Control of degree of sizing through measurement of contact angle and surface energy

Sharma A, Chauhan VS, Chakrabarti SK, Varadhan R

ABSTRACT

Paper during lithographic printing, printing with water based inks, gluing operations and paperboard converting, and water based coating requires controlled hydrophobicity. Contact time of aqueous solutions with paper during all these applications is of milliseconds. Industries use various methods e.g. Cobb & Hercules size test to measure 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 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. Understanding the behavior or interaction of water molecules in contact with paper surface is highly essential to control the sizing of paper. Attempts have been made to observe the wettability of paper through the measurement of both contact angle and $Cobb_{60}$ tests, and find the relationship between the two. In this regard, paper handsheets prepared in laboratory, sized with different sizing chemicals viz. rosin, AKD and ASA, as well as various commercial writing & printing paper samples were analyzed. The effect of filler viz. talc, GCC and PCC has also been shown on the sizing behavior of paper. Generally, the contact angle value decreases with increase in Cobb value. In case of some commercial paper samples, it has been found that the contact angle may not be the same at same Cobb values. In some cases, the contact angle values were higher even at higher Cobb values. The values of contact angle were different with different sizing chemicals even at same Cobb values. This study opens-up an arena to select the right contact angle for a particular grade of paper and fix-up the degree of sizing.

Keywords: $Cobb_{60}$, contact angle, hydrophobicity, sizing and surface energy

Introduction

Most grades of paper and boards, excluding those used for tissues and hygiene applications need to be resistant to wetting and penetration by liquids. Sizing is defined as a process wherein chemical additives are introduced to provide paper or paperboard with this resistance. Sizing of paper is performed in order to reduce the paper's tendency when dry to absorb liquid, with the goal of allowing inks and paints to remain on the surface of the paper, and to dry there rather than be absorbed into the paper. This provides a more consistent, economical, and precise printing, painting, and writing surface. This is achieved by curbing the paper fibers' tendency to absorb liquids by capillary action [1].

There are two types of sizing; internal and external. Internal sizing is applied to almost all papers and especially to all those that are machine made, while surface sizing is added for the highest grade viz. bond, ledger and writing papers. Internal sizing chemicals used in papermaking at the wet-end are alkenyl succinic anhydride (ASA), alkyl ketene dimer (AKD) and rosin. By making the paper web more hydrophobic, the sizing agents influence dewatering and retention of fillers and fibers in the paper sheet. Next to paper quality, main effect of internal sizing agent is on runnability of the paper machine [2, 3].

Over the years, a large number of methods have been developed for measurement of the degree of sizing (viz. hydrophobicity). On the basis of the nature of the methods, they can be grouped roughly as follows [4]:

- Methods which assess the penetration of the liquid in the z-direction of the sample (e.g., Currier test, KBB test, NBS method, Hercules size test (HST), fluorescent dye size test, dry indicator test, ink flotation test, ferric thiocyanate test, lactic acid test)
- Methods which assess the absorption of the test liquid (e.g., Cobb test, water immersion test, edge-wick or Klemn capillary rise test)
- Tests which measure a surface property that implicitly or explicitly depicts the degree of sizing or hydrophobicity (eg. contact angle test, drop test, curl test)

The purpose of all these methods is to provide rapid means of accessing aqueous liquid resistance, suitable for process and product control, in as reproducible a way as possible.

Contact time of aqueous solutions with paper during printing and other end-applications is of milliseconds. The most widely used test in Indian paper industries is $Cobb_{60}$ wherein a water column is rested on the paper surface with definite duration. It gives the amount of water absorbed by a paper substrate in 60 seconds. Interaction of water molecules with paper in the time scale can not be determined through this test, though it is very essential for the above said end operations. The measurement of contact angle and surface energy is an advance method used to determine the hydrophocity of paper worldwide which represents the rate of penetration of water into the paper surface with respect to time. The contact angle for a drop of aqueous liquid increases as the paper surface

Thapar Centre for industrial research & Development, Research and Competency Division in Pulp & Paper, BILT Campus,
Yamuna Nagar, - 135001 (India)

becomes hydrophobic and, conversely, decreases as the surface becomes more wettable. Contact angle measurement with several liquids of known surface tension and polarity can also give calculated value of surface energy of solid surface [5].

