

Carboxy Methyl Cellulose As A Protective Colloid For ASA Particles

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ABSTRACT

The purpose of paper sizing is to provide hydrophobicity to the paper either by acidic, neutral or alkaline sizing agents. At present ASA (Alkenyl succinic anhydride) sizing in alkaline process conditions is dominating over paper industries. ASA is fast curing size, with faster rate of hydrolysis when comes in contact with water. Cationic starch is the most commonly used stabilizer for making ASA emulsion with high starch to ASA ratio of around 3:1 and the prepared emulsion has a shelf life of only few minutes. Attempts have been made to improve the emulsion stability by providing the hydrophobic encapsulation to the ASA particles providing better colloidal stability in terms of particle size distribution, Cobb value and contact angles. Carboxy methyl cellulose with different molecular weights have been studied and it was found that the coverage to the ASA surface provided by the continuous layer of low molecular weight CMC gives better colloidal stability up to 2 hours without using organic acids for pH reduction.

Keywords: ASA, Contact angle, Surface energy, Cationic starch, CMC, Hydrolysis

Introduction

Alkenyl succinic anhydride (ASA) is a fast reactive sizing agent for cellulosic fiber to attribute hydrophobicity. Sizing develops in paper on machine with ASA while with alkyl ketene dimers (AKD) hydrophobicity develops with the passage of time. ASA is produced from the reaction of an isomerized olefin with maleic anhydride which attributes reactive functionality to the ASA, while the long chain alkyl group provides the hydrophobic properties. The resulting succinic anhydride group is extremely reactive and forms a complex with hydroxyl groups on cellulose, starch and water^{2,3,4}. However, there are a few problems with the ASA sizing: (a) poor stability of ASA emulsion and (b) the sticky behavior of hydrolyzed ASA⁵. ASA hydrolyses in aqueous emulsion to form alkenyl succinic acid, which is unfavorable to sizing. To avoid hydrolysis, ASA emulsion is used within a few minutes from the time of preparation⁶. The parameters which determine the stability of ASA are pH, temperature, viscosity of emulsifying agent and the particle size of ASA in emulsion. The smaller the particles, the greater will be the exposed surface area and better the sizing efficacy. Protective covering of ASA particles with any other cationic/anionic polymeric molecule shield the exposed area of the ASA particles without interfering in its reaction with cellulose molecules. If the continuous phase of the emulsion encapsulates a particle or droplet, the polymer segments avert the aggregation between the ASA particles and acts as a stearic barrier against adhesion. This will reduce the hydrolysis rate of ASA emulsion and protect the emulsion stability.

Cationic starch is mostly used as protective colloid for making the ASA emulsion. Though the molecule is effective, it offers the stability to the emulsion for a few minutes. Scientists throughout the world are working to find the alternative molecule for enhancing the emulsion stability. The present communication is based on the study of encapsulation of ASA particles with the carboxy methyl cellulose as protective colloid in terms of particle size distribution, sizing behavior such as Cobb value and contact angle.

Experimental

Materials

Bleached pulp was collected from an integrated pulp and paper mill using bleaching sequence of $C_6E_{OP}D_1D_2$. ASA oil (pale yellow in color), cationic starch (tapioca based) of neutral pH with degree of substitution of 0.035 and carboxy methyl cellulose of different molecular weight were used during the experimentation. Cationic fatty acid condensation product as fixing agent and poly aluminum chloride (PAC) having 17% alumina was used during the stock preparation.

Methods

Pulp was dispersed in a disintegrator and refined in PFI mill (model 516 of HAMJERN MASKIN, Norway) to 28 ± 1 °SR. Cationic starch of 3% consistency was cooked at 90 ± 2 °C for 30 minutes with continuous stirring using a mechanical agitator. ASA emulsion was prepared at

ambient temperature using a high shear mixer with the addition of ASA oil gradually to the dispersion of cationic starch or CMC. The ASA content of 1% was maintained in all the emulsions while the ASA to protective colloid ratio was varied. Distilled water was used for preparation of different chemical solutions. The CMC solutions were prepared with the gradual addition of CMC in hot water at 75° C and stirring at 2000 RPM for 20 min. Distilled water was used for the preparation of different chemical solutions.

