Optimization of ASA Emulsion and Impact of Filler on ASA Sizing

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ABSTRACT

The sizing performance of ASA depends upon the stability of the ASA emulsion also, in addition to other factors. For fine dispersion of ASA oil, cationic starch is used to prepare the ASA emulsion at the paper machine site. The pH of cooked cationic starch is generally reduced to below 4.0 with the help of citric acid or adipic acid before emulsification to reduce the chances of hydrolysis of ASA during emulsification and to some extent on storage for few minutes. As the cationic starch and these acids are quite expensive, attempts have been made to reduce the starch consumption and substitute the expensive acids by low-cost chemicals. It has been possible to reduce the starch to ASA ratio in the emulsion from 3 to 2, resulting in cost saving. It is also possible to use PAC alone or alum alone in place of citric acid to reduce the pH of starch slurry. The optimum dosing of different chemicals has also been determined for preparation of ASA emulsion.

In India, talc is extensively used as filler in the production of writing & printing papers due to its availability at low cost. Few mills, after switching over to neutral or alkaline sizing, have started using ground calcium carbonate (GCC) also to get better optical properties. Precipitated calcium carbonate (PCC) has been reported to have even better bulk and optical properties and it is being used in several modern mills abroad. The fillers are expected to affect the sizing performance to a varying degree, depending upon their nature. These three fillers have been studied to observe their effect on performance of ASA alkaline sizing and also on optical and strength properties. Sizing performance decreases on loading the paper with GCC or PCC but it slightly improves with talc due to its non-wetting nature. Optical properties of PCC are better than those of GCC and talc, which is also reflected in the paper sheets with these fillers. Paper containing PCC exhibited superior bulk, smoothness and stiffness. Due to fine particles of PCC, the strength properties were inferior when PCC was loaded to the paper as compared to those with talc and GCC.

INTRODUCTION

The purpose of internal sizing is to make paper more resistance to liquid penetration. Rosin, AKD and ASA are the common chemicals used for internal sizing. Paper industry is trying to convert acid sizing to alkaline sizing. This was largely driven by the availability of low cost, high brightness calcium carbonate. The increased strength of an alkaline sheet permitted higher filler levels [1]. With an alkaline sheet, an alternative to the conventional rosin-alum sizing is required. This gives two choices, alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA).

AKD has been used in the paper industry as a sizing agent since it was developed in 1950. ASA first appeared in the early 1960's, but did not become common until the mid 80's. Both AKD and ASA are commonly described as reactive alkaline sizes because they form covalent bonds with cellulose, and neutral or alkaline pH values are employed in the papermaking system.

AKD is usually manufactured by chlorinating a fatty acid using phosphorus trichloride followed by dimerisation of the resulting product with tri-methyl amine to form a waxy solid material. This is then melted and later emulsified with cationic stabilizers such as cationic starch or polymers. Since AKD has a relatively slow rate of hydrolysis as compared to ASA, this operation is carried out at a central manufacturing facility, and emulsion is shipped as a ready to use product to the paper mill. There has been considerable research into both the mechanism of AKD sizing and its performance on the paper machine. Though it is a good alkaline sizing agent but has some drawbacks:

- Since AKD is a wax, this size can cause slipperiness on the final sheet.
- The relatively slow reactivity of the AKD can mean that the sheet is unsized by the time it reaches the size press. This has led many paper makers to over dry the sheet to achieve some curing. Full cure in the paper or board may not occur until some hours after the sheet has been manufactured. The curing of the AKD can be enhanced through addition of a cationic polyamideamine-epichlorohydrin resin or bicarbonate ions to the wet end [2].

Due to the above-mentioned problems with AKD sizing, paper industry is shifting from AKD to ASA sizing, especially for copier paper.

Alkenyl succinic anhydride (ASA) is produced from the reaction of an isomerised olefin with maleic anhydride. The maleic anhydride molecule supplies the reactive anhydride functionality to the ASA, while the long chain alkyl portion provides the hydrophobic properties associated with this size. The resulting succinic anhydride group is extremely reactive and will complex with hydroxyl groups on cellulose, starch and water. High reactivity of ASA molecules provides some of its major advantages. The sizing takes place on the machine itself without excessive drying [1, 3-4]. The ASA sizing is preferred over AKD sizing in manufacturing of copier paper as AKD, being a wax, has a problem of paper slipping during printing and photocopying. However, there are two problems with the ASA sizing: (a) poor stability of ASA emulsion and (b) the sticky behaviour of hydrolyzed ASA [5]. ASA hydrolyses easily in aqueous emulsion to form alkenyl succinic acid, which is detrimental to sizing. Once prepared, ASA emulsion should be used

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within few minutes of time [6].