Young established the well-regarded Young's Equation which defines the balances of forces caused by a wet drop on a dry surface. If the surface is hydrophobic, the contact angle of a drop of water will be larger. The Young's equation gives the following relation [4],

$$\acute{y}_{SV}\ \ \acute{y}_{SL} = \acute{y}_{LV} * \cos \Theta$$

where $\acute{y}_{SL}$, $\acute{y}_{LV}$, and $\acute{y}_{SV}$ are the interfacial tensions between the solid and liquid, the liquid and vapor, and the solid and vapor, respectively. The equilibrium contact angle that the drop makes with the surface is denoted by Θ. This is the basic equation for the model estimation of the surface tension/surface energy of the solid surface. The effect of surface tension of substrate on wetting behavior is shown in Figure 1.

Understanding the behavior of water molecules with reference to paper is highly essential to control the hydrophobicity in paper. Attempts have been made to draw the significance of the contact angle over $Cobb_{60}$ test and thereby drawing a relationship in the interaction of water droplets and water column in contact with paper.

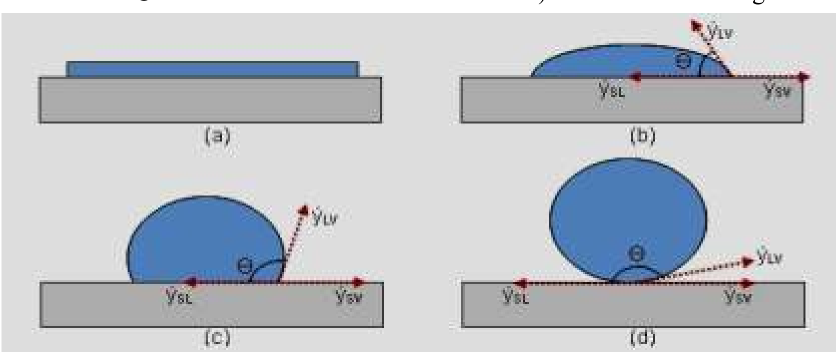

Figure 1: Different wetting behavior of substrates of different surface tension; a) complete wetting on high surface tension substrate (Θ=0°), b) partial wetting on lower surface tension substrate (Θ<90°), c) partial wetting on low surface tension substrate (Θ>90°), d) no wetting on very low surface tension substrate (Θ~180°)

EXPERIMENTAL

Materials

The pulp used in this study was taken from a paper industry in northern India which utilizes mixed hardwood and bamboo fibers (80:20 ratio). Pulp was refined to 30 °SR in PFI Mill.

The AKD sizing emulsion (15% solids) and rosin sizing chemical were taken from BASF India Ltd. and Ivax Paper Chemicals respectively. The ASA was prepared in laboratory using ASA oil of BASF India Ltd.

Different types of commercial fillers such as magnesium silicate (talc), ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) were used in ASA and AKD sizing whereas, in neutral sizing only talc and GCC were used.

Commercial writing and printing grade papers of 70 & 80 g/m^2 were collected from different paper mills in India and abroad.

Methods & Analytical Techniques

Paper handsheets of 70 g/m^2 were prepared on Lab Handsheet Former for all the experiments with 15% ash content.

$Cobb_{60}$ was estimated using standard Cobb tester as per TAPPI Test Method T 441 om-98. The test was performed for 60 seconds. Contact angle and surface energy of paper were determined on Drop Shape Analyzer (Kruss, model: DSA-10). The contact angle was measured for 60 seconds in 1 second interval using Sessile Drop method.

In case of AKD sizing, handsheets were prepared at pH of 8 and cured in oven at 105°C for 15 minutes after standard pressing and air-drying of handsheets. Neutral sizing experiments were carried out at 6.8-7.0 pH. The pH of filtered water used in all neutral sizing experiments was maintained using poly aluminium chloride.

A few preliminary experiments were carried out to optimize the process chemicals and conditions. The dosage of retention aid for all fillers was optimized as 200 g/t of pulp to maintain the first pass ash retention in paper. Optimized chemicals and conditions were used/ maintained in further experiments. The zeta potential of pulp slurries was maintained at around -10 to -12 mV.

