Role of AKD and ASA Emulsions in Improving Hydrophobicity of Recycled Fiber Based Paper

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ABSTRACT

Due to the shortage of native fiber and environmental regulations, the demand of recycled fibers is increasing with time. Generally, the recycled fibers comprising alkaline sizing chemicals; alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA) are imported for use in India. The dose of sizing chemicals depends upon various parameters such as type of raw material and filler. The present study deals with the use of AKD and ASA emulsions at different dose levels in bleached recycled fibers with three commercially available fillers; talc, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) at 15% ash level. The $Cobb_{60}$ and contact angle of the sheets were compared and the relationship between $Cobb_{60}$ vs. contact angle was developed and compared for both AKD and ASA with all fillers. Due to different particle size, shape and charge characteristics, the fillers affected the hydrophobicity of paper differently. It was observed that without filler and with talc filler, the $Cobb_{60}$ values were lower in AKD sizing whereas with GCC and PCC fillers those were lower in ASA sizing. The contact angles were higher in ASA sizing as compared with AKD sizing. The $Cobb_{60}$ vs. contact angle relationship was also better in ASA sizing than AKD sizing which showed that the former is a better sizing chemical for such grade of bleached recycled fibers. The contact angle of 105^o, which is considered fairly good for writing and printing paper grades, could be achieved at 25-30 and 38-48 g/m^2 $Cobb_{60}$ values in AKD and ASA sizing, respectively with all three fillers. These results showed that there is no worth adding higher dose of sizing chemicals in pulp based on only $Cobb_{60}$ values, rather it would be advisable to consider contact angle along with $Cobb_{60}$ for the same.

Keywords: *Contact angle, $Cobb_{60}$, Filler, Paper, Recycled fiber, Sizing*

Introduction

In papermaking, sizing is the process by which a sizing chemical provides hydrophobicity to paper i.e. resistance to liquid wetting, penetration and absorption. It is generally measured through $Cobb_{60}$, Hercules size test and contact angle. The most widely used test in the paper industry is $Cobb_{60}$ wherein a water column is rested on the paper surface for 60 seconds and the amount of water absorbed by the paper per unit area is reported. Contact time of aqueous solutions with paper during the various printing applications is of milliseconds. Despite being of paramount importance, the interaction between water molecules and paper over the short time scale cannot be determined through the water absorption ($Cobb_{60}$) test. Contact angle is the improved technique in this respect to measure the hydrophobicity of paper. The contact angle for a drop of aqueous liquid increases as the paper surface becomes hydrophobic and, conversely, decreases as the surface becomes wet [1-3]. Understanding the behavior or interaction of water molecules in contact with paper surface is highly essential to control the sizing of paper [1].

Cellulose is hydrophilic with a high surface energy. The porous structure of paper acts like a 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 some protection against liquid absorption [3, 4]. Commercially, sizing could be done in acidic, neutral and alkaline conditions. Alkaline sizing has numerous benefits over acidic sizing, which are already discussed in literature so much. There are mainly two alkaline sizing chemicals; alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). Both ASA and AKD are considered effective and have been used as internal sizing agents in papermaking for many years [1, 2, 5-9]. The exact mechanism of these agents is not known clearly with researchers considering that any chemical bond between cellulose and AKD is not responsible for paper sizing, and they have raised doubts about the cellulose reactive mechanism of AKD [3, 10, 11].

Both AKD and ASA have their own positive impacts and limitations for use as sizing chemicals in papermaking. AKD, a wax based emulsion having good stability, is shipped as a ready to use chemical to the paper mills, however ASA, an oil based chemical, is emulsified on site just before its addition to pulp due to its low stability as compared with the former [12]. It is highly required to use the ASA emulsion within few minutes of its emulsification. Though AKD is a good sizing agent, it has some drawbacks such as being wax it causes the slipperiness to the final sheet. Slow reactivity of AKD can mean that the sheet is unsized by the time it reaches the size press. Over drying of sheet is required to achieve some curing. ASA 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, it hydrolyses

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easily in aqueous emulsion to form alkenyl succinic acid, which is detrimental to sizing [2, 3, 12].

Moreover, the different inorganic fillers; talc, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), are used in the production of paper. The morphology, ionic nature, particle size distribution (PSD), specific surface area and shape of the filler particles affect the sizing characteristics of paper. In general, filler has a larger surface area than fiber that can consume more amount of sizing chemicals than the latter. This can ultimately reduce the hydrophobicity of paper [13]. However, the basic nature of the filler particles (hydrophilic/hydrophobic) will have a significant role in the consumption of sizing chemical and improving hydrophobicity of paper.