ASA emulsion is prepared with cationic starch in different ASA to starch ratios. Generally, it is presumed that higher the cationic starch to ASA ratio in the emulsion, better will be the stability. Reduction of cationic starch in the emulsion will be economical if the quality of emulsion is not compromised. The pH of cationic starch slurry is kept low, generally 4.0. Lower the pH, longer will be the emulsion stability. Generally, citric acid or adipic acid is used to reduce the pH of cationic starch slurry before preparation of ASA emulsion [1,4]. As these acids are little expensive, it is desirable to substitute them by low cost chemicals like acetic acid, alum and PAC.

The paper makers use fine minerals (fillers) to achieve the desired properties of paper like opacity, smoothness and brightness. Another common goal of filler use is to decrease the net cost per mass of materials in paper. The dry surface area of fillers is typically in the range of 4-20 m^2/g [7]. Although the fillers can improve various paper characteristics, they may deteriorate the strength properties and affect the performance of sizing chemicals. In Indian paper industry, talc (magnesium silicate), GCC and PCC are the most common fillers. Papers made from these fillers have different sizing performance, physical and optical properties due to difference in their basic characteristics. In the late 1980's and early 1990's, it was found that paper containing PCC filler could lose its sizing with time. Considerable research went into the mechanism and various promoters were found that could reduce, but did not eliminate the problem. The cause was eventually traced to free lime present in the PCC, and now PCC manufacturing processes have been improved to ensure that this is no longer an issue [8]. It has been mentioned that the presence of excess Ca^{2+} ions are detrimental to sizing [9]. Surprisingly calcium salt of ASA is hydrophobic in nature [10].

In this paper, the results on the study of different ASA to starch ratios and use of low-cost chemicals to reduce the pH of cationic starch slurry for preparing ASA emulsion and its impact on ASA sizing have been summarized. Attempts have been made to observe the effects of three common fillers, namely, talc, ground calcium carbonate and precipitated calcium carbonate on ASA sizing and paper properties.

EXPERIMENTAL

MATERIALS

Bleached pulp was collected from an integrated pulp & paper mill using bleaching sequence C_D-E_{OP}-D_1-D_2. ASA oil of pale yellow in colour (Raisafob mf 18-A) was used through out this study. Tapioca based cationic starch (Raisamyl 50941) of neutral pH with degree of substitution 0.035 was used for ASA emulsification and also in stock. Cationic poly acrylamide (Percol-47) (with talc and GCC) and anionic poly acrylamide (Percol-2305) (with PCC) were used as retention aid. M/s Ciba Specialty Chemicals supplied cationic starch, ASA and retention aid. Cationic fatty acid condensation product (Cartaflex-K) used as fixing agents for the fines was supplied by M/s Clariant. Poly aluminum chloride (PAC) having 17% alumina, iron free alum, acetic acid and citric acid were procured from the local suppliers. The following fillers were used in this study: 1) talc (Finex, monoclinic structure), 2) GCC (hexagonal structure), and 3) PCC (scalenohedral structure) slurry of 25% solids prepared at the site of a paper mill.

Methods

Cationic starch 2-3% consistency was cooked at 90±2^{0}C for 30 minutes with continuous stirring using a mechanical agitator. The pH of cooked cationic starch was reduced to 4.0 using different chemicals. In some of the experiments, the optimized dose of PAC was also added to the slurry. ASA emulsion was prepared at ambient temperature using a high shear mixer by slow addition of ASA to the cooled cationic starch slurry. The ASA content of 1% was maintained in all the emulsions while the ASA to starch ratio was varied from 1:2 to 1:3.

Pulp was disintegrated in a British disintegrator and refined in PFI mill (model 516 of HAMJERN MASKIN, Norway) to 28±1 ^{0}SR. The fibre suspension was prepared in the disintegrator in a batch process. Different materials were added to the suspension and agitated for 30 seconds each at ambient temperature. Distilled water was used for preparing different chemical solutions. The following sequence of addition of different materials in stock was used: Cartaflex-K, PAC, starch, ASA emulsion, filler and retention aid. Hand sheets of 70 g/m^2 were prepared according to Tappi standard T 205 sp-02, pressed and air-dried.

