = PDA, 5 = Recorder.

Experimental Setup

Figure 2 shows the experimental setup of flocculation process was used in previous work [8]. Fines of 0.1 % consistency was added to flocculation vessel (beaker) and mixed at a selected stirring rate N (rpm). Fines suspension was circulated by a peristaltic pump via a transparent tube passing the photo cell of Photometric Dispersion Analyzer (PDA) [16]. The PDA out put signals; voltage of direct current (Dc) and voltage ratio (R) of alternating to direct currents were plotted versus time by a recorder. Retention aids were added to fines after initiating steady state; CF was added first followed by PEO.

Flocculation Readings

The Dc signal is one reading resulted from the light intensity transmitted through fines suspension indicates particle concentration. Ratio reading R is the ratio of alternating to direct current voltages. Alternating voltage represents the root mean square (rms) of transmitted light and indicates the rms of particle number, while ratio R indicates particle size taken as a measure of flocculation intensity [16]. In this work, reading R was taken as vertical distance the pen moved in arbitrary unit (A.U.). Both Dc and R readings were plotted versus time (t) by a recorder. Measures of fines flocculation shown in (Fig.3) were: initial rate of flocculation $r_f (= A_m / \tau)$, the slope of curve R at initial time; flocculation amplitude A_m , the reading R at equilibrium denoting the maximum floc size; characteristic time of flocculation τ

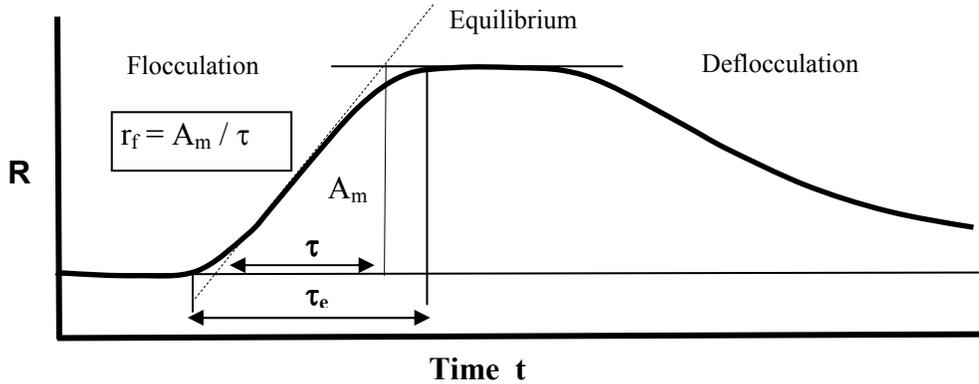


Fig.3: Measures of fines flocculation.

the time denoting flocculation fastness; equilibrium time τ_e , the time needed to reach equilibrium; deflocculation was also noticed after reaching equilibrium as a drop in reading R with time. Deflocculation rate (r_d) was considered as the slope of drop in reading R at initial deflocculation.

Results and Discussion

Taking flocculation amplitude A_m (floc size) as a measure of floc quality, characteristic time of flocculation τ as a measure of flocculation fastness and operation cost, and considering both CF and G roles in flocculation process, two experiments were performed to characterize fines flocculation with CF-PEO retention aid. In first experiment, fines flocculation was performed at

low and constant stirring rate $N = 50$ (rpm), constant PEO (0.08 mg/gm fines), and variable CF. Significant increases in amplitude A_m and initial rate r_f are shown (Fig.4) with the increase in CF, which are attributed to CF role in stiffening the PEO coils and strengthening the bridging