RESULTS & DISCUSSION

Sizing Performance of ASA with Different Fillers

The paper handsheets of different $Cobb_{60}$ values were prepared in lab with various dosages of ASA. Table 1 shows the effect of ASA sizing with talc on hydrophobicity of paper. The contact angle up to a $Cobb_{60}$ value of 40.2 g/m^2 is quite constant with respect to time but at higher $Cobb_{60}$ values, the contact angle is not consistent. At 44.2 g/m^2 $Cobb_{60}$ value, it decreases from 100.5 to 98.8° in 60 seconds, but at 78.2 g/m^2 $Cobb_{60}$ value, it decreases from 104.1 to 13.4°. Wetting of paper surface as reflected through high $Cobb_{60}$ value and low contact angle, and presence of water column are the causative factors for more absorption of water in the soft sized condition. In spite of similar contact angles after 20 seconds in both the cases, the contact angle after 60 seconds are largely different. From these results it can be suggested that in ASA sizing with talc, the paper can be manufactured up to $Cobb_{60}$ value of 32 g/m^2 without any relative change of wetting behavior on paper. The surface energy decreases with increasing contact angle.

Table 1: Sizing performance of ASA sizing with talc

$Cobb_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
22.9	122.2	122.4	122.7	122.9	122.9	122.8	122.6	122.6	10.25
24.1	116.5	116.4	117.5	117.8	117.7	117.5	117.5	117.4	12.94
32.2	110.0	108.8	107.6	107.7	107.4	107.4	107.3	108.1	18.22
40.2	102.6	102.5	102.2	103.2	103.3	102.3	103.4	102.6	21.48
44.2	100.5	100.2	100.2	99.8	99.4	99.3	98.8	99.9	23.07
78.2	104.1	104.0	101.7	97.5	84.5	46.9	13.4	95.0	26.09

Measurement of contact angle in different sizing conditions over the period of 0 to 60 seconds depicts the capillary absorption behavior of water droplets in contact with paper. When the $Cobb_{60}$ value changes from 22.9 to 32.2 g/m^2, contact angle changes from

122.6 to 108.1° over a period of 60 seconds. This clearly demonstrates that the paper is having sufficient water resistance characteristics over this time range.

The similar trend was seen in ASA sizing with GCC (Table 2). Though, the values were quite different, the trend was very similar to previous case. Up to 28.4 g/m^2 Cobb$_{60}$ value, the contact angle was stable from 0 to 60 seconds. But, at higher Cobb$_{60}$ values, it decreased with time. The drop of contact angle is more pronounced softer sized papers.

Table 3: Sizing performance of ASA sizing with PCC

Cobb$_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
26.4	117.0	117.8	116.8	116.9	117.2	117.9	117.7	117.8	12.99
30.1	106.2	106.2	106.1	105.8	105.6	105.1	105.1	106.1	19.72
32.5	104.9	104.8	104.8	104.5	104.4	104.4	104.3	104.6	21.01
35.4	102.1	102.1	101.9	101.8	101.8	101.9	101.8	101.8	23.68

Table 2: Sizing performance of ASA sizing with GCC

Cobb$_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
24.2	117.6	118.7	119.3	119.7	119.2	119.4	119.6	119.0	12.10
28.4	112.6	114.3	114.3	114.3	113.9	113.6	113.1	113.7	14.73
48.8	101.1	101.3	101.0	100.8	97.3	95.9	95.4	99.4	23.40
53.2	100.6	100.1	98.4	96.8	95.8	95.3	95.6	97.5	24.60
63.8	91.5	91.0	90.2	88.4	85.1	91.1	78.7	86.9	31.14
78.9	97.5	96.4	88.9	78.4	71.6	70.8	70.5	79.8	35.63

Similar to talc and GCC, in ASA sizing with PCC, the contact angle up to 35.4 g/m^{2}Cobb$_{60}$ value, does not change with respect to time. It is very stable for initial contact of water droplet to 60 seconds. The Cobb$_{60}$ vs. contact angle behavior in ASA sizing is shown in Figure 2. In case of ASA sizing paper can be manufactured with a Cobb$_{60}$ value of 30-32 g/m^2 corresponding to contact angle of 105° which is a good value for writing and printing grade papers.