Image analyzer (Buehler, USA) was used for measuring particle size distribution of ASA emulsion. With the help of software, the size of all the particles of a slide prepared from the emulsion was determined. Stock properties viz. potential & cationic demand and zeta potential were measured using particle charge detector (Mutek PCD 03 pH) and Zeta potential meter (Mutek SZP 06), respectively. The ash content of hand sheets was determined as per Tappi standard T211 om-93. First pass ash retention was also calculated from the ash contents in the hand sheet and Buchner sheet prepared from the same stock.

The air-dried sheets were conditioned for 4 hours in the paper-testing lab, maintained at 23^0±1C and 50±2% relative humidity as per Tappi standard T 402 sp-98. $Cobb_{60}$ values of 5 sheets of each ASA-sized samples were determined by using distilled water on smooth side as per Tappi standard T 441 sp-98. . Contact angle and surface energy were determined by drop shape analysis system (DSA 10-MK2 of KRUSS, Germany) having DSA1 program for calculation of surface energy. It measures automatically the contact angle and surface energy of the water drop on the surface of the paper with the help of software. Optical properties of hand sheets viz. brightness, whiteness, L*, a*, b*, yellowness, opacity and scattering coefficient were measured using Datacolor (Spectraflash SF 30). Physical strength properties viz. tear index, tensile index, breaking length, burst index, gurley porosity were measured by L & W instruments. Stiffness was measured by Taber V-$_5$ Stiffness tester.

RESULTS AND DISCUSSION

Emulsion characteristics at different ASA to starch ratios

General characteristics of cationic starch used in preparation of ASA emulsion are given in Table 1. It can be seen that the cationic starch is little alkaline and anionic demand is quite high, 2472 **µeq/l**.

Table 1 General characteristics of cationic starch (1% cooked)

Parameters	Value
pH	7.7
Potential, mV	+775
Anionic demand, µeq/l	2472.0
Degree of substitution, mol/mol	0.035

Table 2 Particle size distribution of ASA emulsion

Particle size, m	% of particles	
	Starch to ASA ratio of 3	Starch to ASA ratio of 2
< 0.5	49.1	46.5
0.5 - 1.0	37.9	47.1
1.0 – 2.0	11.1	6.0
2.0 – 3.0	--	--
> 3	1.8	0.3

Table 3 Characteristics of stock at different ASA doses and ASA to starch ratios

Starch to ASA ratio	ASA, kg/TP	Potential, mV	Charge, eq/l	Conductivity, mS	Zeta potl, mV	Alkalinity as $CaCO_3$, mg/l
3	2.2	-246	-6.0	0.603	-5.5	302
	1.5	-272	-6.8	0.601	-6.3	302
2	2.2	-252	-6.3	0.591	-13.9	300
	1.5	-281	-12.4	0.601	-16.7	300

