Efficacy of ASA Sizing with Agro-Residue and Recycled Pulps Using Different Fillers

Sharma Ashish, Kakkar Shaveta, Chauhan Vipul S., Chakrabarti Swapan K. & Varadhan R.

Thapar Centre for Industrial Research & Development, Yamuna Nagar -135 001, Haryana, (India)

ABSTRACT

Paper industries are shifting from neutral to alkaline sizing process. Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are two main sizing agents used in alkaline sizing; the latter is the dominating one. Due to the shortage of wood fiber, the demand of agro-residue based and recycled fiber is increasing with time. The dosage of sizing agent depends upon various parameters related to the raw material, filler and wet-end chemistry of papermaking process. The higher dosage of sizing chemicals creates problems in machine runnability through the formation of sticky materials. It is important to optimize the dosage of the sizing agent for the respective pulp furnish for cost saving and cleaner system. In the present work, two agro-residue based pulps; bleached wheat straw and bleached bagasse along with recycled pulp were used. The ASA emulsion prepared in the lab was added in all the pulps at different dosage and with three commercially available fillers; talc, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). The $Cobb_{60}$ and contact angle of the sheets were compared for all the pulps and fillers. The bleached recycled pulp was having better $Cobb_{60}$ vs. contact angle relationship as compared to both agro-residue based pulps. The analysis of hydrophobicity of paper through the contact angle test showed that there is no need to add higher dosage of ASA emulsion in pulp. The contact angles were quite stable even up to the $Cobb_{60}$ value of 40 g/m^2.

Keywords: *Sizing, Agro-residue pulp, Recycled pulp, Contact angle,* $Cobb_{60}$

Introduction

The term 'sizing' used in papermaking is the process by which a chemical additive provides paper and paperboard with resistance to liquid wetting, penetration and absorption. Industries use various test methods like $Cobb_{60}$, Hercules size test and contact angle to measure the surface wettability of paper. The most widely used test in Indian paper industries is $Cobb_{60}$ wherein a water column is rested on the paper surface in 60 seconds. Interaction of water molecules with paper in the time scale can not be determined through the water absorption test i.e. $Cobb_{60}$ test. On the contrary, the rate of absorption of water into the paper surface with respect to time is of paramount importance. The measurement of contact angle and surface energy are the advanced methods in this respect to determine the hydrophocity of paper [1]. Understanding the behavior or interaction of water molecules in contact with paper surface is highly essential to control the sizing of paper.

The predominant current commercial types of sizing agents are rosin based, wax based and synthetic based cellulose reactive materials. Cellulose is the hydrophilic substance which has a high surface energy. The porous structure of paper acts like sponge in the presence of liquid. The purpose of the sizing agents is to reduce the surface energy of the cellulose so that it can have a protection against liquid absorption. The sized papers are used for a number of end applications such as writing and printing paper, water resistant wrapping and liquid packaging. Sizing just retard the liquid not totally prevent liquid movement [2].

Paper fiber consists of cellulose and hemicelluloses, which have a strong, natural tendency to interact with water. There are two basic categories of sizing agents - acid and alkaline. Acid sizing agents are intended to use in acid papermaking systems, traditionally at less than pH 5. Analogously, alkaline sizing agents are intended for use in alkaline papermaking systems, typically at a pH greater than 6.5. The most common alkaline sizing agents are alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). Both ASA and AKD have been used as internal sizing agents in papermaking since last many years and their use is increasing with time and the new developments in process technologies [3-10].

Both ASA and AKD are the cellulose reactive sizing agents. AKD has slow rate of hydrolysis as compared to ASA so it is shipped as ready to use product to the paper mill while ASA emulsion is prepared on site. Though AKD is a good sizing agent but has some drawbacks such as being wax it causes the slipperiness in the final sheet. Slow reactivity of AKD can mean that the sheet is unsized by the time it reaches the size press. So over drying of sheet is required to achieve some curing. Due to the above mentioned problems with AKD, paper industries are preferring to use the ASA sizing. 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. However, ASA also has some drawbacks such as it hydrolyses easily in aqueous emulsion to form alkenyl succinic acid, which is detrimental to sizing [11-16]. So, it is highly required to use the ASA emulsion within few minutes of its emulsification.