Stock was prepared with the addition of different components in the following sequence: pulp, CFA (cationic fixing agent), PAC (poly aluminium chloride), cationic starch and then ASA. The retention aid (cationic polyacrylamide) was added in the thin stock while adding the chemicals in pulp slurry under constant agitation. Hand sheets of 70 g/m² were prepared according to Tappi standard T 205 sp-02, pressed and air-dried.

Image analyzer (Buehler, USA) was used for measuring the particle size distribution of ASA emulsion. Stock properties viz. potential, cationic demand, zeta potential and conductivity were measured using particle charge detector (Mutek PCD 03 pH) and Zeta potential meter (Mutek SZP 06) respectively. The air dried sheets were conditioned for 2 hours in the paper testing lab, maintained at 23±1°C and 50±2% relative humidity as per

Tappi standard T 402 sp-98. Cobb₆₀ values of 5 sheets of each set were determined with distilled water on smooth side as per Tappi standard T 441 sp-98. Contact angle and surface energy were determined by drop shape analyser (DSA 10-MK2 of KRUSS, Germany) having DSA1 program for calculation of surface energy.

Results And Discussion

General characteristics of cationic starch and carboxy methyl cellulose (CMC) used in preparation of ASA emulsion are shown in Table 1. The cationic starch and CMC are having degree of substitution of 0.035 and

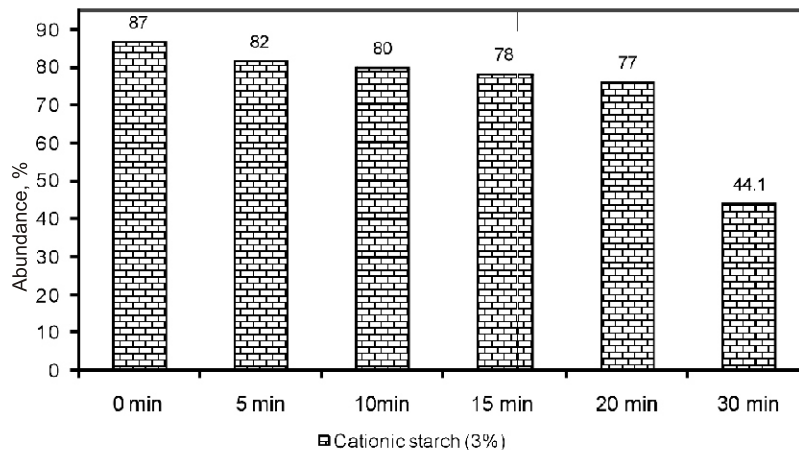


Fig 1: Effect of time on abundance of ASA particle below 1 micron in the emulsion prepared with cationic starch

Table 1: General characteristics of different protective colloids at 0.1% concentration

Parameter	Cationic starch	CMC-1	CMC-2	CMC-3
pH	7.4	5.9	6.0	6.2
Charge	Cationic	Anionic	Anionic	Anionic
Potential (mV)	+737	-617.8	-663.0	-722
Anionic demand (meq/l)	+1939.3	--	--	--
Cationic demand (meq/l)	--	2892	3324	3802
Molecular weight	--	Low	medium	high
Viscosity, cp (1% w/v)	2460 [#]	22*	27*	32*

[#] Viscosity at 75°C & 20 RPM, *Viscosity at 100 RPM & room temperature

0.6-0.95 respectively. The cationic starch is slightly alkaline in nature and its anionic demand is quite high i.e. 1939.3 µeq/l.

Three grades of CMC having low to high molecular weight were used in the study; CMC-1 of low molecular weight and highly anionic, CMC-2 and CMC-3 are of medium and high molecular weight respectively. The latter two are anionic in nature having cationic demand of 3324 and 3802 µeq/l respectively.

