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# Optimization of Alkaline Sizing to Reduce the Sizing Cost

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# Contents

# Nomenclature

| | |
|---|---|
| AKD | Alkyl ketene dimer |
| APAM | High molecular weight anionic polyacrylamide flocculant |
| ASA | Alkenyl ketene dimer |
| BBS | Bleached bagasse |
| BRC | Bleached recycled |
| BWS | Bleached wheat straw |
| CFA | Cationic fatty acid condensation product |
| CIE | International Commision on Illumination (French: Commission Internationale de l’Eclairage) |
| CPAM | Medium to high molecular weight cationic polyacrylamide flocculant |
| CPF | Low molecular weight cationic polyamine fixing agent |
| CS | Cationic starch |
| CSF | Canadian standard freeness |
| GCC | Ground calcium carbonate |
| ISO | International Standards Organization |
| L&W | Lorentzen & Wettre |
| MHB | Bleached mixed hardwood blended with bamboo |
| MHW | Bleached mixed hardwood |
| o.d. | Oven dry |
| $^{o}$SR | Schopper-Riegler number |
| PAC | Poly aluminum chloride |
| PCC | Precipitated calcium carbonate |
| w/v | Weight by volume |

# EXECUTIVE SUMMARY

Sizing is the process by which a chemical additive provides paper and paperboard with resistance to liquid wetting, penetration and absorption. Since protection against aqueous liquid is the usual concern, sizing generally produces water repellency. The predominant current commercial types of sizing agents are based on rosin, wax and synthetic 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 paper are used for a number of end applications such as writing and printing paper, water resistant wrapping or milk carton etc. Sizing just retards the liquid and does not totally prevent liquid movement. The factors which determines the extent to which any of these liquid movement phenomenon occurs is the $Cobb_{60}$ value and contact angle. Presently, sizing in alkaline conditions is the predominant over sizing in acid and neutral conditions. The driving force which compelled the paper manufacturers to shift from acid to alkaline sizing is as brief up as follows:

- Difficulty in using calcium carbonate as filler in acid papermaking system
- Corrosion in equipment and pipelines
- Ageing effect in sized papers
- Reduced brightness and high cost of sizing

There are two types of sizing agents used in alkaline sizing which are Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Both are cellulose-reactive chemicals. AKD has slow rate of hydrolysis as compared to ASA so it is shipped as ready to use product in the form of emulsion to the paper mill while ASA emulsion is prepared on site. Though AKD gives good sizing characteristics to paper but has some drawbacks such as being wax it causes slipperiness to the final sheet of paper. Slow reactivity of AKD can mean that the sheet is unsized by the time it reached the size press, so over-drying of the sheet is required to achieve some curing. Due to the above mentioned problems with AKD, paper manufacturers are shifting towards the ASA sizing. Similar to AKD, ASA also has some drawbacks. Due to very high rate of hydrolysis, it is emulsified on-site just before its addition in pulp suspension. The hydrolysis of ASA emulsion is, somewhat, 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 sizing chemicals also help in reducing the papermaking cost in addition to the 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 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 dosage of sizing agents in presence of different fillers for all types of pulp furnishes used in India.

The process problems, raw material characteristics and comparatively higher cost are the main factors responsible for inefficient use of alkaline sizing. Optimization of filler and other wet-end chemicals are very important to achieve the desired hydrophicity in paper with minimum cost. To overcome the above problems and to convert from neutral sizing to environment friendly alkaline sizing, detailed study on optimization of alkaline sizing agents with Indian raw material was required. There was a need to study the efficacy of alkaline sizing agents on Indian papermaking furnishes such as hardwood, agro-residues and recycled fibers with the utilization of commercial fillers and other wet-end chemicals. This project was planned to study all above factors with both AKD and ASA sizing chemicals with five different verities of pulp furnishes used in India such as bleached mixed hardwood blended with bamboo (MHB), bleached mixed hardwood (MHW), bleached wheat straw (BWS), bleached bagasse (BBS) and bleached recycled (BRC) pulp. Three types of fillers; talc, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), were also used at 15% ash level. The GCC were procured from three different sources whereas PCC were procured from two different sources.

The pulp furnishes were evaluated to generate the data and understand their fiber morphology, charge, zeta potential and other characteristics. The fiber length of the BRC pulp was highest among all pulp furnishes. The anionicity of the BBS pulp was higher than other pulp furnishes.

Three AKD emulsions from different sources were evaluated and used in papermaking to select the best one in terms of particles size distribution, charge demand and hydrophobicity of the paper. The AKD requirement for PCC was highest followed by GCC and talc to achieve similar hydrophobicity of paper. The contact angle of the hardwood pulp furnishes were higher than that of agro-residue based pulp furnishes.

Two ASA oil samples were procured from different sources and their emulsions were prepared in laboratory. The particle size distribution and stability of the emulsions were evaluated. In ASA sizing, the contact angle of the paper was more as compared that in AKD sizing.

The bound and unbound forms of AKD in paper were also determined. It was observed that the quantity of AKD which is bound to the fiber is less than that of AKD in unbound state which is present in the paper.

## BACKGROUND

The paper industry uses sizing agents to give paper and paperboard some degree of resistance to wetting and penetration by aqueous liquids. This is necessary because paper fiber consists of cellulose and hemicellulose, 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. A wide variety of paper products must be sized to an appropriate degree such that the interaction of aqueous fluids with paper can be controlled. For this purpose, various sizing agents depending upon neutral or alkaline papermaking systems have been used by papermakers. The most common sizing agents for fine paper made under alkaline conditions are alkenyl succinic anhydride (ASA), alkyl ketene dimer (AKD) and/or combination of both. The use of said alkaline sizing agents is more prominent worldwide since many years and it is increasing with time and with new developments in process technologies [1-8].

AKD is usually manufactured by chlorinating a fatty acid with phosphorus trichloride followed by dimerisation of the resulting product with tri-methyl amine to form a waxy solid material. This is melted and 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 [9].

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. ASA hydrolyses easily in aqueous emulsion to form alkenyl succinic acid, which is detrimental to sizing. ASA emulsion is prepared with cationic starch in different ASA to starch ratios. 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 [10-15]. Once prepared, ASA emulsion should be used within few minutes.

The alkaline paper is comparatively environmental friendly and durable. Both types of sizing agents have a reactive functional group that covalently bonds to cellulose fiber;

hydrophobic tails of the size molecule are oriented away from the fiber. The nature and orientation of these hydrophobic tails cause the fiber to repel water. The amount of fine paper produced under alkaline conditions has been increasing rapidly, encouraged by cost savings, the ability to use precipitated calcium carbonate (PCC), an increased demand for improved paper permanence and brightness, and an increased tendency to close the wet-end of the paper machine.

Studies are also going on the quantification of sizing agents in paper. Since last few years, papermakers are trying to optimize size chemicals dosages on the basis of their retained proportions into paper. These studies are also useful to get good hydrophobicity in paper as well as to decrease sizing cost. The effect of bound and unbound chemicals has also been studied [16].

In India also, some work has been done on alkaline sizing but due to lack of knowledge of process and suitable chemicals required, it is not completely adopted by Indian papermakers. The process problems, raw material characteristics and comparatively higher cost are the main factors responsible for it. Optimization of filler and other wet-end chemicals are also very important to achieve the desired hydrophicity in paper with minimum cost.

As very little research has been done in India to understand the alkaline sizing with AKD and ASA and its dependency/behavior on/with different wet end chemicals and fillers, detailed lab study has been undertaken on alkaline sizing to have in depth knowledge to improve the process and conditions (effect on optical, strength and other functional properties of paper), and exploring the ways and means to reduce the sizing cost.