Due to the diversity in the raw material for making paper, the colloidal charge demand of the pulp furnishes vary which eventually affect the demand of the wet-end additives and sizing chemicals [2]. Overdosing of sizing chemicals causes the deposit problem on the wire part of machine and hence adversely affects the machine runnability. It is highly desired to optimize the dose of sizing chemicals to react with fiber and provide the required extent of sizing to paper. As very little research has been carried out on the emerging raw materials such as recycled fiber, this study was devised to understand the behavior of both AKD and ASA sizing with the recycled fibers in the presence of talc, GCC and PCC fillers.

Experimental

Materials

The bleached recycled pulp was procured from a pulp and paper mill in southeast India. The pulp was used as such without refining. Various wet-end chemicals such as AKD emulsion, ASA oil, cationic starch, citric acid, cationic fatty acid condensation product (FAC), cationic polyamine based fixing agent (PFA), poly aluminum chloride (PAC), talc, GCC, 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 particle size determination of the AKD/ASA emulsions and fillers was done using Laser scattering particle size distribution analyzer (Horiba LA950S2). Talc was first wetted with ethanol whereas both GCC and PCC were wetted with sodium hexa meta phosphate and then dispersed with deionized water to make 10% (w/v) filler slurry for measuring particle size. A Mutek particle charge detector (PCD 03 pH) was used to examine the ionic behavior and colloidal charge of 10% (w/v) slurry of fillers. A Mutek system zeta potential meter (SZP 06) was used to determine the charge of fillers in the form of zeta potential.

Cationic starch of 3% solids (w/v) was cooked at 90±2^{0}C for 30 minutes with continuous agitation. ASA emulsion was prepared at ambient temperature using a high shear mixer with the addition of ASA oil gradually to the cationic starch. Ratio of ASA to cationic starch was kept as 1:3 for making the ASA emulsion. The pH was maintained as 3.8-4.0 using citric acid. Distilled water was used for the preparation of different chemical solutions. The AKD and ASA emulsions were characterized in terms of pH, colloidal charge and particle size. For the latter, the emulsions were diluted to 0.5% solids and 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 following sequence of addition of different materials in stock preparation was used for AKD and ASA sizing; 1) For AKD sizing: pulp (1% consistency), PFA, cationic starch, AKD emulsion, filler, filtered water (to dilute the pulp slurry to 0.4% consistency) and retention aid chemical; 2) For ASA sizing: pulp (1% consistency), FAC, PAC, cationic starch, ASA emulsion, filler, filtered water (to dilute the pulp slurry to 0.4% consistency) and retention aid chemical. Paper handsheets of 70 g/m^2 were prepared with 15% ash content, and pressing and drying were done 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 sheets were conditioned for 24 hours at 23±1^{0}C and 50±2% relative humidity as per TAPPI test method T 402 sp-98.

The hydrophobicity of paper was measured through Cobb$_{60}$ and contact angle tests. The Cobb$_{60}$ of the handsheets was measured using Cobb sizing tester as per TAPPI test method T 441 om-98. The contact angle of the handsheets was measured on Kruss drop shape analyser (model: DSA 10, Kruss) as per TAPPI test method T 458 cm-94. The DSA 10 measured the dynamic contact angle at 1 second intervals over a total 60 seconds by drawing a tangent at the contact where the water and the paper surface intersect. The arithmetic average of all 60 readings of dynamic contact angle values was also calculated and termed as average contact angle.

Results and Discussion

Characteristics of Input Materials

The ^{0}SR of bleached recycled unrefined pulp was 28. Other physico-chemical and morphological properties are given in Table 1. The average fiber length, width, coarseness and fines content of the recycled pulp were 853 µm, 19.2 µm, 82.3 µg/m and 9.2%, respectively. The cationic charge demand of the pulp was 14.3 µeq/L. The ISO brightness, air permeance and Bendtsen

Table 1: Different characteristics of bleached recycled pulp

Particular	Value
Average fiber length, µm	853
Average fiber width, µm	19.2
Coarseness, µg/m	82.3
Fines (Length weighted), %	9.2
^{o}SR of unrefined pulp	28
Charge demand, µeq/L	-14.3
Brightness, % ISO	80.2
Air permeance, Gurley s/100mL	5.6
Bendtsen roughness, mL/min	181

roughness of 70 g/m^2 sheets made from the recycled fibers were 80.2%, 5.6 s/100mL and 181 mL/min, respectively.