Sizing Performance of AKD with Different Fillers

AKD sizing results also show almost similar trend. The contact angles were quite stable with all fillers up to Cobb$_{60}$ value of 30 g/m^2. But an increase in Cobb$_{60}$ value decreases the stability of contact angle (Table 4-6). The Cobb$_{60}$ vs. contact angle behavior in AKD sizing is shown in Figure 3. In AKD sizing, it can be seen that up to a Cobb$_{60}$ value of 32-33 g/m^2, the average contact angle values with all fillers are around 105°. Here, the contact angle with all fillers are almost comparable.

Table 4: Sizing performance of AKD sizing with talc

Cobb$_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
21.2	114.9	112.1	112.0	112.1	111.9	111.8	111.1	111.9	16.41
29.8	108.8	106.8	105.9	105.5	105.7	105.8	105.9	106.8	21.44
41.1	102.8	102.0	101.8	101.2	100.9	100.2	99.3	100.9	23.87
53.8	93.8	92.9	91.1	90.5	77.3	78.9	71.8	91.2	30.01

Table 5: Sizing performance of AKD sizing with GCC

Cobb$_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
22.6	113.8	111.5	111.3	111.1	110.9	110.7	110.1	111.0	16.54
29.7	109.8	109.4	109.5	109.2	109.1	109.0	108.8	109.3	17.47
41.4	95.0	94.0	93.8	93.4	91.5	90.6	89.4	92.4	27.73

Table 6: Sizing performance of AKD sizing with PCC

Cobb$_{60}$, g/m^2	Contact angle, °								Surface energy, mN/m
	Time interval, s								
	5	10	20	30	40	50	60	Avg.	
25.5	113.0	111.2	111.1	111.3	110.4	110.2	110.1	110.9	16.73
34.6	107.9	104.9	104.1	104.1	104.0	103.8	103.3	105.0	21.90
47.7	95.9	93.6	91.0	90.3	90.2	88.7	87.1	91.4	32.11
61.7	86.7	83.0	80.2	72.3	62.8	59.1	54.7	77.4	36.82

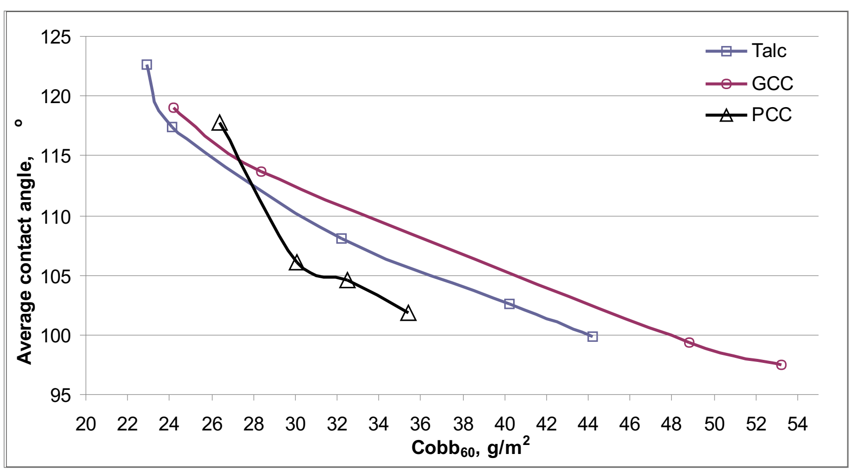

Figure 2: Cobb$_{60}$ vs. contact angle behavior of different fillers with ASA sizing

Sizing Performance of Rosin with Different Fillers

Rosin sizing was performed with only talc and GCC. The behavior of rosin as sizing agent is quite different to that with ASA and AKD. In rosin sizing, the contact angle behaviour was quite different with talc and GCC. The contact angle values were very good with talc. It is seen that to have a contact angle value of around 105°, the Cobb$_{60}$ values required with talc and GCC were 33 and 22 g/m^2 respectively (Figure 4). More dosage of rosin size is required in case of GCC while targeting harder sizing of paper.