## OBJECTIVES

- Optimization of chemicals for economical alkaline sizing
  - Development of methods to determine the retention of sizing agents in paper
  - Study the effect of various process parameters on alkaline sizing of agro, recycled and wood fibres

## SCOPE

- Bleached pulp furnishes: Mixed hardwood (MHW), mixed hardwood blended with bamboo (MHB), wheat straw (BWS), bagasse (BBS), and recycled (BRC)
- Fillers: talc, GCC, PCC to achieve 15% ash level in paper
    - Talc from one supplier
    - GCC from three different suppliers (GCC-1, GCC-2, GCC-2)
    - PCC from two different suppliers (PCC-1, PCC-2)
- AKD sizing: AKD emulsion from four different suppliers (AKD-1, AKD-2, AKD-3, AKD-4)
- ASA sizing: ASA oil from two different suppliers
- Retention aids of different molecular weights and charge densities

# EXPERIMENTAL

## 1. Materials

### 1.1 Pulp

MHW: bleached mixed hardwood pulp furnish collected from an integrated pulp and paper mill in southern India

MHB: bleached mixed hardwood blended with bamboo furnish collected from an integrated pulp and paper mill in northern India

BBS: bleached bagasse pulp furnish collected from an integrated pulp and paper mill in northern India

BWS: bleached wheat straw pulp furnish collected from an integrated pulp and paper mill in northern India

BRC: bleached recycled pulp furnish collected from an integrated pulp and paper mill in southern India

### 1.2 Wet-End Chemicals

- Alkyl ketene dimer (AKD) emulsion from four different suppliers
- Alkenyl succinic anhydride (ASA) oil from two different suppliers
- Cationic starch (CS)
- Low molecular weight cationic polyamine fixing agent (CPF)
- Cationic fatty acid condensation product (CFA)
- Poly aluminum chloride (PAC)
- Retention aid: a medium to high molecular weight cationic polyacrylamide flocculant (CPAM) and a high molecular weight anionic polyacrylamide flocculant (APAM)

### 1.3 Fillers

- Talc (hydrated magnesium silicate)
- GCC (grounded calcium carbonate) from three different suppliers
- PCC (precipitated calcium carbonate) from two different suppliers

### 1.4 Materials for Determination of Bound and Unbound AKD in Paper

- Soxhlet extraction system

- Test tube with ground joint
- Gas chromatograph (NUCON 5765)

1.4.1 Chemicals

- 0.4 M potassium hydroxide in 90 % ethanol
- M hydrochloric acid
- Isooctane
- Internal standard: dotriacontane ($C_{32}H_{66}$) dissolved in isooctane (0.5 mg/ml)

1.4.2 GC Column And Conditions

- BPX-5 column of 30 m length, inner diameter 0.53 mm, film thickness 1.25 µm

## 2. Methods/ Procedures

### 2.1 Refining of Pulp

Pulp was refined to attain $30^0$ SR in PFI Mill (manufactured by HAMJERN MASKIN) following TAPPI Test Method T 248 sp-00.

### 2.2 Characterization of Sizing Chemicals

AKD 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. The resolution in Image Analyzer was set to 1000 magnification. The size of emulsion particles was determined with the help of software.

### 2.3 Cooking of Cationic Starch

Cationic starch was dispersed to 1% (w/v) slurry by mixing it with distilled water. The dispersed slurry was taken into a beaker and placed into water bath. The temperature was raised to gelatinize the slurry. Continuous mild stirring was given to the slurry. The slurry was then cooked at $90^0$C for about 30 minutes. It was then cooled at ambient temperature and was used in wet-end as a strength aid.

### 2.4. Stock Preparation

2.4.1. AKD Sizing

In case of AKD sizing, different components (chemicals and additives) were added to the pulp slurry in the following order with continuous stirring:

a) CPF

b) Cationic starch

c) AKD

d) Filler

e) Filtered water of pH 7.5 to make a pulp slurry of 0.3-0.4% consistency

f) Retention aid

### 2.5. Making of Handsheets on Sheet Former

Handsheets of 70 g/$m^2$ were made on sheet former as per TAPPI Test Method T 272 sp-97.

### 2.6. Sheet Pressing and Drying

Sheets pressing and drying was done according to TAPPI Test Method T 218 sp-02.

### 2.7. Conditioning of Handsheets

The conditioning of handsheets was done following TAPPI Test Method T 402 sp-98 at 23±$1^0$C and 50±2% relative humidity for at least 4 hours.

## 3. Analytical Techniques

### 3.1. Moisture in Pulp

Moisture content of pulp was determined as per TAPPI Test Method T 210 cm-86.

### 3.2 Freeness of Pulp

The extent of refining of pulp, CSF, was determined as per TAPPI Test Method T 227 om-99.

### 3.3 Characterization of Filler

This includes optical properties (brightness, L*, a*, b*, etc.), particle size distribution, particle structure and chemical formula, moisture content, ionic behavior, charge demand, zeta potential, and the pH of the filler suspension.

Optical properties: Optical properties of filler were determined as per TAPPI Test Method T 646 om-02. At first, a compact dice of filler having smooth surface was prepared in a small cylinder with the help of compression plate, plunger and arbor press. Optical properties were checked in Datacolor brightness tester as per the instructions given in the manual.

Particle size distribution: Particle size distribution of filler was determined with MICROSCAN II (Quanta Chrome Corporation, USA). It utilizes soft X-ray to measure particle concentration in a sedimentation cell.

Particle Structure and Chemical Formula: The crystallographic structure of the fillers was determined by X-Ray Diffraction (D-Max IIIC from Rigaku, Japan) using Cu-Kα radiation.

Chemical composition was determined using Energy Dispersive Spectrometer (TN-5500 from Tractor Northern); an attachment to Scanning Electron Microscope (JSM-840A from JEOL, Japan).

pH: Filler suspension (10% w/v) was filtered through a 300 micrometer screen and the pH of the filtrate was measured with the help of pH meter.

Ionic Behavior and Charge Demand: 10 ml of 10% (w/v) filler slurry filtered through 200 micrometer screen was taken as the sample. The charge was measured on Mutek PCD 03 pH and the sample was titrated with cationic/ anionic polymer to neutralize the charge. The PCD 03 pH analyzed the colloidal dissolved charge in the form of streaming potential and given the relative charge demand to neutralize the solution.

Zeta Potential: About 500 ml sample of 10% (w/v) filler was taken and mixed thoroughly before measurement. The zeta potential was measured with SZP 06. The SZP 06 gives the surface charge of materials.

### 3.4. Ionic Behavior and Charge Demand of Pulp Slurry

The pulp slurry was filtered through 200 micrometer screen and 10 ml of the filtrate was taken as the sample. The charge was measured on Mutek PCD 03 pH Particle Charge Detector and the sample was titrated with cationic/ anionic polymer to neutralize the charge.

### 3.5 Zeta Potential of Pulp Slurry

About 500 ml pulp slurry (0.33% consistency) was taken and mixed thoroughly before measurement. The zeta potential of the pulp slurry was measured with SZP 06.

### 3.6 Ash Content in Paper

The ash content of the hand sheet was determined as per TAPPI Test Method T 211 om-93 at 525$^0$C. The ash content and first pass ash retention were calculated with the following formula:

$$\text{Ash content, \%} = \frac{\text{(Crucible + ash) weight} - \text{Crucible weight}}{\text{Handsheet weight}} * 100$$

$$\text{First pass ash retention, \%} = \frac{\text{Handsheet ash, \%}}{\text{Buchner sheet ash, \%}} * 100$$

### 3.7 $Cobb_{60}$ Test

$Cobb_{60}$ value was determined as per TAPPI Test Method T 441 om-98. The total time used in the $Cobb_{60}$ measurement was 60 seconds. Hence, $Cobb_{60}$ is reported and calculated with the following formula:

$Cobb_{60}$, g/m$^2$ = (Final weight of handsheet, g – Initial weight of handsheet, g) * 100

### 3.8. Contact Angle & Surface Energy

Contact angle and surface energy was determined using KRUSS DSA 10 contact angle meter. In this method, the contact angle between air and liquid on a paper surface is taken as a measure of the resistance of the paper surface to wetting by the liquid. The contact angle is measured for 60 seconds on 1 second interval. The contact angle at 5, 10, 20, 30, 40, 50 and 60 seconds has been shown, and a weighted average contact angle of each second is also shown. With the DSA-1 program, the surface energy is also determined. The weighted average surface energy of each second is shown.