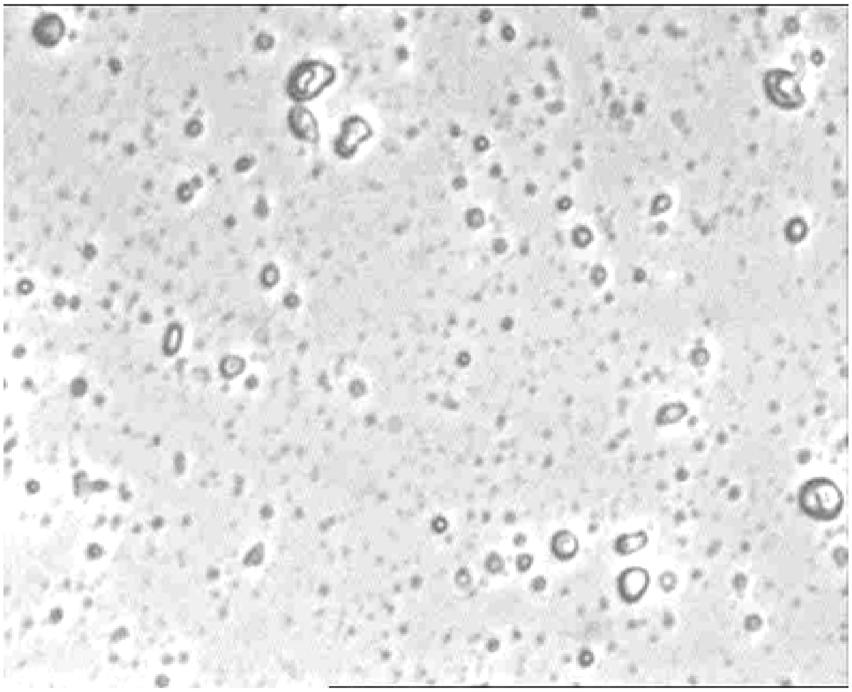

Fig. 1 Micrograph of ASA emulsion, starch to ASA ratio of 3

By using this cationic starch with optimized dose of citric acid (0.12 g/l) and PAC (8.9 g/l) for controlling the foam and particle size, ASA emulsions were prepared using ASA to starch ratios of 1: 3 and 1:2. The particle size distribution of emulsion with ASA to starch ratio of 1:2 is found better than that of 1:3 ratio (Table 2). Over 93% of particles in case of 1:2 ratio are found to be <= 1.0 **m, whereas** 88% of particles are <= 1.0 **m in case of 1:3 ratio.** It can also be seen that there are few bigger particles present in case of 1:3 ratio, whereas no such kind of big particles are visible in 1:2 ratio as shown in figures 1 & 2.

After addition of all the components in the stock, it was characterized for different parameters (Table 3). From table 3, it can be seen that potential, charge and zeta potential are more towards negative side in case of ASA to starch ratio 1:2 than those with the ratio of 1:3. This is due to lesser proportion of cationic starch in the former case.

The sizing performance at higher ASA dose (2.2 kg/TP) in both the cases (at different ASA to starch ratios in emulsion) are comparable whereas at lower ASA dose (1.5 kg/TP), a remarkable difference in sizing performance is observed (Table 4). This may be due to the smaller particles of ASA emulsion in case of 1:2 than in 1:3 ratios.

The change in contact angle (with water on the hand sheet) as a function of time was also recorded for different sized sheets using ASA emulsions of both the types (2:1 and 3:1 ratios of cationic starch to ASA). The results are shown in Fig. 3. It is clearly seen that the contact angles at different ASA doses is higher in case of ASA to starch ratio of 1:2 than those with 1:3 ratio. The change in contact angles with time in case of ASA to starch ratio of 1:2 is much better than that with 1:3 ratio. Moreover, at higher doses of ASA, there was slight increase in contact angle whereas it decreased slightly with time at lower doses of ASA.

Replacement / elimination of citric acid for preparation of ASA emulsion

From the above results, it was decided to keep ASA to starch ratio of 1:2 while preparing ASA emulsion. Next target was to replace/ eliminate the citric acid in the emulsion with the low-cost

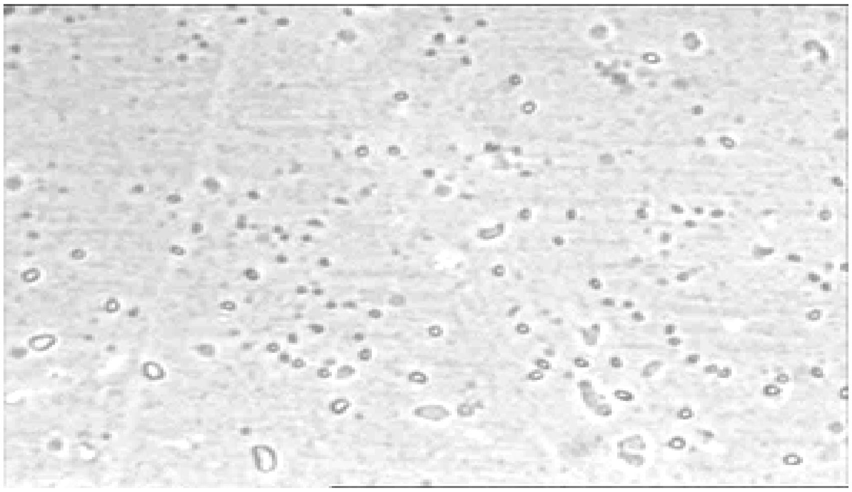

Fig. 2 Micrograph of ASA emulsion, starch to ASA ratio of 2

Table 4 Sizing performance of ASA at different doses and ASA to starch ratio

Starch to ASA ratio	ASA, kg/TP	Cobb, g/m^2	Contact angle, degree	Surface energy, mN/m
3	2.2	27.3	119.5	12.76
	1.5	79.9	92.3	27.66
2	2.2	27.8	119.8	12.69
	1.5	73.2	93.8	27.16