Fast rate of hydrolysis is the main drawback of ASA emulsion which need to be controlled with the efficient use of sizing agent at appropriate dose and dosing point. Overdosing of ASA causes the deposit problem on the wire part of machine and hence adversely affects the machine runnability. Optimized dosage of ASA is required for economy and cleaner system. In India, there is diversity in the raw materials for making the paper which is a big challenge for the paper industries. The charge demand of the pulp furnish thus varies which eventually affects the demand of the wet-end additives and sizing agents. Overdosing of the wet-end additives disturbs the wet-end chemistry. It is thus required to optimize the dose of sizing agents and to know how much quantity of sizing agent is required in real time to react with fiber and provide the required extent of sizing.

As very little research has been carried out on Indian raw materials such as agro-residue based pulps and the recycled pulps, this study was envisaged to understand the behavior of ASA sizing with the said pulp furnishes in the presence of papermaking grade fillers, and to provide the optimized conditions to the papermakers.

Experimental

Materials

Two agro-residue based pulps; bleached bagasse and bleached wheat straw pulp were procured from two different integrated pulp and paper mills in northern India. The bleached recycled pulp was procured from an integrated pulp and paper mill in southeast India. The pulps were used as such without refining/beating. The ^{o}SR of all the pulps was around 28-29. Various wet-end chemicals such as alkenyl succinic anhydride (ASA) oil, cationic strength additive (CSA), cationic fatty acid condensation product (CFA), poly aluminum chloride (PAC), talc, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), medium to high molecular weight cationic polyacrylamide (CPAM) and high molecular weight anionic polyacrylamide flocculant (APAM) were procured from different suppliers in India.

Methods

The Cationic starch of 3% solids (w/v) was cooked at 90±2^{0}C for 30 minutes with continuous stirring using an 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. Ratio of ASA to cationic starch was kept as1:3 for making the ASA emulsion. Distilled water was used for the preparation of different chemical solutions. ASA emulsion was characterized in terms of pH and particle size distribution. For the latter, first the mother emulsion was diluted to 0.5% solids. Slides were prepared to check the particle size under Image analyzer (Buehler, USA) at 100x magnification. The size of emulsion particles was determined with the help of software. The cationic starch for the use at wet-end was further diluted to 1% (w/v).

The following sequence of addition of different materials in stock preparation was use pulp (1% consistency), cationic fixing agent (CFA), poly aluminum chloride (PAC), cationic starch, ASA emulsion, filtered water (to dilute the pulp slurry to 0.4% consistency) and retention aid. Paper handsheets of 70 g/m^{2} were prepared according to Tappi test method T 205 sp-02, and were pressed and air-dried as per Tappi test method T 218 sp-02.

The cationic charge demand and zeta potential of the papermaking slurry were measured with Particle charge detector (Mutek PCD 03 pH) and Zeta potential meter (Mutek SZP 06) respectively. The air dried sheets were conditioned for 24 hours in the controlled room at 23±1^{0}C and 50±2% relative humidity as per Tappi test method T 402 sp-98. Cobb$_{60}$ values of 5 sheets of each set were determined with distilled water on smooth side as per Tappi test method T 441 sp-98. The contact angle and surface energy were determined with Drop shape analyzer (DSA 10-MK2 of KRUSS, Germany) using the Sessile drop method.

The particle size determination of the fillers was measured on Laser scattering particle size distribution analyzer (Horiba LA950S2). The talc fillers were wetted with ethanol whereas both GCC and PCC were wetted with sodium hexa meta phosphate and the wetted fillers were then dispersed with deionized water to make 10% (w/v) filler slurry.