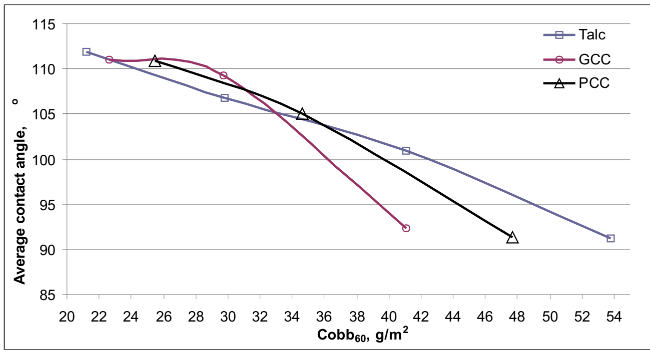

Figure 3: $Cobb_{60}$ vs. contact angle behavior of different fillers with AKD sizing

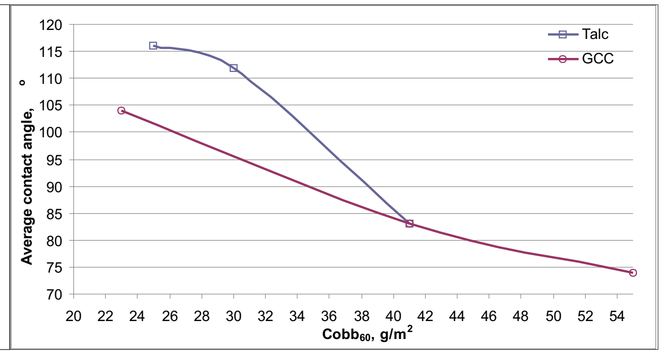

Figure 4: $Cobb_{60}$ vs. contact angle behavior of different fillers with neutral rosin sizing

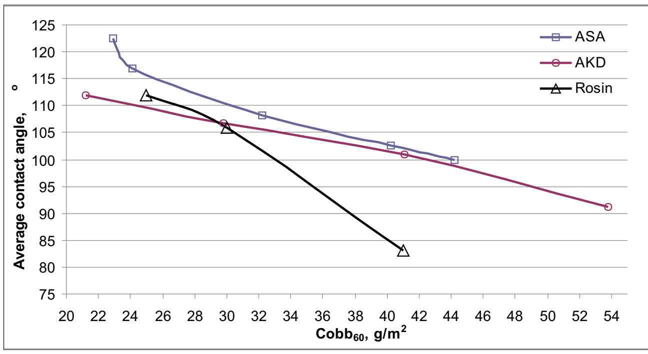

Figure 5: $Cobb_{60}$ vs. contact angle behavior of different sizing agents with talc

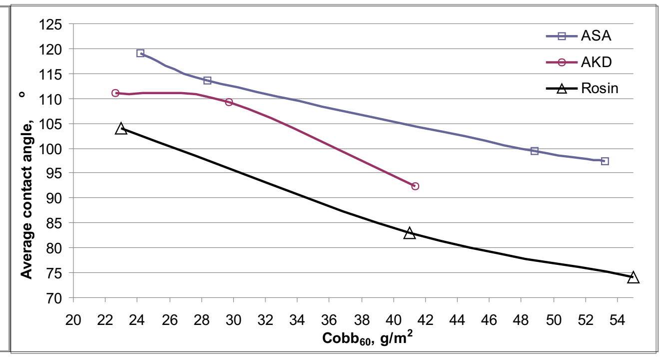

Figure 6: $Cobb_{60}$ vs. contact angle behavior of different sizing agents with GCC

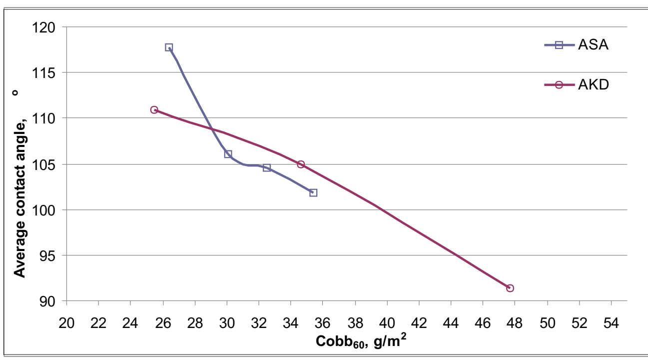

Figure 7: $Cobb_{60}$ vs. contact angle behavior of different sizing agents with PCC