Chemical dosing, g/l				ASA, kg/TP	Cobb, g/m^2	Contact angle, degree	Surface energy, mN/m
Citric acid	PAC	Acetic acid	Alum				
0.12	8.9	--	--	1.2	33.8	106.1	19.42
				1.5	26.4	117.8	12.99
--	8.9	0.06	--	1.2	45.0	102.9	21.29
				1.5	26.8	117.0	13.09
--	--	--	0.4	1.2	39.8	100.1	24.01
				1.5	30.0	106.4	20.43
--	8.9	--	--	1.2	36.0	102.5	23.61
				1.5	25.1	117.9	13.01

Table 5 Sizing performance of ASA emulsions prepared by using different chemicals for pH adjustment of cationic starch

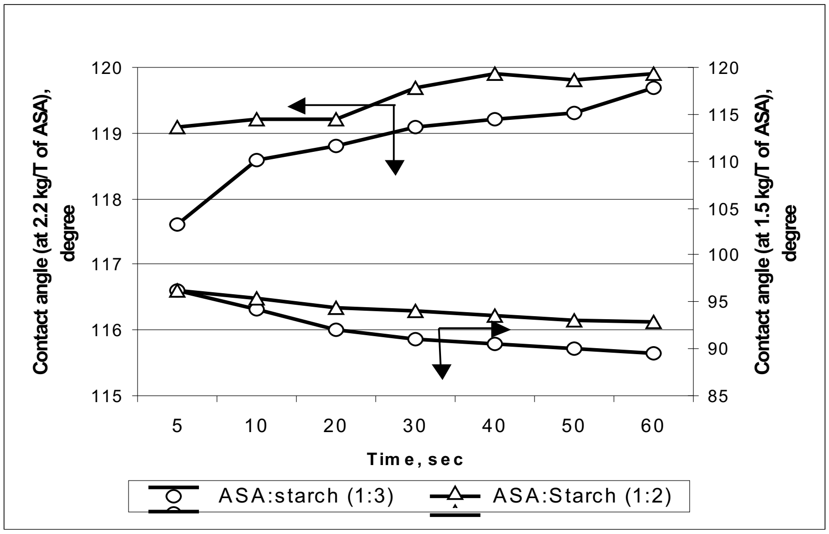

Fig. 3 Contact angle as a function of time at different ASA doses for different starch to ASA ratios

chemicals like alum, acetic acid and PAC.

When only PAC was added to the starch slurry before preparation of ASA emulsion, sizing performance was comparable to that with the citric acid and PAC for pH adjustment (Tables 5). PAC and acetic acid combination gave poor performance at lower dose. Results with only alum in the emulsion were also good. These substitutes used for the replacement of citric acid in ASA emulsion have no appreciable effect on wet end parameters like cationic demand, zeta potential, conductivity and total alkalinity, etc. (not shown)

Impact of filler on ASA sizing

The optical properties viz. brightness and whiteness of PCC are best as compared to those of GCC followed by talc (Table 6). The particles of PCC are smaller followed by those of talc and GCC. PCC carries cationic charge whereas talc and GCC have anionic charge. Except talc, PCC and GCC have shown good dispersion in water. Talc is non-wetting in nature.

The experiments with fillers were conducted using ASA to starch ratio of 1:2 in ASA emulsion and pH of starch was adjusted to 4.0 with citric acid and optimized dose of PAC (8.9 g/l of emulsion) was also added. As mentioned earlier in Table 2, 93.6 % particles of emulsion were less than 1 µm.

Filler loading of 5, 10 and 15% was studied with all the three fillers. The first pass ash retention (FPAR) increased from 70 to 81% on increase in the talc loading from 5 to 15% (results not shown) whereas the values for the same loading were 60 to 70% of GCC and 58 to 69% of PCC (with anionic poly acryl amide as retention aid).

Table 7 shows stock preparation data at 15% ash and 1.5 kg/TP of ASA. The cationic demand of stock increases when GCC or talc is added in to the stock. This is due to the anionic nature of both talc and GCC. However, due to cationic nature of PCC, the cationic demand of stock with PCC is lower than that with GCC and talc. The same trend is also reflected in the values of zeta potential.