Table 2: Sizing behavior of ASA emulsion with cationic starch as protective colloid

ASA , kg/t	Cobb ₆₀ , g/m ²	Contact angle, °								Surface energy, mN/m	Potential, mV	Charge demand, µeq/l	Conductivity , mS	Zeta potential, mV	pH
		Time interval, s													
		5	10	20	30	40	50	60	Avg.						
2.0	25.2	116.9	117.4	120.0	120.7	120.9	120.8	121.3	120.3	11.49	-214.3	-6.8	0.481	-4.1	7.9
1.8	27.2	114.6	114.3	114.2	114.5	115.0	114.9	114.8	114.5	14.54	-220.0	-7.1	0.499	-4.7	7.9
1.5	32.3	108.3	108.4	108.2	108.2	108.1	108.0	108.0	108.2	17.78	-235.5	-7.3	0.501	-5.8	7.9
1.2	42.3	102.6	102.5	102.2	103.2	103.3	102.3	103.4	102.6	21.48	-239.1	-7.5	0.494	-7.3	8.0
1.0	50.3	97.8	102.2	102.7	102.8	102.2	102.5	102.1	102.2	21.69	-260.3	-7.8	0.502	-7.5	7.9

Cationic starch as protective colloid

With cationic starch as protective colloid in combination with citric acid (0.12 g/l) and PAC (8.9 g/l) for controlling the particle size and foam respectively, ASA emulsions were prepared with ASA to starch ratio of 1: 3. It was observed that abundance of ASA particles which was initially 87% below one micron decreased to 77% after 20 min of time (Fig.1). ASA dosage, resultant Cobb₆₀ and contact angle of the sized paper sheets with the use of cationic starch as protective colloid are given in Table 2. At ASA dose of 1.5 kg/t of pulp, the Cobb₆₀ was 32.3 g/m² and contact angle was 108.2°. This particular ASA dose was taken as reference for further analysis and comparison of stability of ASA emulsion prepared with the specific protective colloids under study. Coalescence of ASA particles took place after retention time of 20 minutes and the emulsion was destabilized at a faster rate.

Carboxy methyl cellulose as protective colloid

The ASA emulsion was prepared using carboxy methyl cellulose (CMC-1) with ASA to CMC ratio of 1:1 and 1:0.5. It was observed that there is a sharp decline in abundance of ASA particles less than one micron with passage of time, when the ASA to CMC ratio was 1:0.5 for making ASA emulsion (Fig.2). However, when it was prepared with

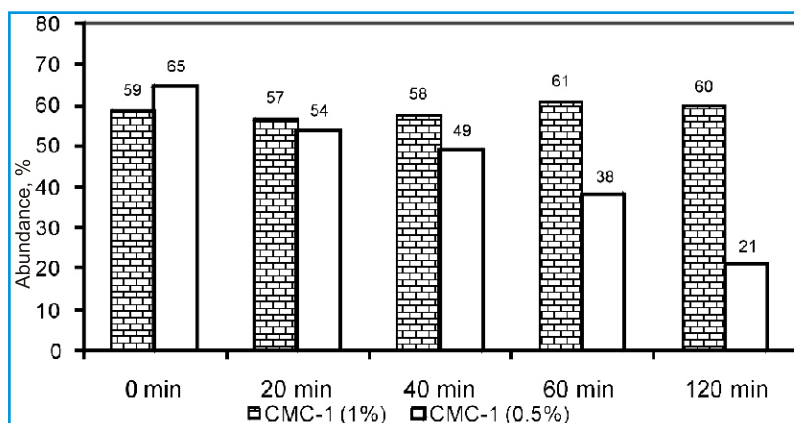


Fig 2: Effect of time on abundance of ASA particles below 1 micron (Emulsion prepared with CMC-1 at different concentrations)