### 3.9. Procedure for Determination of Bound and Unbound AKD in Paper

#### 3.9.1. Determination of Unreacted AKD in Paper

The unreacted AKD is extracted by Soxhlet extraction with dichloromethane (DCM). Paper samples are cut in small pieces and taken in extraction thimble. Then 200 ml of DCM is taken in round bottom flask and 1 ml of internal standard (IS) is added in DCM. The temperature is maintained at 60–70$^0$C and extraction is continued for 24 hrs. After extraction, the thimble is taken out from the extraction column and the paper samples are used for the estimation of reacted AKD. DCM is collected in round bottom flask and evaporated in distillation unit. The solvent is recovered and the residue is left in round bottom flask that contains the unreacted AKD. The round bottom flask containing the residue is dried in oven. Then the residue is dissolved in minimum volume (2 ml) isooctane. If the sample dries too much, 2 ml iso-octane is added and then it is heated in a water bath to dissolve it. Then 1 µl of the samples is injected in GC immediately. The sum of the area of the three biggest ketone peaks is calculated.

#### 3.9.2. Determination of Reacted AKD in Paper

The paper sample (about 2.5 g) is taken out from the thimble, refluxed with 50 ml 0.4 M KOH in 90 % ethanol and 1 ml IS at 90$^0$C for 2 hrs. The solution obtained has dark yellow colour. Then the solution is cooled and acidified with 1 M HCl to a pH 4. The colour changes from dark yellow to pale yellow colour. Now the solution is poured into a separating funnel and extracted with warm iso-octane (5*20 ml). The isooctane is evaporated in distillation unit, dry residue is collected and oven dried. Finally the residue is dissolved in minimum volume of isooctane (2 ml) and 1 μl is injected in GC.

## 3.10. Determination of Bound and Unbound ASA in Paper

### 3.10.1. Pretreatment of Sample

2 g of dry sample is needed for carrying out the analysis. The paper sample is cut into pieces of 1x1 cm size. The dry content of the sample is determined and the appropriate amount of sample is weighed into a boiling flask, freezed and freeze dried.

### 3.10.2. Analysis

30 ml acidic acetone, 1 ml of the internal standard (0.1 mg/ml C17:0 STD-solution) and anti-bumping granules is added to the dry sample. The unbound ASA is extracted by refluxing the sample for 4 hours after which the solvent is separated from the sample.

### 3.10.3. Determination of Unbound ASA

The acetone phase, containing the unbound ASA, is further treated as follows:

The collected acetone is transferred into a separation funnel. 90 ml of deionized water is added and the mixture is extracted with MTBE. The MTBE extraction is performed three times, the total MTBE volume being 120 ml. The MTBE is collected in a round-bottomed boiling flask and then dried with a rotary evaporator until about 2 ml remains. The remaining MTBE is pipetted into a pear shaped flask. The boiling flask is flushed with about 2 ml MTBE and the MTBE is transferred into the pear shaped flask.

The extract is dried under nitrogen and the final drying of the sample is done in a vacuum desiccator (40°C, 30 min).

*Methanolysis*

N.B! The acidic methanol is stored in the freezer. The methanol bottle shall be warmed up before opening in order to avoid the humidity in the air to condense in the methanol solution.

2 ml of 2 M HCl in anhydrous methanol is pipetted to the dry sample. The screw cap of the pear shaped bottle is immediately closed after the addition. Otherwise the humidity in the air can spoil the methylation.

Check that the screw cap is tightly closed. The sample is then heated in an incubator at 105°C for 3 hours. The sample is allowed to cool down for about 15 min, where after the methanol is evaporated in a rotary evaporator and finally dried in a vacuum desiccator (40°C, 30 min).

200 µl methanol was added to the dry sample. The sample should be completely dissolved in the methanol before transferring it to the auto sampler vial. After the transfer the sample is ready for GC analysis.

### 3.10.4. Determination of Bound ASA

The sample, paper or pulp, containing the bound ASA is further treated as follows:

The paper sample is displacement washed in a Bühner funnel with acetone, 3x30 ml. This treatment ensures that the standard is washed away. The acetone is displaced. After washing the sample is transferred into a bottle where after the sample is air dried overnight.

*Methanolysis*

N.B! The acidic methanol is stored in the freezer. The methanol bottle shall be warmed up before opening in order to avoid the humidity in the air to condense in the methanol solution.

10 ml of 2 M HCl in anhydrous methanol and 1 ml of the C17:0 standard solution in methanol is pipetted to the dry sample. The screw cap of the bottle is immediately closed after the addition. Otherwise the humidity in the air can spoil the methylation. Check that the screw cap is tightly closed. The sample is then heated in an incubator at 105°C for 5 hours.

The sample is allowed to cool down for about 15 min, where after the methanol phase is collected and transferred to a separation funnel. An equivalent volume of deionized water is added to the funnel. The mixture is extracted with MTBE ($V_{MTBE} = V_{MeOH} + V_{water}$) and the MTBE phase is collected in a pear shaped flask. The MTBE is evaporated in a rotary evaporator and finally dried in a vacuum desiccator (40°C, 30 min). 200 µl methanol is added to the dry sample. The sample should be completely dissolved in the methanol before transferring it to the autosampler vial. After the transfer the sample is ready for GC analysis.

### 3.10.5. Calculation of Result

#### *3.10.5.1. Response factor of the method*

The relative response factor of the method is determined by using ASA calibration solutions made from distilled ASA. Using distilled ASA a stock solution with the concentration of 1 mg ASA/ml acetone is prepared. ASA calibration solutions, with concentrations 0.05, 0.1 and 0.5 mg/ml acetone, are prepared by appropriate dilution of the stock solution. 1 ml of the calibration solution is transferred into a pear shaped bottle together with 1 ml of the C17:0 standard (0.1 mg/ml) in acetone. The solvent is evaporated under nitrogen and then dried in a vacuum desiccator (40°C, 30 min). 2 ml acidic methanol is added to the dry sample where after the sample is heated in an incubator at 105°C for 3 hours. The solvent is evaporated after finished methanolysis under nitrogen and dried in a vacuum desiccator (40°C, 30 min). 200µl methanol is added to the dried sample.  ready for analysis by GC.

The relative response factor of the method is defined as:

$$R_f = \frac{Area_{(ASA)} * m_{(ISTD)}}{Area_{(ISTD)} * m_{(ASA)}}$$

where:

$Area_{(ASA)}$ = the area of the ASA group

$m_{(ASA)}$ = amount of ASA used (mg)

$Area_{(ISTD)}$ = the area of heptadecanoic acid

$m_{(ISTD)}$ = amount of the heptadecanoic acid (mg)

The value of the relative response factor is calculated as an average of the values achieved with the calibration solutions.

The response factor is checked every time ASA determinations are done, e.q., by running a 0.1 mg/ml calibration solution as a sample.

*3.10.5.2. Calculation of the result*

The result of both the bound and the unbound ASA is calculated as follows:

$$m_{ASA} = \frac{Area_{(ASA)} * m_{(ISTD)}}{Area_{(ISTD)} * m_{(sample)} * R_f}$$

$Area_{(ASA)}$ = the area of the ASA group

$m_{(sample)}$= amount of sample (g)

$Area_{(ISTD)}$ = the area of heptadecanoic acid

$m_{(ISTD)}$ = amount of the heptadecanoic acid (mg)

$R_f$ = the relative response factor

# RESULTS AND DISCUSSION

## 1. Characterization of Input Materials

Prior to performing experiments, the characterization of pulp, wet-end chemicals along with fillers was made to understand their chemical behavior towards papermaking process and paper properties.

### 1.1. Pulps

All pulps furnishes were characterized for the determination of their physico-chemical and morphological properties.