The sizing performance with different fillers at 1.5 kg/T of ASA is shown in

Serial No	Parameters	Talc	GCC	PCC
01	Brightness, % ISO	88.8	94.4	97.2
02	CIE Whiteness	81.7	88.4	93.3
03	Nature	Anionic	Anionic	Cationic
04	Colour	White	White	White
05	pH of 5% slurry	10.3	9.2	10.3
06	Dispersion in water	Poor	Good	Good
07	Moisture, %	0.2	0.1	-
08	Particle size < 2 µm, mass%	20.90	11.34	29.70

Table 6 general characteristics of fillers

Filler	Potential, mV	Charge, µeq/l	Conductivity, µS	Zeta Potential, mV	Total Alkalinity, ppm
None	-238	-6.5	0.478	-10.6	300
Talc	-264	-7.7	0.514	-12.7	302
GCC	-207	-7.1	0.493	-11.1	306
PCC	-261	-7.0	0.525	-11.1	308

Table 7 Stock preparation data with different fillers at 15% ash loading and 1.5 kg/TP ASA

Filler	Cobb, g/m^2	Contact angle, degree	Surface energy, mN/m
No filler	26.4	117.8	12.99
Talc	25.5	119.8	12.78
GCC	30.5	106.3	19.63
PCC	34.8	104.2	21.03

Table 8 Performance of ASA sizing with different fillers at 15% ash loading

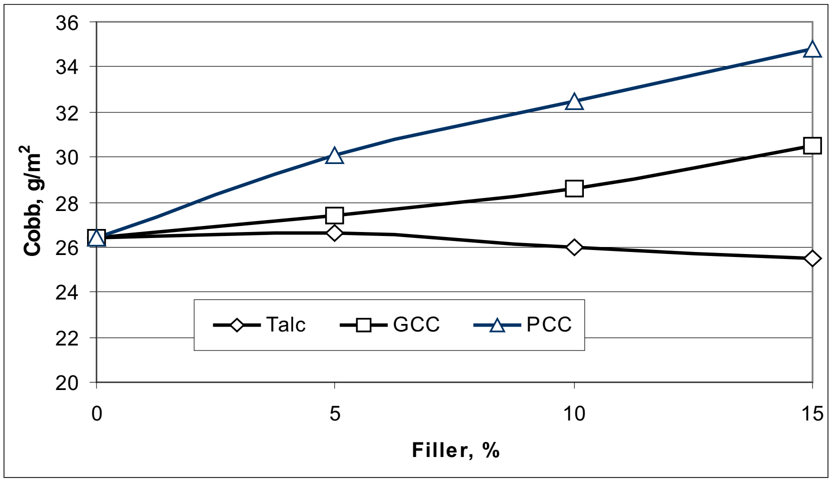

Fig. 4 Sizing performance in terms of Cobb value as a function of filler content

Table 8. By adding talc in the stock, it is observed that the sizing performance has slightly improved. This may be due to non-wetting nature of the talc. Whereas with the addition of GCC and PCC, the sizing performance has deteriorated. This may be due to hydrophilic nature of GCC and PCC and the finer particles of PCC, having more surface area, which might have adsorbed more ASA as compared to that by talc and GCC particles. Thus, more ASA adsorbs on to the surface of PCC and passes from the wire. Figures 4 & 5 show the effect on sizing by increasing the filler content in stock. The sizing performance increases with the increase in talc content due to its non-wetting nature. However, opposite is the trend with GCC and PCC due to their hydrophilic nature.

Different fillers impart optical properties differently when they are added to the stock. These are recorded in Table 9. All the paper sheets made with different fillers have shown good optical properties in terms of brightness, whiteness, opacity, yellowness and scattering coefficient in comparison to blank (without filler). Brightness, whiteness and opacity of the sheets are best with PCC followed by GCC and talc. Scattering coefficient also follows the same trend however; the yellowness follows the opposite trend as expected. Thus, it can be inferred that PCC imparts best optical properties to the paper, followed by GCC and then talc.

Comparison of physical properties of paper sheets made with different fillers is given in Table 10. Bulk of the paper sheet is lower with talc, comparable with GCC and higher with PCC as compared to the blank (without filler). PCC sheet has highest bulk and stiffness as compared to that with talc and GCC. When we compare strength properties viz. breaking length, burst index, tear index, PCC is found inferior than talc and GCC. This might be due to the small particles of PCC (as shown inTable 1, PCC particles are finer than those of talc and GCC). The filler of smaller particles cover more surface of the fibre per unit mass of the filler, reducing fibre-to-fibre bonding, which results in lower strength. Because GCC particles are bigger, they cover less area of fibre per unit mass, giving better fibre-to-fibre bonding. Thus, reduction in strength properties with GCC is much less as compared to that with PCC and talc. Also PCC plays an important role on paper smoothness. The smoothness of paper sheets with PCC is much better than that containing talc and GCC.