Results and Discussion

Characterization of Input Materials

The pulp furnishes were characterized for the physico-chemical and morphological properties. The average fiber length and width of bleached recycled (BRC) pulp were highest among all three pulp furnishes probably due to the presence of long fibered imported waste paper in the BRC pulp. They were lowest in case of bleached bagasse (BBS) pulp. The width of BRC fibers was highest (19.2 m) followed by bleached wheat straw (BWS) (17.9 m) and BBS (15.1 m) pulp. The coarseness BRC pulp was also highest (82.3 g/m) followed by BBS (67 g/m) and BWS (73.1 g/m). The fines were highest in BWS pulp followed by BBS and BRC pulp (Table 1).

The ^{0}SR of unbeaten agro-residue and recycled pulps was around 27-28. The colloidal charge and surface charge on all pulps were negative. The cationic charge demand of BBS pulp was highest (22.3 eq/l) followed by BRC (14.3 eq/l) and BWS (11.2 eq/l). The ISO brightness of BBS pulp was highest (86.2%) followed by BRC (80.2%) and BWS (78.2%). The air permanence was measured for the sheets prepared from the pulps . It was higher for agro-residue pulps than that of recycled pulp. The Bendtsen roughness of paper was highest in case of BRC (181 ml/min) followed by BBS (71 ml/min) and BWS (43 ml/min) (Table 2).

Among all three fillers used in this study, GCC was pre-dispersed to around 60% solids (w/v) whereas PCC and talc were collected in powder form and dispersed in lab with filtered water prior to their addition to pulp stock. The optical properties of PCC was highest followed by GCC and talc. All fillers were alkaline in nature. GCC and talc were anionic whereas PCC was cationic in nature. The colloidal charge demand of GCC filler was quite high (3.90 eq/g) whereas for talc it was 1.72

Table 1: Fiber morphology of different agro-residue and recycled pulps

Particular	BBS	BWS	BRC
Average fiber length, mm	0.586	0.751	0.853
Average fiber width, m	15.1	17.9	19.2
Coarseness, g/m	67.5	73.1	82.3
Fines (Length weighted), %	16.0	21.7	9.2

Table 2: Different characteristics of agro-residue and recycled pulps

Particular	BBS	BWS	BRC
Potential, mV	-370	-310	-552
Charge demand, eq/l	-22.3	-11.2	-14.3
^{0}SR of unbeaten pulp	27	27	28
Brightness, % ISO	86.2	78.2	80.2
Air permeance, Gurley s	75.3	49.0	5.6
Bendtsen roughness, ml/min	71	43	181

Table 3: General characteristics of fillers

Particular	Talc	GCC	PCC
ISO Brightness, %	89.7	94.4	95.8
pH of 5% slurry	10.3	9.3	9.7
Median particle size (volume weighted), µm	10.7	2.8	4.8
Colloidal charge demand, µeq/g	1.72 (cationic)	3.90 (cationic)	6.94 (anionic)
Zeta potential, mV	-267	-195	+159

eq/g. The anionic charge demand required to neutralize the charge of PCC filler was 6.94 eq/g (Table 3).