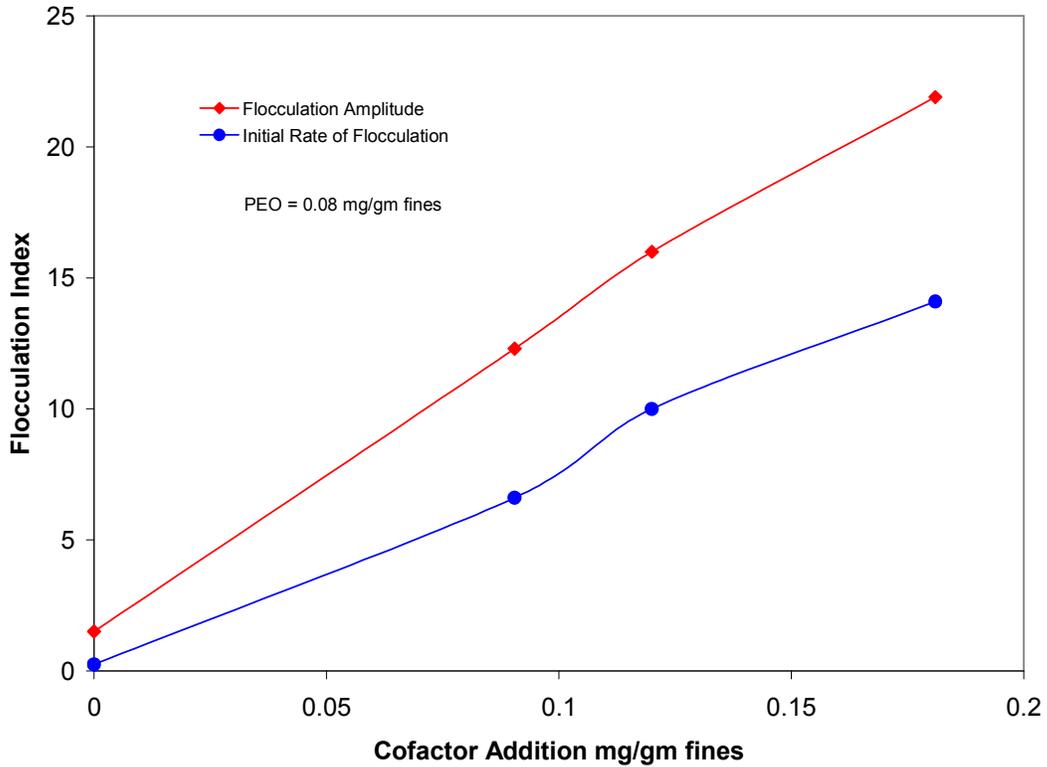


Fig.4: Effect of cofactor addition on fines flocculation at constant PEO in a beaker at low shear rate, $N = 50$ (rpm).

bonds between the coils and the surfaces, enhancing flocculation rate [6,7]. The transient flocculation was also recorded in all performed runs with deflocculation after equilibrium. No

more detail are given in this work on the transient behavior, since sufficient information showing the transient behavior causes were recorded in our previous work. In this work, we notify to deflocculation just to show the importance of the equilibrium time τ_e in flocculation process to avoid deflocculation, which occurs after equilibrium. The deflocculation rate r_d in performed runs was, comparatively with flocculation rate r_f , estimated very small with a scale a round r_d/r_f (≈ 0.13), indicating that flocs will destruct in longer time sufficient to save flocs.

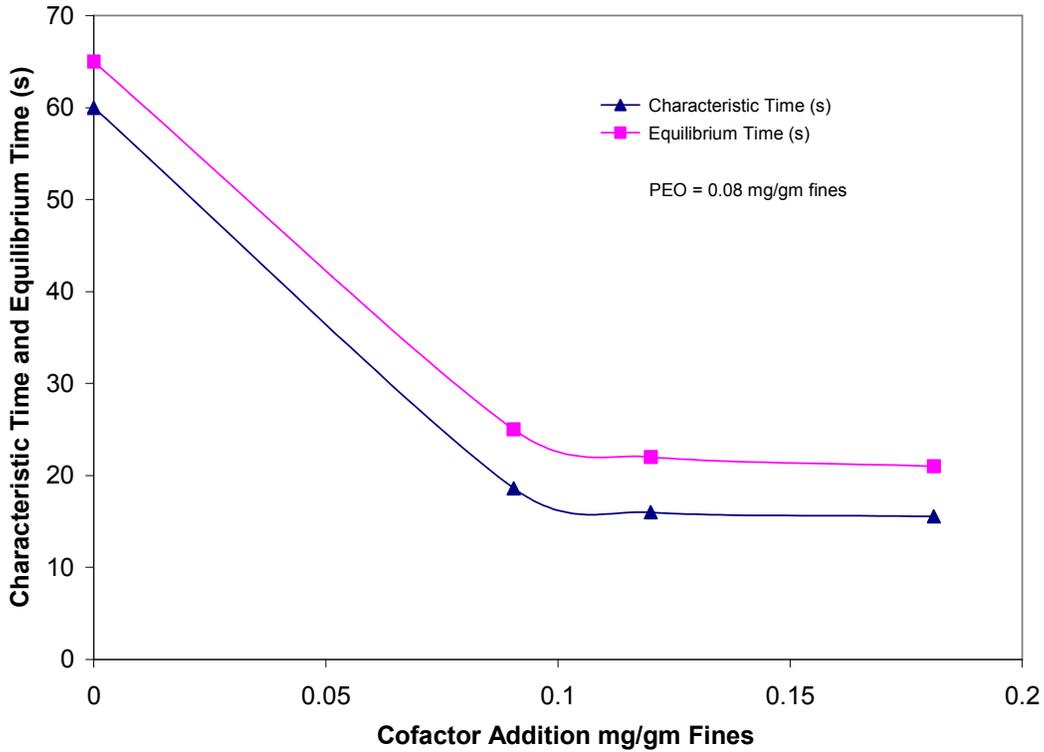


Fig.5: Effect of cofactor addition on characteristic time and equilibrium time of flocculation at constant PEO in a beaker at low shear rate, $N = 50$ (rpm).