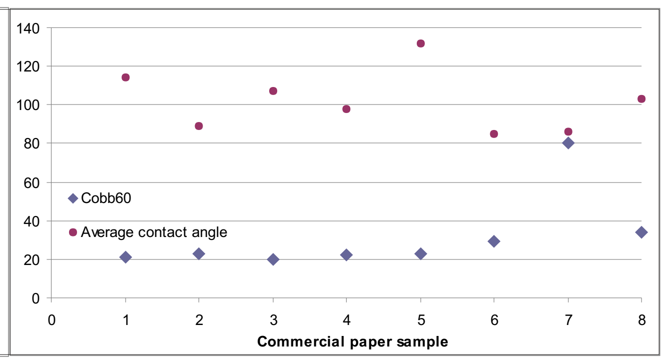

Figure 8: $Cobb_{60}$ vs. contact angle behavior of different commercial paper samples of 70 g/m^2 (sample 1-8, Indigenous papers; sample 7-8, imported papers)

Behavior of Sizing Agents with Talc

Figure 5 shows the $Cobb_{60}$ vs. contact angle behavior of different sizing agents with talc. For a specific $Cobb_{60}$ value, contact angle was the highest with ASA sizing followed by AKD and rosin. On the other hand to have a contact angle value of around 105°, the $Cobb_{60}$ values required with ASA, AKD and rosin sizing were around 37, 34 and 30 g/m^2 respectively. This points out that the sizing behavior of alkaline and neutral sizing agents are quite different and in case of alkaline sizing higher $Cobb_{60}$ can be maintained by lowering the size dose.

Behavior of Sizing Agents with GCC

Figure 6 shows the $Cobb_{60}$ vs. contact angle behavior of different sizing agents with GCC. It is shown that the $Cobb_{60}$ vs. contact angle behavior is extremely different for different sizing agents when GCC is used as a filler. To have a contact angle value of around 105°, the $Cobb_{60}$ values required with ASA, AKD and rosin sizing were around 41, 37 and 22 g/m^2 respectively. With usage of GCC as filler, alkaline sizing with ASA performs in a much better way as compared to AKD and rosin.

Behavior of Sizing Agents with PCC

The $Cobb_{60}$ vs. contact angle behavior of ASA and AKD with PCC is shown in Figure 7. It can be seen that with PCC, both the sizing agents show almost similar trend but AKD gives slightly better sizing behavior under high $Cobb_{60}$ values.

Sizing Behavior of Commercial Paper Samples

Sizing behavior of different writing and printing grade paper samples collected from paper mills in India and abroad was evaluated through the measurement of $Cobb_{60}$ and contact angle. Figure 8 shows the paper samples of 70 g/m^2. Though, the $Cobb_{60}$ values of indigenous paper samples 1 to 5 were 20-22 g/m^2, the contact angles were in the range of 90 to 135°. This

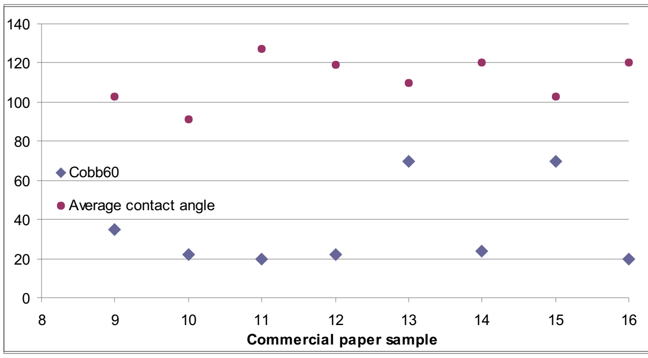

Figure 9: $Cobb_{60}$ vs. contact angle behavior of different commercial paper samples of 80 g/m^2 (sample 9-12, Indigenous papers; sample 13-16, imported papers)

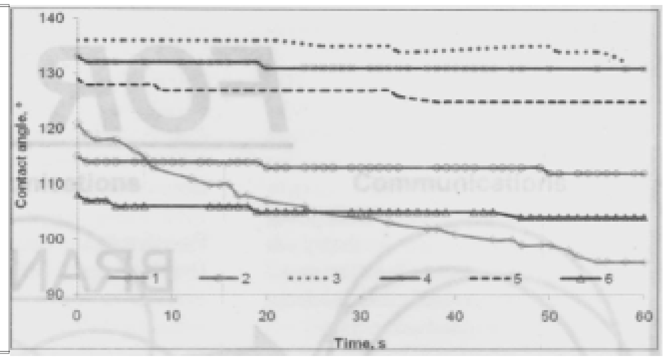

Figure 10: Contact angle behavior of different commercial paper samples with respect to time ($Cobb_{60}$ of sample 1 to 5, 20 g/m^2; sample 6, 35 g/m^2)