The average fiber length and width of bleached recycled (BRC) pulp were highest probably due to presence of long fibered imported waste paper. These properties were almost comparable for bleached mixed hardwood (MHW), bleached mixed hardwood blended with bamboo (MHB) and bleached wheat straw (BWS) pulps, and were lowest in case of bleached bagasse (BBS) pulp. The width of BRC fibers were highest (19.2 μm), followed by (18.5 μm), BWS (17.9 μm), MHB (17.4 μm) and BBS (15.1 μm) pulp. The coarseness of MHW pulp was highest (95.4 μg/m) followed by BRC (82.3 μg/m) and BWS (73.1 μg/m) whereas that of MHB and BBS was almost comparable (64-67 μg/m). The fines were highest in BWS pulp followed by BBS, MHW, BRC and MHB pulp (Table 1).

The freeness levels of pulps were also different. The $^{0}$SR of unbeaten hardwood pulps was around 20-21 whereas that of agro-residue and recycled pulps was around 27-28. The colloidal charge and surface charge on all pulp samples were negative. The cationic charge demand of BBS pulp was highest (22.3 μeq/l) followed by MHB (15.4 μeq/l), BRC (14.3 μeq/l), BWS (11.2 μeq/l) and MHW (10.5 μeq/l). The ISO brightness of MHW pulp was highest (89.7%) followed by MHB (88.6%), BBS (86.2%), BRC (80.2%) and BWS (78.2%). The air permanence was measured for the handsheets prepared from the pulps having almost comparable freeness level of around 27-29 $^{0}$SR. It was higher for agro residue furnishes than that of hardwood furnishes. It was highest for BBS (75.3 s/100ml) followed by BWS (49 s/100 ml), MHB (18.1 s/100 ml), MHW (12.5 s/100ml) and BRC (5.6 s/100ml). The Bendtsen smoothness of paper made from the pulps at constant freeness levels was also different for different pulps. The higher Bendten value means lower smoothness of paper. The smoothness was highest in case of BWS (43 ml/min) followed by BBS (71 ml/min), MHB (112 ml/min), MHW (120 ml/min) and BRC (181 ml/min). The ash content of MHW, MHB and BBS pulps was around 0.1-0.2% whereas that of BWS and BRC pulps was 1.8 and 5% respectively (Table 2).

### 1.2. Fillers

The three different GCC and two different PCC fillers were used which were procured from different sources. GCC-2 and PCC-2 were pre-dispersed to around 40 and 75% solids (w/v) respectively whereas GCC-1, GCC-2 and PCC-1 were collected in powder form and dispersed in lab using fresh filtered water prior to their addition to pulp stock. The optical properties of PCC-2 was highest followed by GCC-1, PCC-1, GCC-2, GCC-3 and talc. All fillers were alkaline in nature.

GCC-1 and GCC-3 were cationic whereas GCC-2 was anionic in nature. Both PCC fillers were cationic in nature and talc was anionic. The cationic demand required to neutralize the charge of GCC-2 filler was quite high (390 μeq/l) whereas for talc it was only 172 μeq/l. the anionic demand required to neutralize the charge of PCC-1 filler (694 μeq/l) was higher than that of PCC-2 filler (165 μeq/l) (Table 3).

### 1.3. AKD Emulsions

Four AKD emulsions collected from different suppliers were used in this study. As the stability of AKD emulsion was only 2-3 months under specified storage conditions, the fresh AKD emulsions were collected from the same source at an interval of 2-3 months. The AKD-1 and AKD-3 were the examples of AKD emulsions collected from same supplier but at a span of 3 months. Both AKD-1 and AKD-3 emulsions were having around 20.6% solid content. The pH and anionic charge demand of AKD-3 were slightly higher than those of AKD-1. All AKD emulsions were cationic in nature. The anionic charge demand required to neutralize their cationic charge was higher for AKD-5 and AKD-2 whereas that of AKD-1, AKD-3 and AKD-4 was comparable. AKD-1 emulsion was more acidic than other AKD emulsions (Table 4).

The particle size distribution of all AKD emulsions is shown in Table 5 which showed that all AKD emulsions were having almost 100% particles less than 2 micron size expects AKD-2 emulsion. The particle size distribution of AKD-1 was slightly better than that of AKD-3 emulsion. The particles less than 1 micron for AKD-1 and AKD-3 were around 77.5 and 74.7% respectively.

### 1.4. ASA Emulsions

The ASA emulsion was prepared in ASA to starch ratio of 1:3. The particle size distribution of the ASA-1 emulsion prepared in lab shows that around 54% particles were less than 1 micron whereas those were 75% in case of ASA-2. 39% particles of ASA-1 emulsion were in the range of 1 to 2 microns whereas in case of ASA-2 emulsion those were 23%. The total particles of ASA-1 and ASA-2 emulsion less than 2 microns were around 93% and 98% respectively (Table 6).

### 1.5. Other Wet-end Chemicals

The ionic behavior of wet-end chemicals has been measured to understand their chemistry and chemical nature. As expected, the dissolved and colloidal charge on beaten pulp was anionic. The charge on cationic polyamine fixing agent (CPF), cationic starch (CS), alkyl ketene dimer (AKD), and cationic polyacrylmide flocculant (CPAM) was cationic whereas that on anionic polyacrylmide flocculant (APAM) was anionic. The AKD was highly acidic in nature with a pH of 3.8 (Table 7).

## 2. Studies on AKD Sizing

The pH and charge study of pulp slurry after addition of each wet-end chemical shows that the pH of pulp slurry ranged from 7.6 to 7.8. Charge demand was reduced on the addition of chemicals due to their cationic nature. The charge demand of the ready stock was cationic, 5.6 µeq/l (Table 8).

### 2.1. Effect of Moisture on Sizing Performance of Paper

It has been observed that after standard pressing of handsheets i.e. 5 minutes and 2 minutes, around 49% moisture remains in the handsheets. The curing in oven at this moisture provided best hydrophobicity to paper. The time of curing was optimized as 30 minutes at 105 $^{o}$C. The curing time of more than 30 minutes does not show any positive effect on hydrophobicity of paper (Table 9). So, the suitable curing time for paper handsheets in the oven was kept as 30 minutes.

### 2.2. Effect of Natural Curing on Sizing Performance of Paper

It was observed that the atmospheric curing of handsheets does not give hydrophobicity to paper. It always requires accelerated curing in an oven at $105^{0}$C. The natural curing even after five days did not give the same hydrophobicity of paper as it was after accelerated curing. The $Cobb_{60}$ value was decreased from 130 to 116 g/m$^2$ after five days of natural curing, whereas only 30 minutes accelerated curing of handsheets provided 20.6 g/m$^2$ $Cobb_{60}$ value (Table 10).

### 2.3. Effect of pH on Sizing Performance of Paper

The pH of ready pulp slurry was around 7.8 without adding any acid or base. The hydrophobicity of paper was slightly improved on increasing pH from 7.8 to 9 using sodium carbonate whereas it was decreased on decrease in pH. As there was very slight improvement in hydrophocity of paper over a pH of 7.8 (as such), it was decided to perform the further experiments on this pH level (Table 11).

### 2.4. Effect of Cationic Polyamine Fixing Agent on Sizing Performance of Paper

The effect of cationic fixing agent (CPF) with and without cationic starch was studied. It was found that the use of 200 g/t of CPF along with 5 kg/t of cationic starch imparted best hydrophobicity to paper. Increasing CPF dose from 100 g/t to 200 g/t and using cationic starch, the $Cobb_{60}$ value was decreased from 24.4 to 20.4 g/m$^2$. However further increasing CPF dose to 300 g/t increased the $Cobb_{60}$ value to 27.8 g/m$^2$ (Table 12). The optimized hydrophobicity to paper was provided by the combination of CPF (200 g/t) and cationic starch (5 kg/t). Though, the dose of cationic starch was yet to be optimized.

### 2.5. Effect of Cationic Starch on Sizing Performance of Paper

Increasing dosage of cationic starch from 2 to 5 kg/t decreased the $Cobb_{60}$ value from 28.2 to 20.5 g/m$^2$. But further increasing cationic starch dose to 10 kg/t did not have any positive impact on hydrophobicity to paper (Table 13). It was optimized that CPF (200 g/t) along with cationic starch (5 kg/t) provided best hydrophocity to paper.