Estimation of characteristic time of flocculation τ is quite necessary in flocculation processes, since processes having smaller τ are faster and having less operating cost. Comparing τ of flocculation using PEO alone (CF = 0) with τ of flocculation using CF- PEO (Fig.5), increment in CF addition at constant PEO (increment in ϕ) to a value around 0.1 mg/gm fines ($\phi=1.25$) caused a drastic drop in τ from 60 to 15 s. This drop indicates that the rate r_f with CF addition is four times faster than the rate with PEO alone. For CF values larger than 0.1 mg/gm fines ($\phi >1.25$), flocculation fastness determined by $\tau \approx$ (constant) becomes a weak function of CF addition. Taking that CF addition has two actions: increasing flocculation fastness (Fig.5) and increasing floc size (Fig.4), and combining results in Figures 4 and 5, we conclude that for CF addition larger than 0.1 mg/gm fines ($\phi >1.25$); it is seemingly acting to increase floc size only. For more, the characteristic time of flocculation was shown less than equilibrium time ($\tau < \tau_e$). Estimation of τ_e is important to determine maximum floc size A_m and to avoid un-favored deflocculation. Estimation of τ_e was experimentally obtained from flocculation curve (Fig.3) or using numerical methods solving Longmuir equation that fits flocculation [8]. Such results are important to flocculation unit design and cost.

The second experiment (Fig.6) was flocculation runs performed at different stirring rates N , constant CF (0.25 mg/g fines) and constant PEO (0.12 mg/g fines) of moderate ratio ϕ (= 2.1). Results (Fig.6) showed that the increase in stirring rate N caused a decrease in initial rate r_f and amplitude A_m (floc size), and a decrease in characteristic time τ (or τ_e) at stirring rate larger than $N = 240$ (rpm). Furthermore, at low shear rate $N = 50$ (rpm), large flocs were

produced with flocculation fastness of $\tau=15$ s, and comparatively, small flocs were produced with same fastness $\tau=15$ s at high shear rate $N=300$ (rpm). Other runs performed at higher stirring rates N with PEO alone showed no response in ratio reading R (dispersion action) indicating no flocculation due to high detachment rates subjected on flocs, confirming previous work [8,13]. Although CF acted to induce PEO association bridging [6,17] and to strengthen bridging bond at surfaces [6], dispersion by high shears caused to reduce floc size.