Comparison of $Cobb_{60}$ Value

The hydrophobicity of paper increases and wettability decreases on increasing the dosage of ASA emulsion in pulp. The $Cobb_{60}$ value decreases and contact angle increases on increasing the ASA emulsion in pulp. As shown in Fig. 1, the $Cobb_{60}$ value of BRC pulp initially at lower dosage of ASA emulsion was much higher than that of both agro-residue pulps and decreased sharply on increasing the dosage of ASA emulsion. At around 0.8-0.9 kg/t dosage of ASA emulsion, the $Cobb_{60}$ value of BRC pulp was around 80 g/m^2 whereas that was in the range of 40 - 50 g/m^2, moreover it was lesser with BWS pulp (~35-40 g/m^2) than BBS pulp (45-50 g/m^2). At lower dosage of ASA emulsion, the porosity of paper was responsible for the lower $Cobb_{60}$ values with agro-residue pulps which prevented the penetration of liquid through capillary in the fiber matrix. The drop in $Cobb_{60}$ value of agro-residue pulps on increase in ASA emulsion was much lesser than that of BRC pulp; it was almost linear in case of former. When $Cobb_{60}$ value of paper made from different pulps with no filler addition was compared, it was observed that the requirement of ASA dosage was more or less comparable with both agro-residue pulps and slightly lesser with BRC pulp to achieve the $Cobb_{60}$ value below 30 g/m^2. The dosage of ASA required for BBS pulp to achieve 30 g/m^2 $Cobb_{60}$ value was highest (1.88 kg/t) followed by BWS (1.40 kg/t) and BRC (1.37 kg/t) pulp. Among all the pulp furnishes bleached recycled pulp required the least dose of ASA to achieve the 30 g/m^2 $Cobb_{60}$ value.

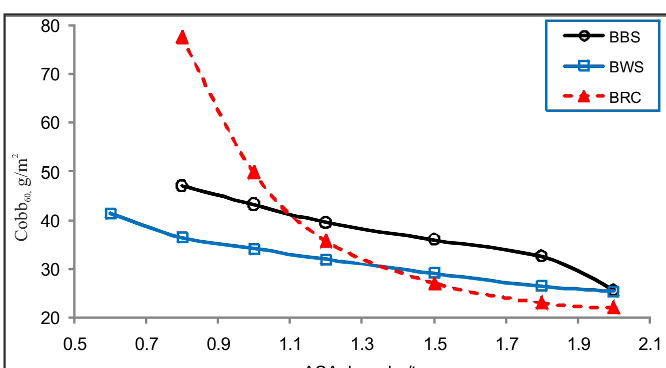

Figure 1: $Cobb_{60}$ values of paper made from different pulp furnishes in ASA sizing (without filler)

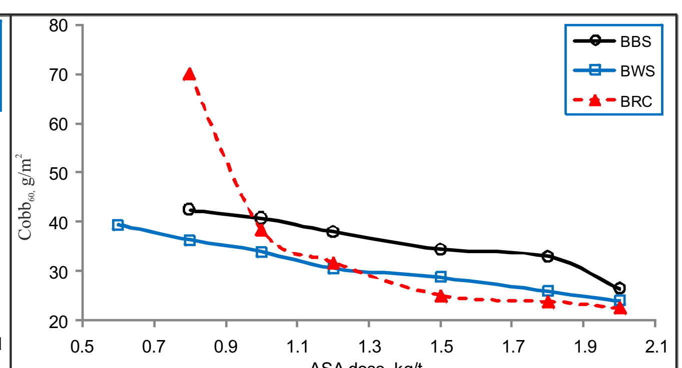

Figure 2: $Cobb_{60}$ values of paper made from different pulp furnishes in ASA sizing with talc filler

Similar to the case with no filler, with talc filler also the difference in dosage of ASA required to achieve the $Cobb_{60}$ value below 30 g/m^2 was not prominent among all pulp furnishes. As shown in Fig. 2, on increasing the dosage of ASA emulsion from 0.8 to 2.0 kg/t the drop in $Cobb_{60}$ value was from 70.0 to 22.7, 42.5 to 26.5 and 36.4 to 24.1 g/m^2 with BRC, BBS and BWS pulp respectively. This showed that talc filler was helpful in decreasing the $Cobb_{60}$ value of agro-residue pulps at lower dosage of ASA emulsion. Similar to the case without filler, with talc filler also the trend of decrease in $Cobb_{60}$ value on increasing ASA dosage was linear. However, the sizing behavior of BWS pulp was slightly better than that of BBS pulp.