### 2.6. Comparison of Different AKD Emulsions

All five AKD emulsions were added in pulp slurry at different dosage keeping the other wet-end chemicals constant in order to understand their effect on hydrophobicity of paper. This study was carried out with MHB pulp. The increasing dosage of AKD emulsion decreased the $Cobb_{60}$ and increased the contact angle of paper. The surface energy was decreased on increasing the contact angle (Table 14-18). The behavior of all AKD emulsions to reduce the $Cobb_{60}$ on increasing their dosage was different. It was observed that the AKD-3 and AKD-4 showed almost similar trend of $Cobb_{60}$ at all dose levels. In case of AKD-1 emulsion, the rate of decrease in $Cobb_{60}$ value on increasing its dosage was comparatively higher than that of AKD-3 and AKD-4. Initially at lower dosage of AKD-1 emulsion, $Cobb_{60}$ value was higher but it reduced rapidly on increasing the dosage of AKD-1 emulsion. The rate of decrease of $Cobb_{60}$ value was highest with AKD-2 emulsion. In order to get around 30 g/m$^2$ $Cobb_{60}$ value of paper, the required dosage of AKD-1, AKD-2, AKD-3, AKD-4 and AKD-5 were around 1.06, 1.25, 0.93, 0.87 and 0.45 kg/t of pulp. The difference in requirement of dosage of AKD emulsion was higher at higher $Cobb_{60}$ values. To get around 25 g/m$^2$ $Cobb_{60}$ value, the dosage required for all AKD emulsions varied from 0.9 to 1.3 kg/t only which showed that at lower $Cobb_{60}$ values, the difference in dosage of AKD emulsion reduces (Figure 1).

The AKD dose vs. contact angle behavior was shown in Figure 2. The contact angle of paper increases on decreasing the $Cobb_{60}$ value. The contact angle behavior was slightly different than that of $Cobb_{60}$ value. The contact angle of paper with AKD-1, AKD-2 and AKD-3 was almost comparable at all dose levels, whereas that with AKD-4 and AKD-5 was higher. The contact angle was highest with lowest dose of AKD-5 emulsion.

**2.7. Studies with Bleached Mixed Hardwood (MHW) Pulp**

2.7.1. Optimization of AKD Sizing

*2.7.1.1. Without filler*

Different dosage of AKD-1 emulsion was used to achieve variable sizing stages. Increasing dose of AKD decreased the $Cobb_{60}$ value and surface energy, and increased the contact angle of paper. At 1.0 kg/t dose of AKD, the $Cobb_{60}$ and contact angle values were 29.3 g/m$^2$ and 109.8$^0$ respectively (Table 19).

*2.7.1.2. With talc*

The similar trend with talc was also observed as in case of pulp only. Increasing dose of AKD decreased the $Cobb_{60}$ value and surface energy, and increased the contact angle of paper. At 0.8 kg/t dose of AKD, the $Cobb_{60}$ value, contact angle, and surface energy were 51.6 g/m$^2$, 85.3$^0$, and 33.77 mN/m respectively. On increasing dose to 1.2 kg/t, the $Cobb_{60}$ value was decreased to 20.4 g/m$^2$, contact angle was increased to 112.6$^0$, and surface energy was decreased to 14.99 mN/m (Table 20). The hydrophobicity of paper in terms of $Cobb_{60}$ value and contact angle was slightly better with talc as compared to those with pulp only. It indicated that talc was helpful in increasing hydrophobicity of paper due to its hydrophobic nature.

*2.7.1.3. With GCC*

Three GCC filler samples procured from different suppliers were used to study the effect of type of GCC filler on paper hydrophobicity. The dose of AKD required to achieve the hydrophobicity in paper similar to the case with talc was quite higher with GCC filler. It was true for all GCC samples (Table 21-23). To achieve 30 g/m$^2$ $Cobb_{60}$ value, the dosage of AKD required for GCC-1, GCC-2 and GCC-3 was around 2.1, 2.5 and 4.8 respectively (Figure 3). The corresponding contact angle at 30 g/m$^2$ $Cobb_{60}$ value for all GCC fillers was around 106$^o$. It showed that the GCC-1 was the best among all GCC fillers used in this study. It also indicated that the physico-chemical properties of filler were quite responsible for their selection to get good sizing characteristics of paper. As the sizing behavior of GCC-1 filler was found better than other GCC fillers, so it was decided to use GCC-1 filler in further experiments.

*2.7.1.4. With PCC*

Two PCC filler samples supplied by different suppliers in India were used to see the effect of type of PCC filler on paper hydrophobicity. Similar to GCC, the dose of AKD required to achieve similar hydrophobicity of paper as in case of talc was quite higher with PCC filler. It was true for both PCC samples. At 2.8 kg/t dose of AKD, the $Cobb_{60}$ and contact angle values for PCC-1 filler were 23.1 g/m$^2$ and 111.2$^0$ whereas those with PCC-2 were 57.2 g/m$^2$ and 91.2$^0$ respectively (Table 24-25, Figure 4). It indicated that the PCC-1 filler gives better sizing properties to paper as compared with PCC-2 filler. As the sizing behavior of PCC-1 filler was found better than PCC-2, so it was decided to use PCC-1 filler in further experiments.

2.7.2. Comparison of $Cobb_{60}$ Values with Different Fillers

When a graph was plotted between AKD dose and $Cobb_{60}$ values of paper made with and without fillers, it was observed that talc filler was showing almost similar trend as without filler at all AKD dose levels. Talc was the best filler to get the desired hydrophobicity of paper at minimum AKD dose followed by GCC and PCC. From Figure 5, it can be seen that to achieve 30 g/m$^2$ $Cobb_{60}$ value, the dose of AKD required without filler and with talc was comparable i.e. around 1.0 kg/t whereas that for GCC and PCC were around 2.1 and 2.6 kg/t pulp respectively.

2.7.3. Comparison of Contact Angle with Different Fillers

The graph plotted between AKD dose and contact angle of paper made with and without fillers is shown in Figure 6. It was observed that talc filler was showing almost similar trend as without filler at all AKD dose levels. To achieve 105$^o$ contact angle, the dose of AKD required without filler and with talc was comparable i.e. around 0.9 kg/t pulp whereas that for GCC and PCC was around 1.9 and 2.4 kg/t pulp respectively.

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

A graph was plotted between $Cobb_{60}$ value and contact angle of paper made with and without fillers to see the effect of filler on $Cobb_{60}$ vs. contact angle relationship. It was seen that the contact angle of paper at 30 g/m$^2$ $Cobb_{60}$ value was almost comparable for all fillers (Figure 7).

### 2.8. Studies with Bleached Mixed Hardwood Blended with Bamboo (MHB) Pulp

2.8.1. Optimization of AKD Sizing

*2.8.1.1. Without filler*

The sizing behavior of MHB pulp was slightly inferior to that of MHW pulp. At 0.8 kg/t dose of AKD, the $Cobb_{60}$ values of MHW and MHB pulps were 53.5 and 78.3 g/m$^2$ respectively. However at higher dose level of AKD, the difference in $Cobb_{60}$ value of MHB and MHW pulps was very less. At 1.2 kg/t dose of AKD, the $Cobb_{60}$ values of MHW and MHB pulps were 22.5 and 24.0 g/m$^2$ respectively (Table 14, Figure 8).

*2.8.1.2. With talc*

The $Cobb_{60}$ value of paper made with talc filler was slightly lower than without filler. At 1.2 kg/t dose of AKD, the $Cobb_{60}$ values with talc and without filler were 21.2 and 24.0 g/m$^2$ respectively. The similar trend was seen on lower AKD dose levels (Table 26). It shows that talc was helpful in decreasing $Cobb_{60}$ value of paper.