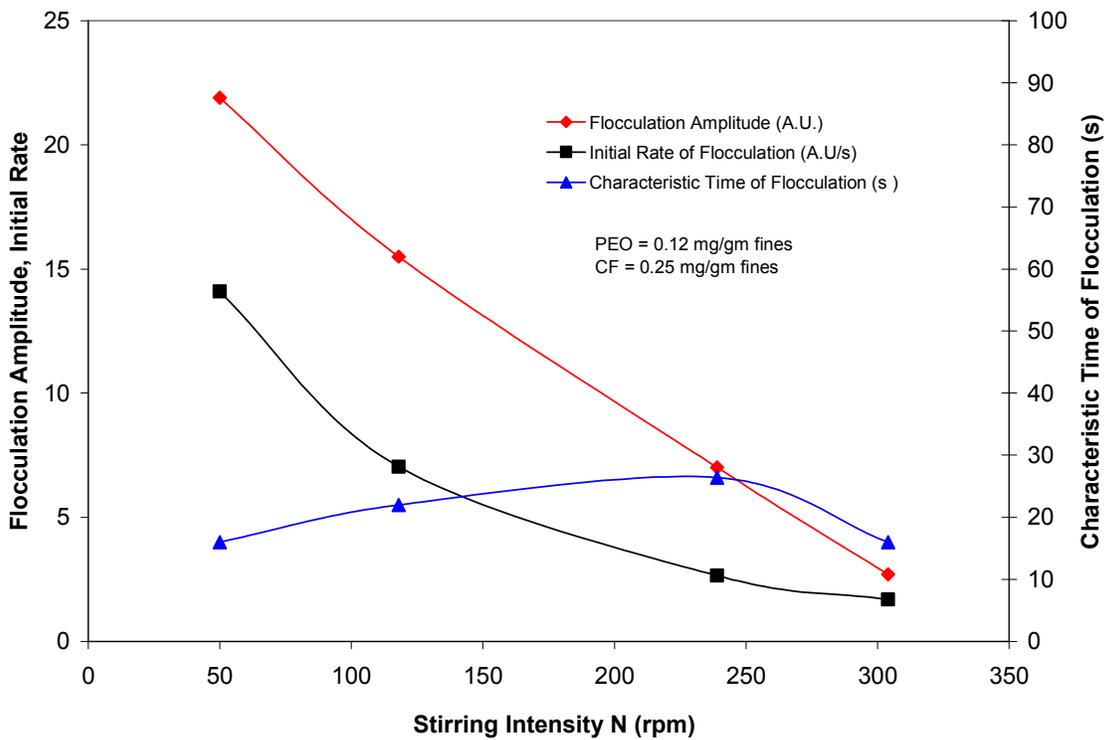


Fig.6: Effect of shearing (Stirring N) on fines flocculation with CF-PEO in a beaker

In flocculation unit, the following times are important; characteristic time τ , equilibrium time τ_e , and residence time (τ_r). Time τ indicates flocculation fastness, and τ_e is the time needed to get maximum floc size with $\tau_e > \tau$. Residence time $\tau_r (=V/Q)$ is the actual time that particle stay in flocculation unit of a volume (V) and volumetric flow rate (Q). These times are important in unit design and should satisfy the order $\tau_r \geq \tau_e > \tau$.

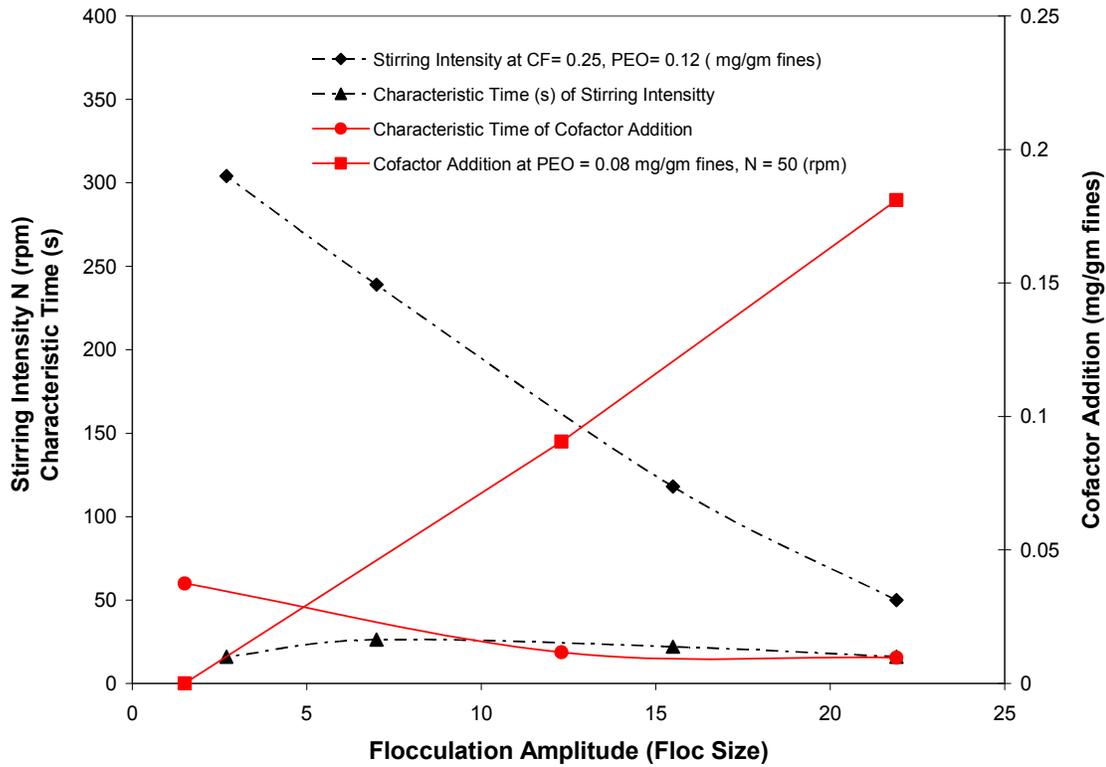


Fig.7: Characterization of fines flocculation with CF-PEO Retention aid, a method to select wanted floc size

In literature [17] PEO alone could flocculate small fines at low shear rates; similarly was for fillers and colloids [21]. Combination of CF-PEO at low and high shear rates also flocculated colloids [8,14]. In this work, results confirmed the CF-PEO ability to flocculate particles in a

large size scale (fines $\leq 76 \mu\text{m}$) and showed that resulted floc size A_m and characteristic time τ were functions of shear rate G (stirring intensity N) and CF to PEO (ratio ϕ) addition. Since floc size determines floc quality, the required quality of floc will be a function of G and ϕ ; say; $A_m = f_1(G, \phi)$. Similarly is characteristic time of flocculation $\tau = f_2(G, \phi)$, which determines flocculation fastness and operating cost, which in turn becoming a function of G and ϕ .