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. Brightness of PCC was the highest followed by GCC and talc. All fillers were alkaline in nature. The median particle size of talc, PCC and GCC was 10.7, 4.8 and 2.8 µm, respectively. Talc and GCC were anionic whereas PCC was cationic in nature. The cationic charge demand of GCC and talc fillers was 1.7 and 3.9 µeq/g whereas the anionic charge demand of PCC filler was 6.9 µeq/g (Table 2).

Table 2: 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 (laser scattering), µm	10.7	2.8	4.8
Colloidal charge demand, µeq/g	1.7 (cationic)	3.9 (cationic)	6.9 (anionic)
Zeta potential, mV	-267	-195	+159

As shown in Table 3, the solids content of the commercial AKD emulsion was 20.8% (w/v) whereas the ASA emulsion was prepared at 1% (w/v) solid in lab. The pH of both the emulsions was acidic (3.3-3.4). Both the emulsions were cationic; AKD was more cationic having an anionic charge demand of 460 µeq/g against 137 µeq/g anionic demand of ASA emulsion. The particle size of ASA emulsion was little coarser than that of AKD emulsion.

Table 3: General characteristics of AKD and ASA emulsions

Particular	AKD	ASA
Total solids (w/v), %	20.8	4.0
pH	3.3	3.4
Anionic charge demand, µeq/g	460	137
Particles less than 1 µm, %	77	56
Particles less than 2 µm, %	100	93

The colloidal as well as surface charge of the pulp stock after addition of all wet-end chemicals was also measured and given in Table 4. The cationic charge demand of the pulp stock in ASA sizing was little higher than that in AKD sizing at the same $Cobb_{60}$ value with all fillers. The surface charge of the pulp stock measured in the form of zeta potential was influenced by the type of the fillers and sizing chemical. Without filler and with talc filler, the anionic zeta potential was more in AKD sizing whereas it was more in ASA sizing with GCC and PCC fillers. The pH of the pulp stock in both AKD and ASA sizing was maintained at about 8.

$Cobb_{60}$ in AKD and ASA sizing

The sizing chemical increases the hydrophobicity of paper; the latter increases with increase in the former. $Cobb_{60}$ values of the paper handsheets were decreased with an increase in the dose of sizing chemical (Figures 1-4). Initially at lower dose levels of AKD/ASA sizing chemical the $Cobb_{60}$ values were decreased at a faster rate than at higher dose levels of the former. At lower dose of emulsions, difference in $Cobb_{60}$ values was more but at higher dose levels it was less.

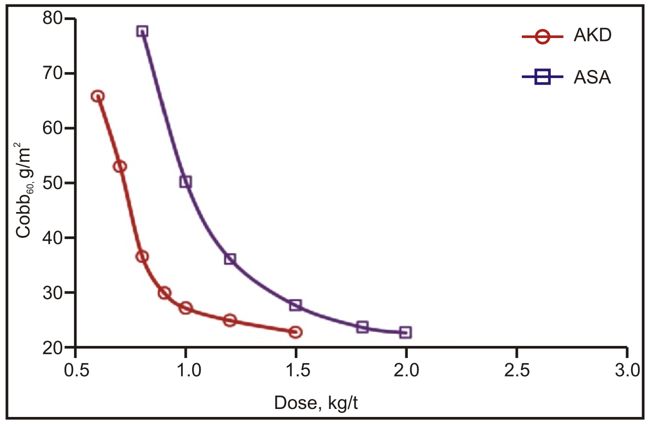

Figure 1: Effect of AKD and ASA sizing on hydrophobicity ($Cobb_{60}$) of recycled fiber based paper *without using filler*

In case of without filler and with talc filler, the trend of $Cobb_{60}$ values with increasing dose of sizing chemicals was comparable (Figures 1-2). The $Cobb_{60}$ values were lower in AKD sizing than ASA sizing. In case of no filler, the required dose of AKD and ASA to achieve 30 $Cobb_{60}$ value was about 0.88 and 1.37 kg/t, respectively (Figure 1).