*2.8.1.3. With GCC*

In this experiment, GCC-1 was used as filler. Similar to the MHW pulp, in case of MHB pulp also the dose of AKD required to achieve a particular $Cobb_{60}$ value was quite high as compared to that with talc filler. To achieve 28.5 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for GCC and talc were 2.2 and 1.0 kg/t. The contact angles were almost comparable with both the fillers at 28.5 g/m$^2$ $Cobb_{60}$ value (Table 27).

*2.8.1.4. With PCC*

In this experiment, PCC-1 was used as filler. Similar to GCC, the dose of AKD required to achieve similar hydrophobicity of paper as in case of talc was quite higher with PCC filler. To achieve a desired $Cobb_{60}$ value, the AKD dose required for PCC was more than double as compared with talc (Table 28).

2.8.2. Comparison of $Cobb_{60}$ Values with Different Fillers

When a graph was plotted between AKD dose and $Cobb_{60}$ values of paper made with and without fillers, it was observed that talc filler was showing the best trend even better than without filler at all AKD dose levels. To achieve 30 g/m$^2$ $Cobb_{60}$ value, the dose of AKD required without filler, and with talc, GCC and PCC was around 1.0, 0.95, 2.2 and 2.65 kg/t respectively (Figure 8).

2.8.3. Comparison of Contact Angle with Different Fillers

Similar to the $Cobb_{60}$ results, contact angle at different dose levels of AKD were again best with talc filler. To achieve $105^o$ contact angle, the dose of AKD required without filler, with talc, GCC and PCC was around 1.0, 0.95, 2.1 and 2.5 kg/t respectively (Figure 9).

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

When a graph was plotted between $Cobb_{60}$ value and contact angle of paper made with and without fillers, it was observed that the contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value was almost comparable for all fillers i.e. 107-$109^o$ (Figure 10).

## 2.9. Studies with Bleached Bagasse (BBS) Pulp

2.9.1. Optimization of AKD Sizing

*2.9.1.1. Without filler*

Different AKD dosage were used to achieve variable sizing stages. Increasing dosage of AKD decreased the $Cobb_{60}$ value and surface energy, and increased the contact angle of paper, similar to the case with previous pulp furnishes. At 1.2 kg/t dose of AKD, the $Cobb_{60}$ value and contact angle were 24.2 $g/m^2$ and $101.7^0$ respectively. To achieve 30 $g/m^2$ $Cobb_{60}$ value, 1.0 kg/t of AKD was required when no filler was used. The anionic colloidal charge of the pulp stock was increased from -5.4 to -8.9 μeq/l with the reduction in AKD dose from 1.2 to 0.6 kg/t. The zeta potential of the pulp slurry was around -8.1 to -9.7 mV (Table 29).

*2.9.1.2. With talc*

The sizing performance of BBS pulp was slightly improved when talc was used as filler. At 1.0 kg/t dose of AKD, the $Cobb_{60}$ value of BBS pulp without filler and with talc were 30.1 and 26.9 $g/m^2$ respectively. The contact angle also increased from 100.9 to $102.7^0$. The similar trend was seen at all dose levels of AKD (Table 30). $Cobb_{60}$ value and contact angle were slightly better with talc as compared to those with pulp only. It indicates that talc was helpful in increasing hydrophobicity of paper due to its hydrophobic nature

*2.9.1.3. With GCC*

The dose of AKD required to achieve similar hydrophobicity of paper as in case of talc was quite higher with GCC filler. To achieve 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for GCC and talc were 2.25 and 0.95 kg/t respectively. The contact angles were almost comparable with both the fillers at this $Cobb_{60}$ value (Table 31).

*2.9.1.4. With PCC*

To achieve a desired $Cobb_{60}$ value, the AKD dose required for PCC was higher than that of GCC and talc. To achieve 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for PCC was 2.35 kg/t. The corresponding contact angle was around $99^0$ which was slightly lower than that in case of GCC and talc (Table 32).

2.9.2. Comparison of $Cobb_{60}$ Values with Different Fillers

The talc filler was showing the best trend even better than without filler at all AKD dose levels. To achieve 30 $g/m^2$ $Cobb_{60}$ value, the dose of AKD required without filler, and with talc, GCC and PCC was around 1.0, 0.95, 2.25 and 2.35 kg/t respectively (Figure 11). All of these values were almost comparable as in case of MHW and MHB pulps.

2.9.3. Comparison of Contact Angle with Different Fillers

Similar to the $Cobb_{60}$ results, contact angle at different dose levels of AKD were again best with talc filler. Though, the contact angle with BBS pulp at constant $Cobb_{60}$ value was slightly lower as compared with MHW and MHB pulps. To achieve $100^o$ contact angle, the dose of AKD required without filler, with talc, GCC and PCC was around 0.9, 0.9, 2.15 and 2.4 kg/t respectively (Figure 12).

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

When a graph was plotted between $Cobb_{60}$ value and contact angle of paper made with and without fillers, it can be seen that the contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value was almost comparable for all fillers i.e. 99-$102^o$ whereas at higher $Cobb_{60}$ value, the difference in contact angle was seen with different fillers (Figure 13).

**2.10. Studies with Bleached Wheat Straw (BWS) Pulp**

2.10.1. Optimization of AKD Sizing

*2.10.1.1. Without filler*

At 1.2 kg/t dose of AKD, the $Cobb_{60}$ value and contact angle were 25.5 $g/m^2$ and $93.2^0$ respectively. Further increasing dose to 1.5 and 2.0 kg/t the $Cobb_{60}$ value was decreased to 24.4 and 23.5 $g/m^2$ respectively. The corresponding average contact angles were 93.9 and $97.5^0$ respectively. To achieve 30 $g/m^2$ $Cobb_{60}$ value, around 0.93 kg/t of AKD was required when no filler was used. The contact angle was quite low with BWS pulp as compared with other pulp furnishes. It was in the range of 83-$84^0$ at 30 $g/m^2$ $Cobb_{60}$ value. The anionic colloidal charge of the pulp stock was increased from -7.2 to -12.8 $\mu$eq/l with the decrease in AKD dose from 2.0 to 0.6 kg/t. The zeta potential of the pulp slurry was between -9.0 to -13.6 mV (Table 33).

*2.10.1.2. With talc*

The requirement of talc for BWS pulp was quite lower than that in case of MHW, MHB and BBS pulps to achieve the same ash level. BWS pulp requires only 190 kg/t of talc filler to achieve 15% ash level whereas it was 250 kg/t in case of other pulps. The trend of AKD dose vs. $Cobb_{60}$ value with talc filler was almost comparable as compared with no filler. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for BWS pulp without filler and with talc was around 0.90 kg/t (Table 34).

*2.10.1.3. With GCC*

Similar to other pulp furnishes, the dosage of AKD emulsion required to achieve similar hydrophobicity of paper was quite higher with GCC filler. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for GCC and talc was 1.88 and 0.90 kg/t respectively. At 30 $g/m^2$ $Cobb_{60}$ value, the contact angle with GCC was slightly lower than that with talc (Table 35).

*2.10.1.4. With PCC*

To achieve a desired $Cobb_{60}$ value, the AKD dose required for PCC was higher than that of talc and almost comparable to that of GCC. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for PCC was around 2.0 kg/t. The corresponding contact angle was around $86.6^0$ which was almost comparable to that in case of talc (Table 36).

2.10.2. Comparison of $Cobb_{60}$ Values with Different Fillers

When a graph was plotted between AKD dose and $Cobb_{60}$ values of paper made with and without filler, it can be seen that BWS pulp shows almost similar trend without filler and with talc at all AKD dose levels. To achieve 30 $g/m^2$ $Cobb_{60}$ value, the dose of AKD required without filler, and with talc, GCC and PCC fillers was around 0.93, 0.90, 1.88 and 2.0 kg/t respectively (Figure 14).

2.10.3. Comparison of Contact Angle with Different Fillers

Similar to the $Cobb_{60}$ results, contact angle at different dose levels of AKD were again best without filler and with talc filler. Though, the contact angle with BWS pulp at constant $Cobb_{60}$ value was relatively lower as compared with MHW, MHB and BBS pulps. To achieve $95^o$ contact angle, the AKD dose required without filler, with talc, GCC and PCC was around 1.65, 1.15, 2.4 and 2.4 kg/t respectively. The results again show that talc filler helps in hydrophobicity of paper (Figure 15).