As shown in Fig. 3, with GCC filler the trend of $Cobb_{60}$ value was comparable to that without filler. This was applicable for all pulp furnishes. Similar to the previous two cases, in this case also the difference in $Cobb_{60}$ value of paper made at lower ASA dosage was observed while at higher ASA dosage of around 2.0 kg/t, the difference was negligible. All pulp furnishes used in this study have given the similar $Cobb_{60}$ value at higher dosage of ASA emulsion with GCC filler. To achieve 30 g/m^2 $Cobb_{60}$ value, the ASA dose required for BBS, BWS and BRC pulp was around 1.86, 1.18 and 1.61 kg/t respectively. This was also observed that when GCC was used as filler the requirement of ASA emulsion was higher with BBS pulp and lower with BWS pulp.

The trend of $Cobb_{60}$ value with PCC filler was slightly different than that with other fillers. It is assumed that being higher in specific surface area, PCC requires more amount of sizing chemicals. This was true at lower dosage of ASA emulsion when there was comparatively higher $Cobb_{60}$ value with all pulp furnishes. However, at higher dosage of ASA emulsion the difference in $Cobb_{60}$ values was negligible even with the use of PCC filler. As shown in Fig. 4, to achieve a good level of paper hydrophobicity i.e. around 30 g/m^2 $Cobb_{60}$ value, the ASA dose required with PCC filler for BRC, BBS and BWS pulp was around 1.89, 1.72 and 1.18 kg/t respectively. Again the requirement of ASA was more with recycled pulp than that with agro-residue pulps. In this also, the BWS pulp required lower ASA dose as compared with BBS pulp.

Comparison of Contact Angle

The measurement of dynamic contact angle in different sizing conditions over the period of 1 to 60 seconds depicts the capillary absorption behavior of water droplet in contact with paper [1]. The average contact angle of the water droplet with paper has been presented in the results. The contact angle behavior of agro-residue and recycled pulps was different with each other. The effect of ASA dosage on contact angle of different pulps in absence of filler is shown in Fig. 5. The average contact angle of BWS pulp was lowest among all pulp furnishes, and it was not much increased on increasing the dosage of ASA emulsion. The contact angle of paper made from BWS pulp was 96.4 and 101.1^0 at 0.8 and 2.0 kg/t dosage of ASA emulsion. The BBS was having comparatively higher contact angle than that of BWS pulp. BRC pulp was having the highest contact angle among all three pulps used in this study. At 0.8 kg/t dosage of ASA, the BBS and BWS pulp were having comparable contact angle of around $96\text{-}97^0$ which was higher

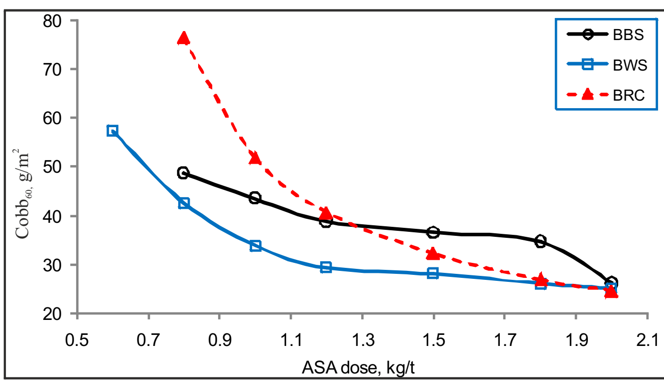

Figure 3: $Cobb_{60}$ values of paper made from different pulp furnishes in ASA sizing with GCC filler