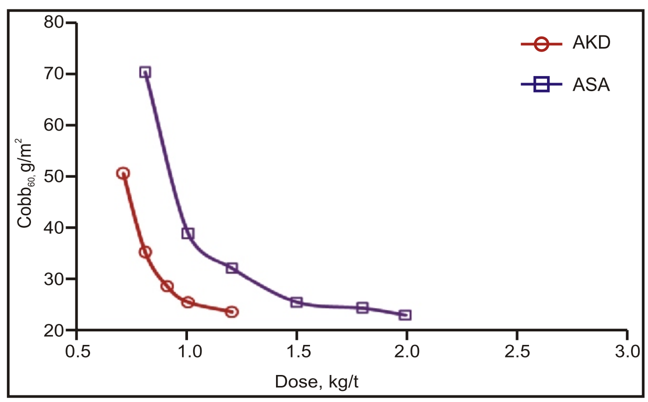

Figure 2: Effect of AKD and ASA sizing on hydrophobicity ($Cobb_{60}$) of recycled fiber based paper *with talc filler*

Table 4: Characteristics of pulp stock for AKD and ASA sizing for getting 30 g/m^2 $Cobb_{60}$ value of paper

Particular	No filler		Talc		GCC		PCC	
	AKD	ASA	AKD	ASA	AKD	ASA	AKD	ASA
Cationic charge demand, µeq/L	10.2	13.3	9.2	11.6	8.2	11.4	8.4	9.4
Conductivity, mS	0.482	0.365	0.482	0.375	0.481	0.392	0.484	0.389
Zeta potential, mV	-24.1	-12.3	-23.9	-19.9	-18.8	-19.1	-23.8	-25.6
pH	8.0	8.0	8.0	8.1	8.0	8.0	8.0	8.1

In case of talc filler, the requirement of dose was slightly reduced to 0.86 and 1.26 kg/t, respectively (Figure 2).

As shown in Figure 3, with GCC filler the requirement of both AKD and ASA emulsions was higher than that with talc filler for getting the same $Cobb_{60}$ value. The dose of AKD and ASA required to get about 30 $Cobb_{60}$ value was increased to about 1.94 and 1.62 kg/t, respectively. In case of GCC filler, it was interestingly observed that the requirement of AKD was more than that of ASA which was just opposite to the case of without filler and talc filler. These results indicated that ASA sizing is more suitable for GCC filler than AKD sizing for getting same $Cobb_{60}$ value of paper. The similar results were also seen with PCC filler, however the dose of both AKD and ASA further increased to about 2.43 and 1.90 kg/t, respectively (Figure 4).

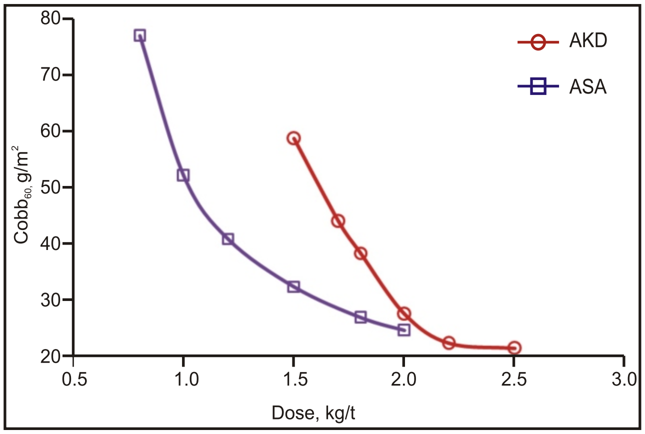

Figure 3: Effect of AKD and ASA sizing on hydrophobicity ($Cobb_{60}$) of recycled fiber based paper *with GCC filler*

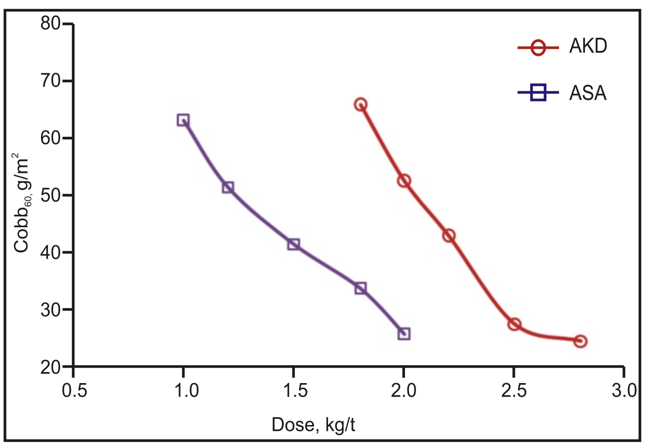

Figure 4: Effect of AKD and ASA sizing on hydrophobicity ($Cobb_{60}$) of recycled fiber based paper *with PCC filler*

Fillers, having a larger surface area than fibers, consume the sizing agent and in addition they cannot be sized because reactive sizing chemicals do not react with them. This can ultimately reduce the hydrophobicity of paper, however this effect depends on the filler, with talc possibly helping the sizing effect due to its own natural hydrophobicity [3, 14]. It is believed that the sizing agents may be lost or rendered ineffective from furnish due to a disproportionate fraction of a sizing agent being absorbed on the high surface area filler in the furnish. Increased loading levels of inorganic fillers are therefore associated with negative effects on sizing efficiency of the filled sheets and increased demand for sizing agents [3, 15].