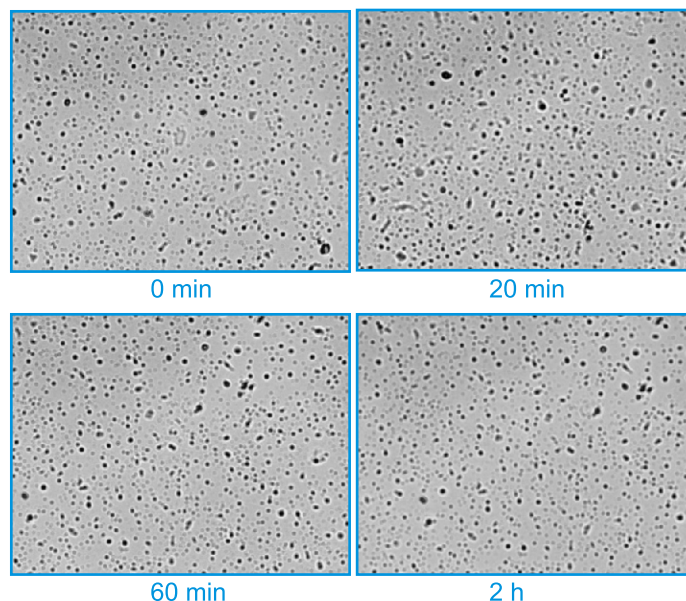


Fig 3: Micrographs showing the colloidal stability of ASA emulsion at different time interval prepared with CMC-1 (ASA : CMC :: 1:1)

ASA:CMC-1 of 1:1 the emulsion was quite stable up to 2 hours. So the sizing behavior was analyzed at 1% concentration of CMC-1. The Cobb₆₀ values and contact angles of the hand sheets prepared by ASA

emulsion prepared with CMC-1 has been found to be very consistent as shown in Table 3. The particle size distribution of ASA in emulsion was unaltered upto 2 hours. It was found that 59-60% particles were less than 1 micron and these remain stable upto 2 hour (Fig.3). The sizing performance was slightly inferior in comparison to the reference prepared with cationic starch. Slightly higher dose of ASA will be required to compensate the sizing.

The ASA emulsion was prepared with other two CMC grades viz., CMC-2 and CMC-3 having medium and high molecular weight with ASA: CMC ratio of 1:1 and 1:2. CMC-2 and CMC-3 were found to be less efficient protective

Table 3: Sizing behavior and stability of ASA emulsion prepared with CMC-1 as protective colloid.

Time, min	Cobb ₆₀ , g/m ²	Contact angle, °								Surface energy, mN/m	Potential, mV	Charge demand, µeq/l	Conductivity, mS	Zeta potential, mV	pH
		Time interval, s													
		5	10	20	30	40	50	60	Avg.						
0	35.8	102.4	101.9	101.9	101.4	101.1	100.5	99.9	101.3	22.27	-265.3	-16.8	0.381	-19.1	8.0
20	35.2	102.8	102.1	101.6	101.2	101.1	100.4	99.5	101.2	22.33	-261.8	-16.4	0.384	-19.5	8.1
40	35.4	102.1	102.2	101.8	101.7	101.0	100.1	98.9	101.1	22.39	-264.5	-16.5	0.385	-19.4	8.1
60	35.8	101.9	102.1	101.9	101.2	100.9	100.2	98.4	100.9	22.51	-266.6	-16.9	0.384	-19.7	8.1
120	36.1	101.2	101.9	101.8	101.1	100.5	100.1	97.9	100.6	22.69	-271.2	-16.2	0.382	-19.1	8.0
180	63.9	85.9	84.0	82.2	78.0	76.1	75.0	70.9	78.9	36.03	-268.3	-16.8	0.388	-19.7	8.1

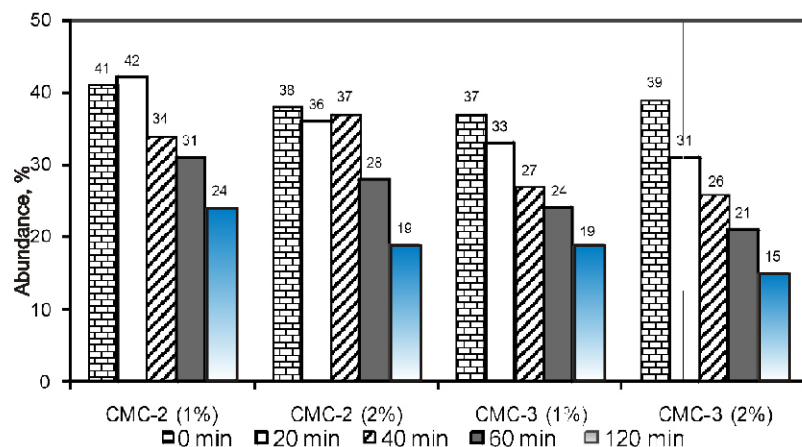


Fig 4:- Effect of time on abundance of ASA particle below 1 micron (Emulsion prepared with CMC-2 & CMC-3 at different concentrations)