CONCLUSION

The particle size distribution and sizing performance is better with the ASA emulsion prepared in ASA to starch ratio of 1:2 than those with the ratio of 1:3. When the pH of cationic starch is reduced with the help of PAC only, the sizing performance of ASA emulsion is quite satisfactory. The foaming problem during preparation of ASA emulsion also reduces when PAC is used. Thus, PAC alone can be used as a better substitute for the replacement of citric acid in pH adjustment of cationic starch for the preparation of ASA emulsion.

GCC and PCC decrease the sizing performance but not the talc. Also by increasing the talc %, sizing is slightly improved due to its non-wetting nature but reverse is the case with GCC and PCC. Optical properties of PCC are better than GCC and talc, which is also reflected in the properties of the paper sheets. Paper made from PCC found to

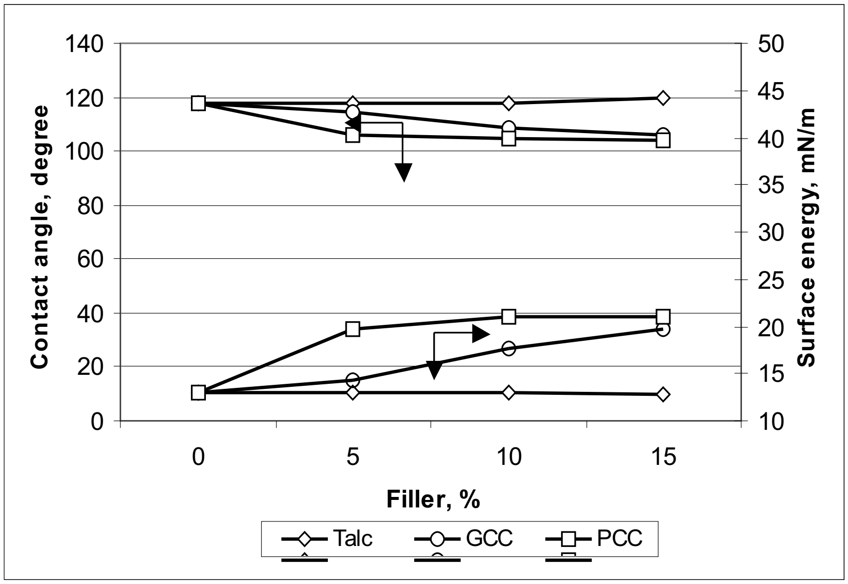

Fig. 5 Sizing performance in terms of contact angle and surface energy as a function of filler content

Properties	No filler	Talc	GCC	PCC
Brightness, % ISO	78.8	82.4	83.5	85.4
CIE Whiteness	57.9	69.4	72.3	74.5
L*	93.28	94.3	94.5	95.6
a*	-0.03	-0.15	-0.16	-0.17
b*	5.48	3.71	3.94	3.98
Yellowness	7.38	6.94	5.92	5.61
Opacity, % ISO	78.2	82.8	84.7	87.6
Scattering coefficient, m^2/kg	29.46	37.87	43.44	57.5

Table 9 Optical properties of paper with different fillers at 15% ash loading

Properties	No filler	Talc	GCC	PCC
Bulk, cc/g	1.45	1.40	1.48	1.55
Breaking length, km	5.222	3.658	3.914	3.406
Burst Index, kN/g	4.95	2.30	2.45	2.04
Tear index, mNm^2/g	8.45	4.96	4.86	4.61
Roughness, ml/min				
- Smooth side	202	157	180	146
- Rough side	561	394	430	405
Double fold, number	148	10	11	9
Gurley porosity, s/100cc	15.16	5.87	4.56	4.61
Stiffness, Taber x10	14.87	8.90	8.05	9.50

Table 10 Physical properties of paper with different fillers at 15% ash loading

be superior in bulk, smoothness and stiffness. Due to fine particles of PCC, the strength properties with this filler are found to be inferior to those with talc and GCC. GCC having bigger particles does not affect the strength properties to the same extent as talc and PCC.

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