Contact Angle in AKD and ASA sizing

The importance of contact angle in the papermaking has already been discussed by the different authors earlier [1-3]. In the Figures 5-8, the average contact angle of the water droplet with paper measured over the period of 1 to 60 seconds has been presented against dose of AKD/ASA emulsion. As expected, the contact angle of paper was increased with increase in the dose of sizing chemicals. As shown in Figure 5, the dose of both AKD and ASA emulsions required to get about 105° contact angle was comparable (1.04-1.10 kg/t). The similar trend was observed with talc filler where the requirement of AKD/ASA was about 1.0 kg/t (Figure 6). The similar results were shown by Ashish et al. [2]; incorporation of talc filler in pulp had no impact on the contact angle of paper. The contact angle was same in both the cases i.e. pulps without filler and with talc filler.

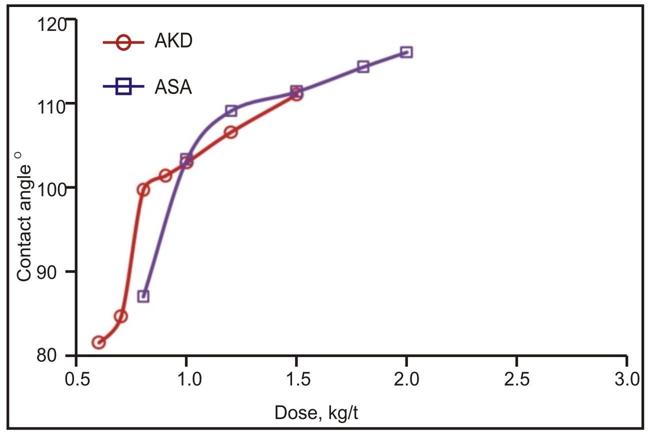

Figure 5: Effect of AKD and ASA sizing on hydrophobicity (contact angle) of recycled fiber based paper *without using filler*

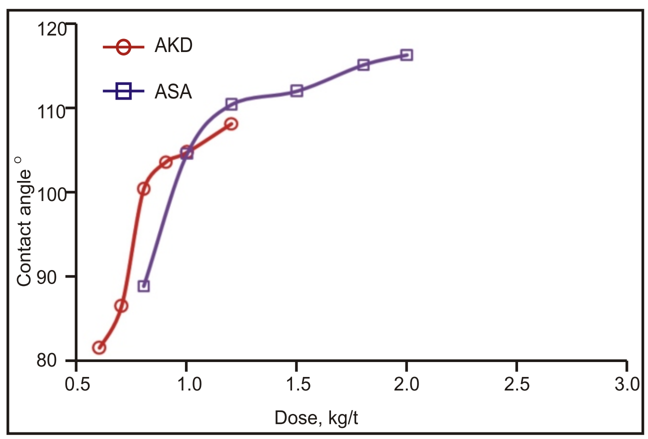

Figure 6: Effect of AKD and ASA sizing on hydrophobicity (contact angle) of recycled fiber based paper *with talc filler*

The above trend of contact angle was changed with the incorporation of both calcium carbonate fillers in paper. With GCC filler to get about 105° contact angle, the dose of ASA was

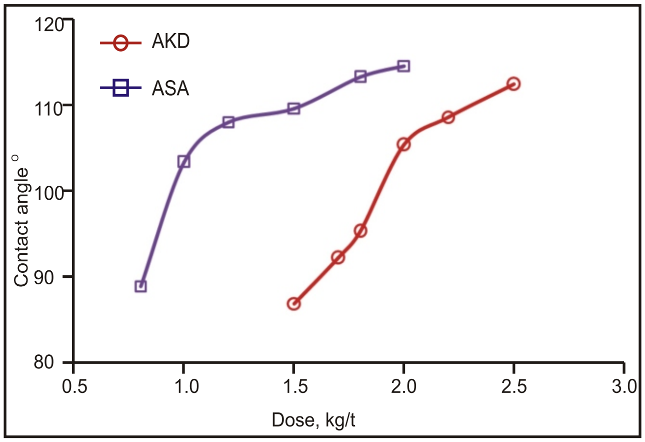

Figure 7: Effect of AKD and ASA sizing on hydrophobicity (contact angle) of recycled fiber based paper *with GCC filler*