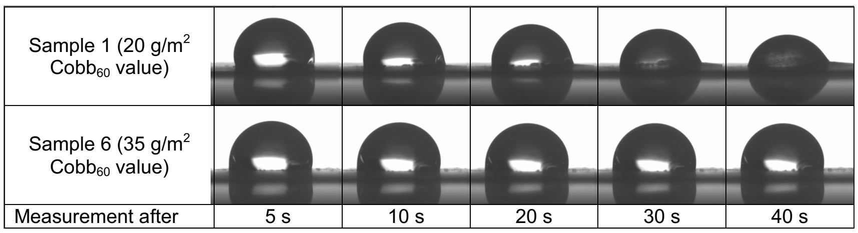

Figure 11: Contact angle behavior of two papers at 60 g/m^2 $Cobb_{60}$ value

shows the misleading indication of $Cobb_{60}$ value. The $Cobb_{60}$ value of imported paper sample 7 was around 80 g/m^2, yet its contact angle was similar to indigenous paper sample 6 of 35 g/m^2 $Cobb_{60}$ value.

The commercial paper samples of 80 g/m^2 were also analyzed to see the $Cobb_{60}$ vs. contact angle behavior (Figure 9). Here also, the $Cobb_{60}$ values of indigenous paper samples 2 to 4 were 20-22 g/m^2, but the contact angles were in the range of 90 to 130°. The imported paper samples 13 and 15 manufactured with around 70 g/m^2 $Cobb_{60}$ value, also show good contact angles of around 105-110°. It again indicates that the contact angle is a better tool to measure the sizing performance of a paper than $Cobb_{60}$.

To understand this behavior in detail and to know the stability of contact angle with time, various commercial paper samples were analyzed (Figure 10). Samples 1 to 5 were of 20-21 g/m^2 and sample 6 was of 35 g/m^2 $Cobb_{60}$ value. Though the $Cobb_{60}$ value of samples 1-5 were same but the contact angle behavior was quite different. Secondly, the contact angle values were quite stable with time for four samples except sample no. 1. On the other hand, the contact angle stability of sample 6 (35 g/m^2 $Cobb_{60}$ value) was also good with time. When sample 1 (20 g/m^2 $Cobb_{60}$ value) is compared with sample 6 (35 g/m^2 $Cobb_{60}$ value), it can be seen that the contact angle stability of sample 6 is much better than sample 1 though there is a quite large difference in $Cobb_{60}$ values. The drop behavior of sample 1 and 6 is shown in Figure 11. It can be seen again that the stability of sample 6 is better than sample 1.

CONCLUSION

To understand the performance of sizing agents, it is essential to use a better tool i.e. contact angle rather than $Cobb_{60}$. The $Cobb_{60}$ value shows the hydrophobicity of paper in a long span of time, whereas contact angle can show the real time behavior of interaction of water droplets with the paper in a defined time interval from 1 to 60 seconds or even more. Depending upon the use, the contact angle of paper can be fixed to represent the aqueous absorption behavior during printing or other end application.

REFERENCES

1. Roberts JC (1996). Neutral and alkaline sizing. In: Paper Chemistry, 2nd ed. Edited by Roberts JC, Chapman & Hall, p.140-160.
2. Neimo L (1999). Internal sizing of paper. In: Papermaking Science and Technology Book 4 'Papermaking Chemistry'. Published by Fapet Oy, p.150-203.
3. Kwok DY, Neumann AW (1999). Contact angle measurement and contact angle interpretation. *Adv. Colloid Interface Sci.* **81**(3):167-249.
4. Gess JM (1992). A perspective on neutral/alkaline papermaking. *Tappi J.* **4**: 79-81.
5. Bajpai PK, Sharma AK, Das S and Varadhan R (2008). Optimization of ASA emulsion and impact of filler on ASA sizing. *IPPTA J.* **20**(3): 99-104.