colloids for ASA emulsion in these two conditions. The particle size distribution of ASA emulsion prepared with CMC-2 and CMC-3 was very broad; only 41 and 37 % of the particles were found to be less than 1 micron in case of emulsion prepared with CMC-2 and 3 respectively (Fig. 4). The emulsion prepared by CMC 2 was stable only upto 20 min where after coalescence of particles took place (Fig 5). With the freshly prepared ASA emulsion the Cobb value and contact angle were 41.5 g/m² and 97.5 degree respectively. The latter remained consistent only upto 20 min (Table 4). ASA emulsion prepared with CMC-3 started losing its stability immediately after its preparation which was reflected by the Cobb₆₀ values and contact angles (Table 5, Fig. 6).

Table 4: Sizing behavior and stability of ASA emulsion prepared with CMC-2 as protective colloid.

Time, min	Cobb ₆₀ , g/m ²	Contact angle, °								Surface energy, mN/m	Potential, mV	Charge demand, µeq/l	Conductivity, mS	Zeta potential, mV	pH
		Time interval, s													
		5	10	20	30	40	50	60	Avg.						
0	41.5	100.1	98.2	98.0	97.50	97.2	96.2	95.8	97.5	24.56	-182.0	18.7	0.374	-23.8	8.0
20	42.5	99.9	97.2	97.0	96.5	95.3	94.2	94.1	96.3	25.28	-181.2	18.4	0.366	-23.1	8.1
40	46.9	98.1	97.2	96.4	95.2	94.1	93.8	92.1	95.3	25.88	-182.1	18.3	0.368	-23.7	8.1
60	52.3	97.8	96.4	96.2	94.5	93.3	92.0	90.0	94.5	27.01	-182.3	18.6	0.369	-23.5	8.1
120	65.2	84.9	83.1	82.1	76.0	74.2	73.2	70.1	77.6	36.77	-183.4	18.5	0.371	-23.9	8.0

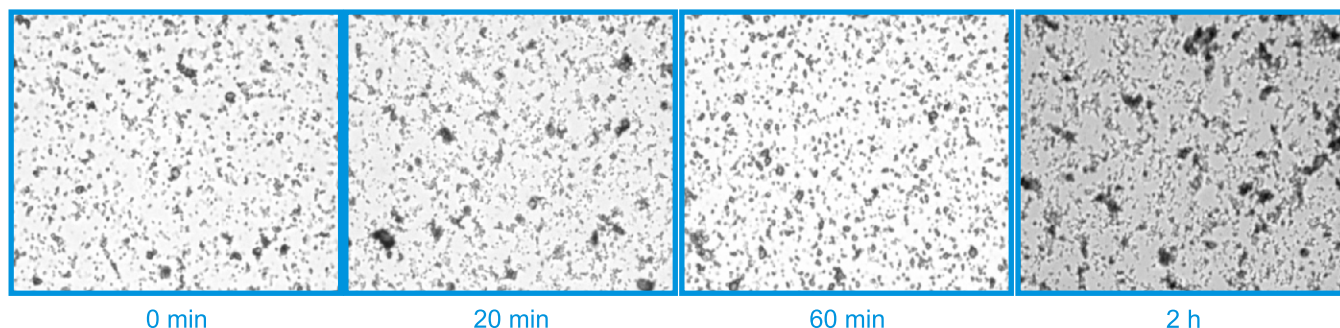


Fig 5: Micrographs showing the colloidal instability of ASA emulsion at different time interval prepared with CMC-2

Table 5: Sizing behavior and stability of ASA emulsion prepared with CMC-3 as protective colloid.