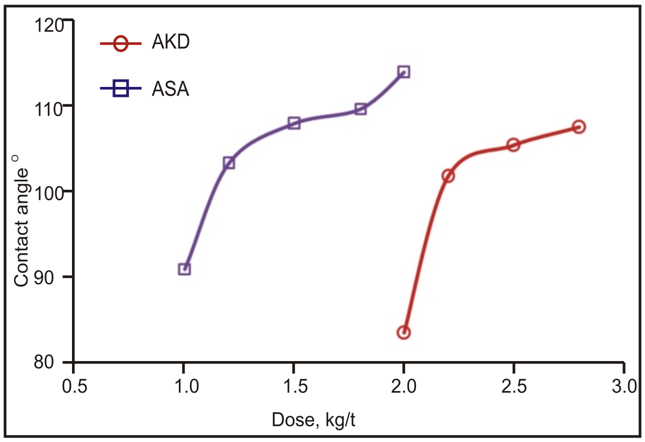

Figure 8: Effect of AKD and ASA sizing on hydrophobicity (contact angle) of recycled fiber based paper *with PCC filler*

comparable to that of talc filler (1.04 kg/t) whereas that of AKD was significantly increased to about 1.99 kg/t (Figure 7). The highest AKD/ASA emulsion dose requirement was with PCC filler among all fillers used (Figure 8). For ASA it was 1.28 kg/t whereas for AKD it was 2.45 kg/t. PCC filler required about 23% higher dose of sizing chemicals as compared with GCC to get about 105° contact angle. Earlier it has been shown that the agro residue based pulp provides comparatively lower values of contact angle than that in recycled pulp in ASA sizing. Moreover, the contact angles were stable with respect to time [2].

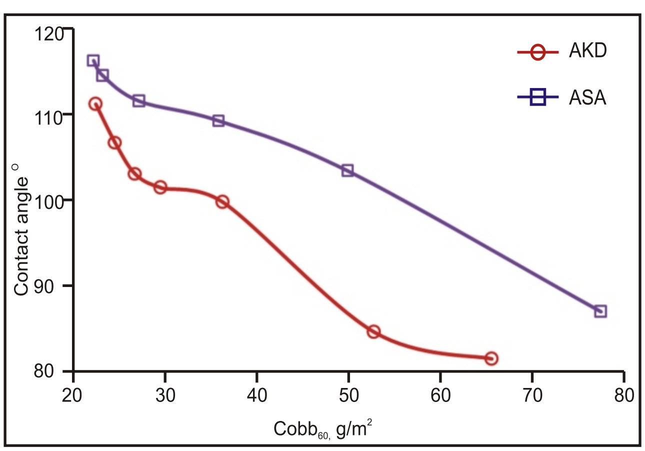

Figure 9: Cobb$_{60}$ vs. contact angle relationship of recycled fiber based paper following AKD and ASA sizing *without using filler*

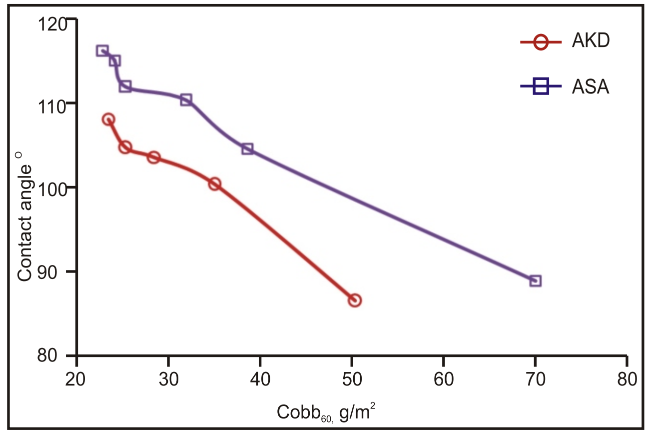

Figure 10: Cobb$_{60}$ vs. contact angle relationship of recycled fiber based paper following AKD and ASA sizing *with talc filler*