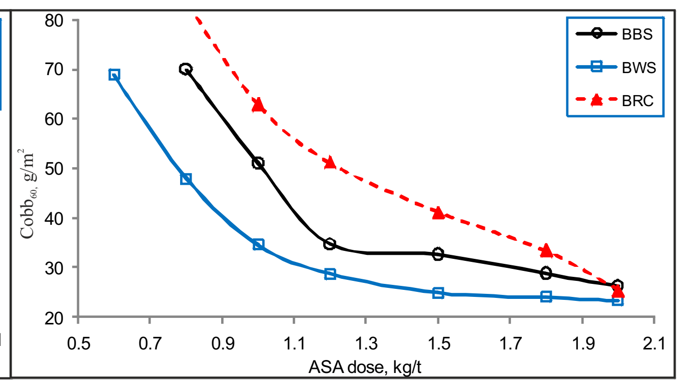

Figure 4: $Cobb_{60}$ values of paper made from different pulp furnishes in ASA sizing with PCC filler

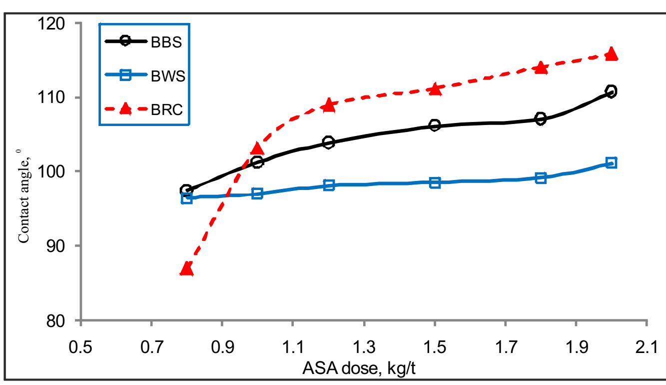

Figure 5: Contact angle of paper made from different pulp furnishes in ASA sizing (without filler)

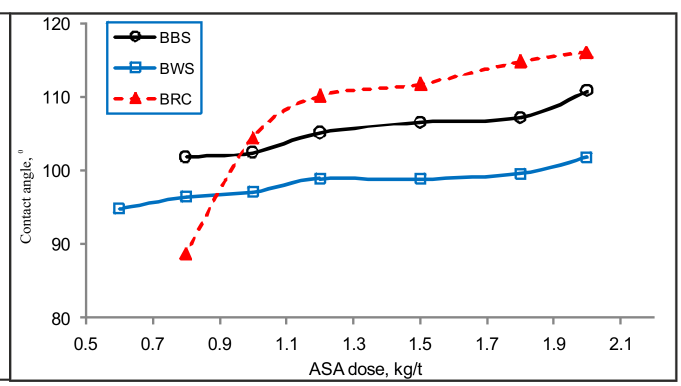

Figure 6: Contact angle of paper made from different pulp furnishes in ASA sizing with talc filler

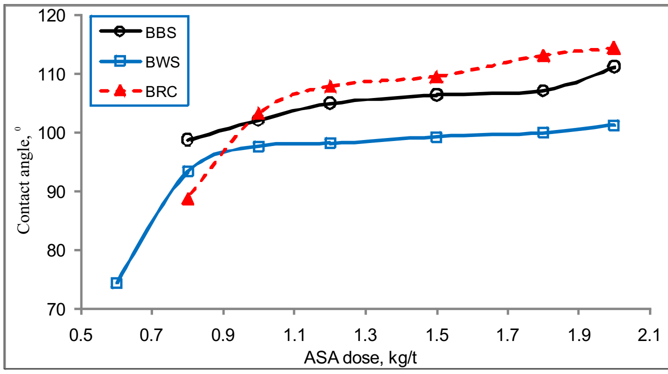

Figure 7: Contact angle of paper made from different pulp furnishes in ASA sizing with GCC filler