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

The $Cobb_{60}$ value vs. contact angle behavior of BWS pulp without filler and with different fillers was comparable. The contact angle of paper at 30 g/m$^2$ $Cobb_{60}$ value was around 84-87$^o$ (Figure 16).

## 2.11. Studies with Bleached Recycled (BRC) Pulp

### 2.11.1. Optimization of AKD Sizing

*2.11.1.1. Without filler*

Different AKD dose were used to achieve variable sizing stages. Increasing dose of AKD decreases the $Cobb_{60}$ value and surface energy, and increases the contact angle of paper. At 1.5 kg/t dose of AKD, the $Cobb_{60}$ value and contact angle were 22.3 g/m$^2$ and 110.8$^0$ respectively. To achieve 30 g/m$^2$ $Cobb_{60}$ value, around 0.9 kg/t of AKD was required when no filler was used. The corresponding contact angle was 101.2$^0$. The anionic colloidal charge of the pulp stock increased from -7.0 to -11.1 μeq/l with the reduction in AKD dose from 1.5 to 0.6 kg/t (Table 37).

*2.11.1.2. With talc*

The sizing performance of BRC pulp was slightly improved when talc was used as filler. At 0.9 kg/t dose of AKD, the $Cobb_{60}$ value of BRC pulp without filler and with talc were 29.4 and 28.3 g/m$^2$ respectively. The contact angle also increased from 101.2 to 103.4$^0$. The similar trend was seen at all dose levels of AKD (Table 38). $Cobb_{60}$ value and contact angle were slightly better with talc as compared to those with pulp only. It indicates that talc was helpful in increasing hydrophobicity of paper due to its hydrophobic nature.

*2.11.1.3. With GCC*

The dose of AKD required to achieve similar hydrophobicity of paper as in case of talc was quite higher with GCC filler. To achieve 30 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for GCC and talc were around 1.95 and 0.85 kg/t respectively. The contact angles with GCC filler were slightly higher than that of talc filler (Table 39).

*2.11.1.4. With PCC*

The dose of AKD emulsion required for PCC filler was comparatively higher than that of GCC and talc. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for PCC was around 2.45 kg/t. The corresponding contact angle was around 105$^0$ which was slightly higher than that in case of GCC and talc (Table 40).

2.11.2. Comparison of $Cobb_{60}$ Values with Different Fillers

When a graph was plotted between AKD dose and $Cobb_{60}$ values of paper made with and without filler, it was observed that talc filler was showing the best trend even better than without filler at all AKD dose levels. To achieve 30 g/m$^2$ $Cobb_{60}$ value, the dose of AKD required without filler, and with talc, GCC and PCC was around 0.9, 0.85, 1.95 and 2.45 kg/t respectively (Figure 17).

2.11.3. Comparison of Contact Angle with Different Fillers

Similar to the $Cobb_{60}$ results, contact angle at different dose levels of AKD were again best with talc filler. To achieve 100$^o$ contact angle, the dose of AKD required without filler, with talc, GCC and PCC was around 0.8, 0.8, 1.9 and 2.15 kg/t respectively (Figure 18).

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

The $Cobb_{60}$ value vs. contact angle relationship with and without fillers was shown in Figure 3. The contact angle of paper at 30 g/m$^2$ $Cobb_{60}$ value was almost comparable for all fillers i.e. 103-105$^o$ whereas at higher $Cobb_{60}$ values, the difference in contact angle was observed with different fillers (Figure 19).

## 2.12. Sizing Behavior of Different Pulps in AKD Sizing

2.12.1. Comparison of $Cobb_{60}$ Value

*2.12.1.1. Without filler*

When $Cobb_{60}$ value of different pulps was compared, it was seen that the difference in dose of AKD required to achieve the $Cobb_{60}$ value below 30 g/m$^2$ was not prominent. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulp was around 0.99, 1.06, 1.01, 0.93 and 0.89 kg/t respectively (Figure 20).

*2.12.1.2. With talc*

Similar to without filler, with talc filler also, the difference in dose of AKD required to achieve the $Cobb_{60}$ value below 30 g/m$^2$ was not prominent. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulp was around 0.97, 1.0, 0.94, 0.9 and 0.87 kg/t respectively (Figure 21).

*2.12.1.3. With GCC*

With GCC filler the dose of AKD required was higher than that of talc and without filler. Moreover, the dose required for different furnishes were also slightly different. To achieve 30 g/m$^2$ $Cobb_{60}$ value, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulp was around 2.15, 2.2, 2.25, 1.9 and 1.95 kg/t respectively. This shows that BWS pulp requires lowest AKD and BBS pulp requires highest AKD when GCC was used as filler (Figure 22).

*2.12.1.4. With PCC*

With PCC filler the dose of AKD required was higher than that of other fillers and were different for different pulp furnishes. To achieve 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulp was around 2.62, 2.65, 2.35, 2.02 and 1.95 kg/t respectively. This shows that the agro-residue pulps require lower AKD as compared with hardwood pulps when PCC was used as filler (Figure 23).

2.12.2. Comparison of Contact Angle

*2.12.2.1. Without filler*

The contact angle behavior of pulps was different with each other. The contact angle of both hardwood pulps i.e. MHW and MHB was more than $110^0$ whereas it was below $100^0$ in case of BWS pulp. BBS pulp has shown comparatively better contact angle than BWS pulp. To achieve around $100^0$ contact angle, the AKD dose required for MHW, MHB, BBS and BRC pulps was around 0.9, 0.96, 0.9, 0.81 kg/t respectively. In case of BWS pulp, this contact angle value could not be achieved even with higher dose of AKD. To achieve around $90^0$ contact angle, the AKD dose required for MHW, MHB, BBS and BRC pulps was around 0.86, 0.91, 0.78, 1.09 and 0.73 kg/t respectively (Figure 24).

*2.12.2.2. With talc*

With talc filler also the contact angle of BWS pulp was lowest and below $100^0$. Again, the contact angle of hardwood pulps was above $110^0$. To achieve around $100^0$ contact angle, the AKD dose required for MHW, MHB, BBS and BRC pulps was around 0.9, 0.9, 0.9 and 0.8 kg/t respectively. To achieve around $90^0$ contact angle, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulps was around 0.83, 0.78, 0.74, 1.05 and 0.72 kg/t respectively (Figure 25).

*2.12.2.3. With GCC*

Opposite to AKD dose vs. $Cobb_{60}$ value, the trend of AKD dose vs. contact angle was worst in case of BWS pulp. To achieve $100^0$ contact angle, the AKD dose required for MHW, MHB, BBS and BRC pulps was around 1.92, 2.08, 2.16 and 1.89 kg/t respectively. This shows that BRC pulp requires lowest AKD dose as compared with other pulp furnishes. To achieve $90^0$ contact angle, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulps was around 1.78, 1.98, 1.94, 2.21 and 1.62 kg/t respectively (Figure 26).

*2.12.2.4. With PCC*

To achieve around $100^0$ contact angle, the AKD dose required for MHW, MHB, BBS and BRC pulps was around 2.22, 2.38, 2.42 and 2.18 kg/t respectively whereas in case of BWS pulp, this contact angle could not be achieved similar to other filler. The doe of AKD required to achieve the same contact angle with PCC filler was slightly higher than that with GCC filler. To achieve $90^0$ contact angle, the AKD dose required for MHW, MHB, BBS, BWS and BRC pulps was around 2.04, 2.18, 2.13, 2.23 and 2.06 kg/t respectively which was almost comparable for all pulp furnishes (Figure 27).

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

*2.12.3.1. Without filler*

The $Cobb_{60}$ value vs. contact angle behavior of MHB pulp was the best among all furnishes. BWS pulp showed the poorest trend. The trend of BBS pulp was better than BWS, and lower than MHW and MHB pulps. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 104, 108, 101, 84 and $101^o$ respectively (Figure 28).