Cobb$_{60}$ vs. Contact Angle Behavior in AKD and ASA Sizing

In order to make the paper with desired hydrophobicity depending upon the printing process, the analysis of Cobb$_{60}$ vs. contact angle behavior with different fillers is an important practice to perform. It has been shown earlier that the contact angles of paper made from recycled fibers are reasonably good in ASA sizing. The contact angle of 100^0 could be achieved at the Cobb$_{60}$ value of 45 g/m^2 or higher with recycled pulp in ASA sizing [2]. The present results showed the similar trend of Cobb$_{60}$ vs. contact angle behavior. As shown in Figure 9, when no filler was used, this behavior was better in ASA sizing than AKD sizing. The contact angle of about 105° could be achieved at the Cobb$_{60}$ value of 25 and 46 g/m^2 in AKD and ASA sizing, respectively from the sheets made from recycled fibers only (Table 5). This showed that in ASA sizing, the paper could be manufactured with comparatively higher Cobb$_{60}$ values which will reduce the sizing chemical cost. In case of talc filler, this much of contact angle value could be achieved at the Cobb$_{60}$ value of 25 and 38 g/m^2 in AKD and ASA sizing, respectively (Figure 10, Table 5). In case of both GCC and PCC fillers, 105° contact angle could be achieved at the Cobb$_{60}$ value of 48 g/m^2 in ASA sizing which was

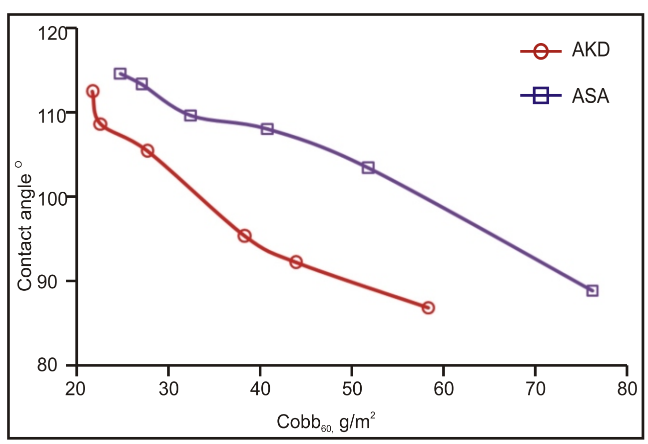

Figure 11: Cobb$_{60}$ vs. contact angle relationship of recycled fiber based paper following AKD and ASA sizing *with GCC filler*

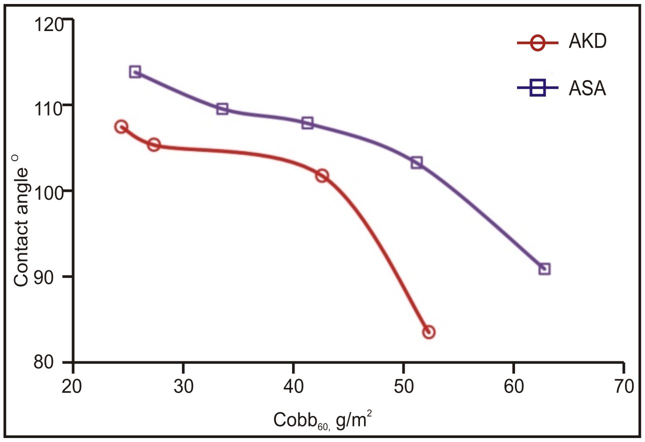

Figure 12: $Cobb_{60}$ vs. contact angle relationship of recycled fiber based paper following AKD and ASA sizing *with PCC filler*

Table 5: $Cobb_{60}$ values of paper at 100 and 105° contact angles with different fillers and sizing chemicals

Particular	Contact angle, 100°		Contact angle, 105°	
	AKD	ASA	AKD	ASA
No filler	35	55	25	46
Talc	35	47	25	38
GCC	33	57	28	48
PCC	44	54	28	48

comparable to the results of no filler, however in AKD sizing 28 g/m^2 $Cobb_{60}$ value was required for the same (Figures 11-12). Sharma et al. [2] showed that the type of filler (talc, GCC and PCC) had no effect on $Cobb_{60}$ vs. contact angle behavior and provided more or less same trend with all fillers.