Time, min	Cobb ₆₀ , g/m ²	Contact angle, °								Surface energy, mN/m	Potential, mV	Charge demand, µeq/l	Conductivity, mS	Zeta potential, mV	pH
		Time interval, s													
		5	10	20	30	40	50	60	Avg.						
0	44.4	99.8	98.4	97.8	96.2	95.5	93.2	92.9	96.2	25.34	-192.3	18.9	0.385	-23.7	8.0
20	47.5	98.2	97.0	96.1	95.1	93.6	92.4	91.9	94.9	26.12	-192.6	18.1	0.388	-23.4	8.1
40	52.3	95.5	95.2	96.1	92.4	91.2	91.0	89.6	92.5	26.52	-193.2	18.5	0.381	-23.9	8.1
60	66.2	84.1	82.0	80.0	74.1	72.2	70.2	67.1	75.6	37.92	-191.2	19.0	0.390	-24.2	8.1
120	71.9	85.4	82.3	79.0	73.5	71.1	65.2	60.2	73.8	39.07	-192.9	19.1	0.391	-24.3	8.0

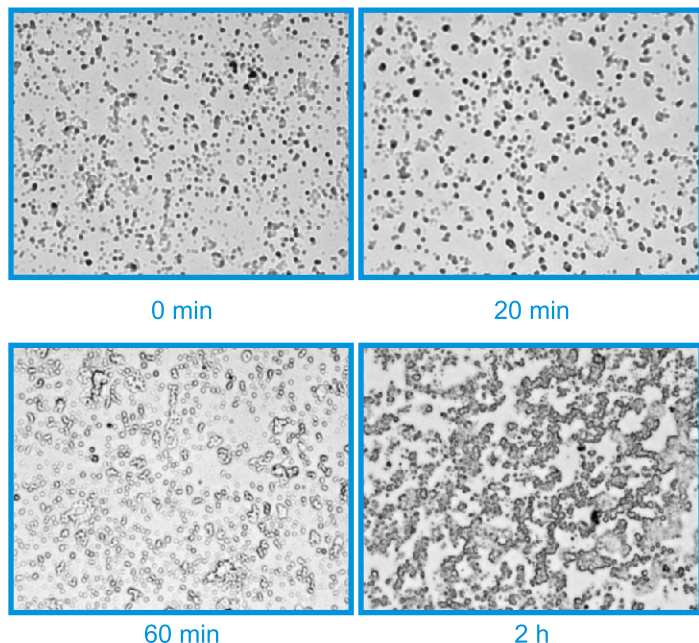


Fig 6: Micrographs representing the particle agglomeration in ASA emulsion at different time interval prepared with CMC-3

Large amount of water are associated with all the samples of carboxy methyl cellulose, suggesting a multilayer arrangement of water molecules about the solute. A change in degree of substitution has some effect on the hydration, but it appears less significant than a change in molecular weight.⁷ This may be the reason for the fast hydrolysis of emulsion prepared with high molecular weight of CMC-2 and CMC-3. During the emulsification of ASA in CMC three things are important: i) molecular weight of CMC, ii) its degree of substitution and iii) number of water molecules associated with the different CMC molecules. In comparison to CMC 1, CMC-2 and 3 are having higher molecular weights and higher degree of substitution. The number of associated water molecules in case of CMC-2 and CMC-3 might be much higher as compared to that in CMC-1. These three factors combinedly form the larger particles of ASA molecules from the zero time with CMC-2 and CMC-3. Higher exposure to water molecules in the CMC structure and tilting the hydrophobic-hydrophilic balance were the causative factors for rapid coalescence of the particles of ASA molecules in CMC-2 and CMC-3. Low molecular weight CMC provides all the prerequisites necessary for the stable ASA emulsion.

Conclusion

Low molecular weight CMC macromolecules appear to encapsulate the ASA particles and provide a stable protective layer to the emulsified ASA particles. The number of particles lesser than 1 micron are comparatively lower i.e. 59-60% with LMW CMC in comparison to cationic starch (87%) initially. The lower amount of CMC (ASA to CMC ratio 1:1) forms stable emulsion.

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