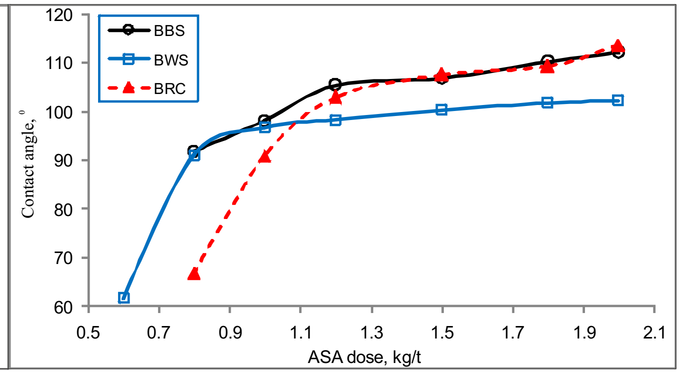

Figure 8: Contact angle of paper made from different pulp furnishes in ASA sizing with PCC filler

than that of BRC pulp (86.9^0) at the same dosage of ASA. The contact angle of the BBS and BRC pulps increased sharply on increasing the ASA dosage. The initially compacted sheet of fibers of BWS pulp provided a good contact angle to the paper at lower dosage of ASA. The availability of pores for the absorption of water was minimal in BWS pulp which might have initially given a higher contact angle to the sheet. However at higher dosage of ASA emulsion, the contact angle could not be increased probably due to smoother fibrous sheet of BWS pulp. It is reported in the literature that the smoother surface of the sample provides lesser contact angle.

The incorporation of talc filler in all the pulp furnishes had no impact on the contact angle of paper (Fig. 6). The contact angle was same in both the cases i.e. pulps without filler and with talc filler. The 105^0 contact angle was achieved with around 1.0 and 1.2 kg/t dosage of ASA with BRC and BBS pulp furnishes respectively; however the same could not be achieved even at the highest dosage of ASA. The effect of GCC and PCC fillers on the contact angle of paper made from all three pulps is shown in Fig. 7 and 8 respectively. The contact angle behavior of paper made with GCC and PCC filler was comparable at all dosage of ASA emulsion. The behavior of pulp furnishes with all three fillers was also comparable at different dosage of ASA.

$Cobb_{60}$ vs. Contact Angle Behavior of Different Pulps

The $Cobb_{60}$ vs. contact angle behavior of all the three pulps without filler is shown in Fig. 9. It was observed that the BWS pulp had the poorest trend of the $Cobb_{60}$ vs. contact angle

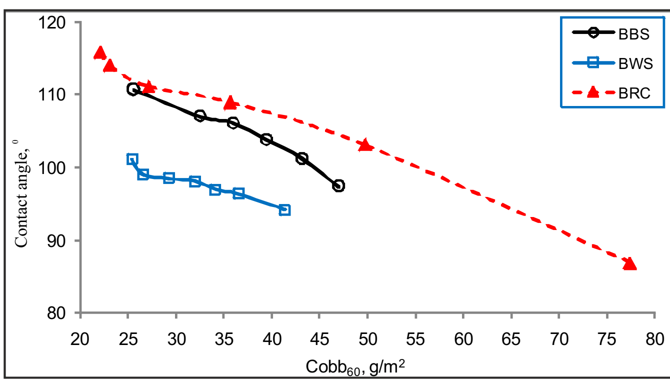

Figure 9: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in ASA sizing (without Filler)

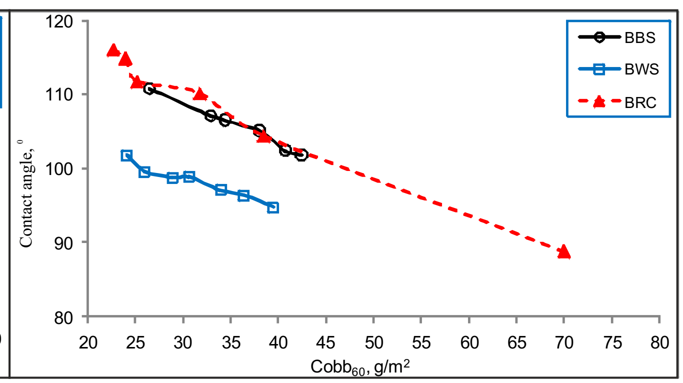

Figure 10: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in ASA sizing with talc filler