The similar trend of $Cobb_{60}$ values could also be observed for 100° contact angle (Table 5). It was observed that in AKD sizing this much of contact angle could be achieved at about 33-35 g/m^2 $Cobb_{60}$ value for the cases of no filler, with talc and GCC filler whereas in case of PCC filler, comparatively higher $Cobb_{60}$ value (44 g/m^2) will give the same contact angle. In ASA sizing, again the requirement of $Cobb_{60}$ value was higher than that in AKD sizing for achieving the 100° contact angle in paper. In ASA sizing, the requirement of $Cobb_{60}$ value was about 54-57 g/m^2 for the cases of no filler, with GCC and PCC filler whereas in case of talc filler, comparatively lower $Cobb_{60}$ value (44 g/m^2) will give the same contact angle, similar to the case of 105° contact angle. As shown in Figures 9-12, the $Cobb_{60}$ vs. contact angle behavior of recycled pulp was better with ASA sizing than AKD sizing. The paper with comparatively much higher $Cobb_{60}$ value may be prepared in ASA sizing for getting a good contact angle whereas in AKD sizing, little hard size paper needs to be prepared for the same. It will increase the dose requirement of AKD emulsion.

Conclusion

The alkaline sizing agents; AKD and ASA, provide dissimilar hydrophobciity in paper. The type of filler added to pulp viz. talc, GCC and PCC had substantial effect on hydrophobicity of paper. For recycled pulp, AKD sizing was found suitable with talc filler whereas ASA sizing was more suitable with GCC and PCC fillers. For all fillers, the contact angles of the sheets following ASA sizing were higher than those obtained by following AKD sizing. The $Cobb_{60}$ vs. contact angle behavior of recycled pulp was also found better following ASA sizing as the contact angle of 105° could be achieved at the $Cobb_{60}$ values of 38-48 g/m^2 as against 25-28 g/m^2 following AKD sizing. The type of filler had no impact on $Cobb_{60}$ vs. contact angle behavior of paper made from recycled fibers.

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References

[1]. Sharma, A., Chauhan, V.S., Chakrabarti, S.K. and Varadhan, R. (2010). Control of degree of sizing through measurement of contact angle and surface energy. Ippta J. 22(2), 143-145.

[2]. Sharma, A., Kakkar, S., Chauhan, V.S., Chakrabarti, S.K. and Varadhan, R. (2012). Efficacy of ASA sizing with agro-residue and recycled pulps using different fillers. Ippta J. 24(3), 93-98.

[3]. Chauhan, V.S. and Bhardwaj, N.K. (2013). Effect of particle size and preflocculation of talc filler on sizing characteristics of paper. Appita J. 66(1), 66-72.

[4]. Hagemeyer, R.W., Kocurek, M.J. and Manson, D.W. (1992). Pulp and Paper Manufacture Series, Vol. 6, Stock Preparation.

[5]. Hodgson, K.T. (1994). A review of paper sizing using alkyl ketene dimmer versus alkenyl succinic anhydride. Appita J. 47(5), 402-406.

[6]. Marton, J. (1990). Practical aspects of alkaline sizing. Tappi J. 73(11), 139-143.

[7]. Shen, W., Parker, I.H., Brack, N. and Pigram, P.J. (2001). A simplified approach to understanding the mechanism of AKD sizing. Appita J. 54(4), 352-356.

[8]. Paul, S.K., Balasubramaniam, S. and Lakshminarayanan, T.K. (2004). Alkaline sizing for manufacture of coloured papers. Ippta J. 16(3), 53-57.

[9]. Hubbe, M.A. (2006). Paper's resistance to wetting A review of internal sizing chemicals and their effects. Bioresources 2(1), 1-40.

[10]. Song, X., Chen, F. and Liu, F. (2012). Study on the reaction of alkyl ketene dimer (AKD) and cellulose fiber. BioResources 7(1), 652-662.

[11]. Yoshida, Y., Heux, L. and Isogai, A. (2012). Heterogeneous reaction between cellulose and alkyl ketene dimer under solvent-free conditions. Cellulose 19, 1667-1676.

[12]. Bajpai, P.K., Sharma, A.K., Das, S. and Varadhan, R. (2008). Optimization of ASA emulsion and impact of filler on ASA sizing. Ippta J. 20(3), 99-104.

[13]. Krogerus, B. (2008). Papermaking Chemistry, 2nd ed., Raimo Alen (ed.), Finnish Paper Engineers' Association, Helsinki, Finland.

[14]. Lindström, T. and Larsson, P.T. (2008). Alkyl ketene dimer (AKD) sizing a review. Nordic Pulp Pap. Res. J. 23(2), 202-209.

[15] Bartz, W.J., Darroch, M.E. and Kurrle, F.L. (1994). Alkyl ketene dimer sizing efficiency and reversion in calcium carbonate filled papers. Tappi J. 77(12), 139-148.