Based on experimental results, we have proposed a method to characterize flocculation process, which is simply plotting G in form of N (rpm), ϕ , and τ in y-axis versus floc size A_m in x-axis. Such plot (Fig.7) shows four curves: one curve is stirring intensity and second curve is its corresponding characteristic time taken as dotted lines. The third curve is cofactor addition and forth curve is its characteristic time taken as solid lines. The method comprises the following steps. One is fixing the wanted floc size (quality) on x-axis. Two is finding the corresponding needed values of N (rpm) and τ using curves of stirring intensity curve and its characteristic time curve. Three is finding the corresponding needed values of cofactor CF (mg/gm) or ϕ and τ using the curve of cofactor addition and its curve of characteristic time. Four is choosing either stirring intensity experiment or cofactor addition experiment; the one is of less operation cost or that satisfying production aim. Assuming that the two experiments are to be done in same flocculation vessel, differences in cost for the two experiments will be operating cost, which is directly proportional to the used CF and N , and inversely to τ . For explanation, let a floc of 15 (A.U.) is the wanted size. We first fix this value on x-axis, and find the corresponding stirring intensity $N = 120$ (rpm), characteristic time $\tau = 22$ (s) and $\phi = 0.25 \text{ mg CF} / 0.12 \text{ mg PEO}$, using

stirring intensity curves. These data are compared with $N = 50$ (rpm), $\tau = 18$ (s) and $\phi = 0.11 \text{ mg CF} / 0.08 \text{ mg PEO}$ that giving the same floc size (15 A.U.), using cofactor addition curves. If the choice is to get less operation cost, mill operator will chose setting at $\phi = 0.11 \text{ mg CF} / 0.08 \text{ mg PEO}$ and $N = 50$ rpm. If the choice is to maintain dispersion at this floc size, the case of a fiber floc dispersion to maintain a homogeneous paper sheet, mill operator will chose the higher stirring setting.

Concluding Remarks

In this work, increasing CF addition at constant PEO with a moderate CF to PEO ratio caused flocculation amplitude (flocs size) and rate to increase by a mechanism of induced PEO association bridging. Such action is related to CF role in stiffening PEO coils that enhances flocculation, and in strengthening bridging bond between PEO coils and surfaces. Addition of CF also caused characteristic time of flocculation to decrease making flocculation faster (less operating time). The no flocculation with PEO alone at high shear rates indicated weak bridging bond by PEO between fines surfaces. Increasing shear rates in fines flocculation with CF-PEO system caused floc size to decrease, and characteristic time to plateau a curve. Characteristic time of flocculation and equilibrium time are important parameters in flocculation unit design. Characterization of fines flocculation with cofactor additions at constant PEO (variable cofactor to PEO ratio) and with shear rate intensities initiated a method to adjust flocculation process at required floc size and production aim.

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Nomenclature

Parameters			
Name	Symbol	Name	Symbol
Amplitude of flocculation (at equilibrium)	A_m	Initial rate of flocculation	r_f
Arbitrary unit	A.U.	Polymer layer thickness	δ
CF to PEO ratio	ϕ	Quantity of PEO added	Γ
Characteristic time of deflocculation	τ_d	Quantity of PEO to maintains full coverage	Γ_m
Characteristic time of flocculation	τ	Ratio reading	R
Capture efficiency	α	root mean square	Rms
Deflocculation rate	r_d	Simple shear rate in beaker	G
Direct current voltage	Dc	Simple shear rate in tube	G_t
Electrical double layer thickness	k^{-1}	Stirring rate (rpm)	N
Equilibrium time	τ_e	Time	t
Flocculation efficiency	η	Volume of a Unit	V
Fractional Coverage	θ	Volumetric flow rate	Q

Substances and Equipments			
Cofactor	CF	Polyethylene oxide	PEO
Photometric Dispersion Analyzer (PDA).	PDA	Sodium naphthalene sulphonate	SNS
Modified phenolic resin	MPR	Sulphonated kraft lignin	SKL
Phenol formaldehyde resin	PFR	Tannic acid	TA