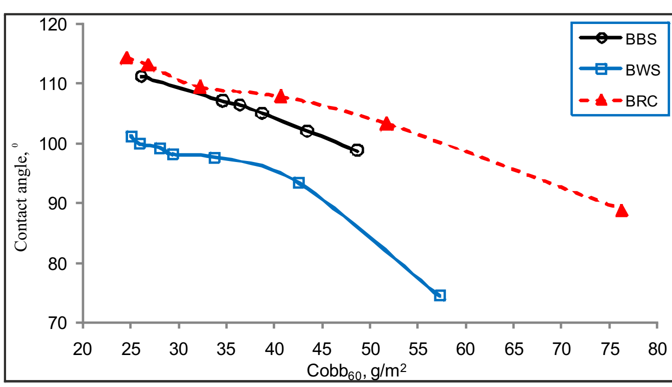

Figure 11: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in ASA sizing with GCC filler

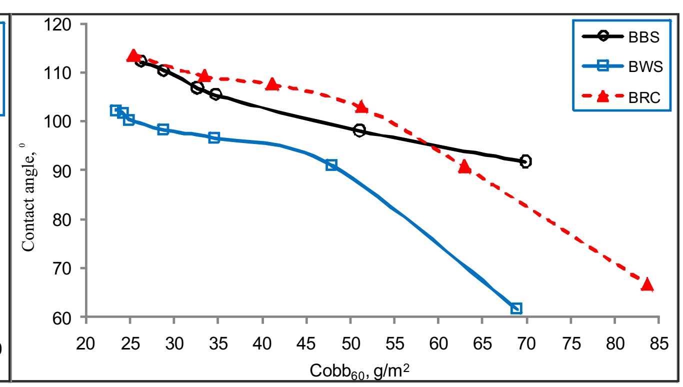

Figure 12: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in ASA sizing with PCC filler

behavior. This trend was comparatively better in case of another agro-residue pulp i.e. BBS pulp. The contact angle of papers at 30 g/m^2 $Cobb_{60}$ value with BBS, BWS and BRC pulps were 108, 98 and 111^0 respectively. The contact angle of around 100^0 could be achieved at the $Cobb_{60}$ value of 45 g/m^2 or higher in case of BBS and BRC pulp. In case of BWS pulp the contact angles were on lower side and stable. A slightly higher contact angle of around 105^0 could be achieved at the $Cobb_{60}$ value of 35 g/m^2 or higher in case of BBS and BRC pulp, however in case of BWS pulp this contact angle value could not be achieved. The $Cobb_{60}$ vs. contact angle behavior of all the three pulps with talc, GCC and PCC fillers is shown in Fig. 10, 11 and 12 respectively. It was observed that the filler had no effect on this behavior and provided more or less same trend.

Conclusion

The sizing behavior of paper depends upon the papermaking fibers along with wet-end additives. The sizing of the paper made from agro-residue pulps was comparatively more stable than that of recycled pulp. The contact angles of the sheets prepared from bleached recycled pulp were quite higher than that of agro-residue pulps. The $Cobb_{60}$ vs. contact angle behavior of the pulps has shown that the contact angle of 100^0 or more can be easily achieved at a $Cobb_{60}$ value of 45 g/m^2 or more in case of bleached bagasse and recycled pulps; the latter showed better sizing behavior. The type of filler had an impact on the development of $Cobb_{60}$ and/or contact angle values separately, however it did not impact the $Cobb_{60}$ vs. contact angle behavior of paper. Under our experimental conditions, it is concluded that there is no requirement of making a hard sized paper (with a $Cobb_{60}$ value of 25 g/m^2 or lesser) from the agro-residue and recycled pulps.

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