*2.12.3.2. With talc*

With talc filler the $Cobb_{60}$ value vs. contact angle behavior of MHW and MHB pulps were almost comparable and best among all pulp furnishes. BWS pulp again showed the poorest trend. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 108, 107, 102, 87 and $103^o$ respectively (Figure 29).

*2.12.3.3. With GCC*

Similar to talc filler, with GCC also the $Cobb_{60}$ value vs. contact angle behavior of MHW and MHB pulps were almost similar and best among all pulp furnishes. BWS pulp again showed the poorest trend. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 109, 107, 102, 85 and $103^o$ respectively (Figure 30).

*2.12.3.4. With PCC*

With PCC filler also the $Cobb_{60}$ value vs. contact angle behavior of MHW and MHB pulps were almost comparable and best among all pulp furnishes. The trend of BWS pulp was again poorest. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 108, 108, 99, 87 and $105^o$ respectively (Figure 31).

# 3. Studies on ASA Sizing

## 3.1. Studies with Bleached Mixed Hardwood Blended with Bamboo (MHB) Pulp

3.1.1. Optimization of ASA Sizing

*3.1.1.1 Without filler*

Different ASA dosage was used to achieve variable sizing stages. Increasing dose of ASA decreased the $Cobb_{60}$ value and surface energy, and increased the contact angle of paper. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle were 25.2 $g/m^2$ and $120.3^0$ respectively. Decreasing ASA dose to 1.0 kg/t increased the $Cobb_{60}$ value to 50.3 $g/m^2$ and decreased the contact angle to $102.2^0$. Even though the $Cobb_{60}$ value was quite high but the contact angle was still almost constant with respect to time. This shows that the contact angle is a better tool to measure the hydrophobicity of paper. The cationic colloidal charge demand of the pulp stock was increased from 6.8 to 8.4 μeq/l with reducing ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry at different ASA dose was in the range of -4.1 to -8.0 mV (Table 41).

*3.1.1.2. With talc*

The sizing performance of MHB pulp was slightly improved when talc was used as filler. The reduction in $Cobb_{60}$ value was observed through the contact angle values which were comparable for without filler and with talc filler at constant dose of ASA. At 2.0 kg/t dose of AKD, the $Cobb_{60}$ value of MHB pulp without filler and with talc were 25.2 and 23.4 $g/m^2$ respectively, whereas the contact angles were around 120.3 to $120.9^0$ respectively. The similar trend was observed at other dosage of ASA emulsion. The cationic colloidal charge demand of the stock suspension was increased from 3.9 to 6.2 μeq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t respectively. The zeta potential of the pulp slurry was -4.1 mV at maximum ASA dose and -6.2 mV at minimum ASA dose (Table 42).

*3.1.1.3. With GCC-1*

The dosage of ASA required to achieve similar hydrophobicity of paper as in case of talc was quite higher with GCC-1 filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC-1 filler were 27.2 $g/m^2$ and $114.8^0$ whereas those were 23.4 $g/m^2$ and $120.9^0$ respectively with talc filler. The cationic charge demand of pulp stock increased from 4.7 to 7.3 μeq/l with the reduction of ASA dose from 2.0 to 1.0 kg/t. The zeta potential of the pulp slurry was -1.8 mV at maximum ASA dose and -7.9 mV at minimum ASA dose (Table 43).

*3.1.1.4. With GCC-2*

The ASA requirement in case of GCC-2 was comparatively lower than that of GCC-1. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC-2 filler were 24.8 $g/m^2$ and $120.01^0$ whereas those were 27.2 $g/m^2$ and $114.8^0$ respectively with GCC-1 filler. At 1.0 kg/t dose of ASA, the difference in $Cobb_{60}$ value and contact angle of paper made using GCC-1 and GCC-2 fillers increased. Here, the $Cobb_{60}$ value and contact angle with GCC-2 filler were 44.6 $g/m^2$ and $102.0^0$ whereas those were 59.5 $g/m^2$ and $94.5^0$ respectively with GCC-1 filler. The cationic charge demand of pulp stock increased from 5.4 to 7.7 $\mu$eq/l with the reduction in ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was -9.0 mV at maximum ASA dose and -16.6 mV at minimum ASA dose (Table 44).

*3.1.1.5. With GCC-3*

The retention of GCC-3 filler was inferior to that of GCC-1 and GCC-2. The addition level of both GCC-1 and GCC-2 fillers was 250 kg/t whereas that of GCC-3 was 300 kg/t to achieve 15% ash in paper. The sizing performance of GCC-3 was almost comparable to that of GCC-1. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC-3 filler were 26.5 $g/m^2$ and $119.3^0$ respectively which were almost comparable to results of GCC-1 filler. The similar trend also was observed at lower dose of ASA. At 1.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC-3 filler were 61.7 $g/m^2$ and $92.5^0$ respectively. The cationic charge demand of pulp stock increased from 5.4 to 7.7 $\mu$eq/l with reduction in ASA dose from 2.0 to 1.0 kg/t. The Zeta potential of the pulp slurry was -4.3 mV at maximum ASA dose and -6.2 mV at minimum ASA dose (Table 45).

As the sizing performance of GCC-2 filler was found better in ASA sizing, so it was used for other furnishes in ASA sizing and termed as GCC (Figure 32)

*3.1.1.6. With PCC-1*

The sizing performance of PCC-1 filler was slightly lower at lower dose of ASA as compared to that of GCC fillers, though at high dose levels of ASA, it was slightly better or comparable to GCC fillers. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC-1 filler were 22.4 $g/m^2$ and $121.1^0$ respectively which were slightly better as compared to those of GCC fillers. At 1.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC-1 filler were 68.4 $g/m^2$ and $83.4^0$ respectively which were slightly inferior as compared to those of GCC fillers. The cationic charge demand of pulp stock increased from 5.1 to 8.1 $\mu$eq/l with reduction in ASA dose from 2.0 to 0.8 kg/t. The Zeta potential of the pulp slurry was -7.8 mV at maximum ASA dose and -10.9 mV at minimum ASA dose (Table 46).

*3.1.1.7. With PCC-2*

The sizing performance of PCC-2 filler was almost comparable to that of PCC-1 filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC-2 filler were 22.0 $g/m^2$ and $121.6^0$ whereas those were 22.4 $g/m^2$ and $121.1^0$ respectively with PCC-1 filler. At 1.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC-1 filler were 65.3 $g/m^2$ and $81.0^0$ respectively which were again comparable to those of PCC-1 filler. The cationic charge demand of pulp stock increased from 5.8 to 7.6 μeq/l with reduction in ASA dose from 2.0 to 0.8 kg/t. The Zeta potential of the pulp slurry was -8.2 mV at maximum ASA dose and -14.9 mV at minimum ASA dose (Table 47).

The sizing performance of both PCC fillers was found comparable. In further experiments, PCC-1 fillers was used for other furnishes in ASA sizing and termed as PCC (Figure 33).

3.1.2. Comparison of $Cobb_{60}$ Values with Different Fillers

The $Cobb_{60}$ value of paper with PCC filler at lower dosage of ASA was inferior to talc and GCC fillers and for the latter two fillers it was almost comparable. To achieve around 25 $g/m^2$ $Cobb_{60}$ value, the ASA dose required without filler and with talc, GCC and PCC fillers were around 2.0, 1.9, 1.8 and 1.74 kg/t respectively, which showed that PCC filler required the lowest dose of ASA as compared to other fillers. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the ASA dose required without filler and with talc, GCC and PCC fillers were around 1.6, 1.36, 1.36 and 1.54 kg/t respectively, which showed that PCC filler required higher dose of ASA as compared with talc and GCC. These results showed a sharp decline in the $Cobb_{60}$ value of paper prepared from PCC filler with increase in ASA dose from 1.5 to 2.0 kg/t (Figure 34).

3.1.3. Comparison of Contact Angle with Different Fillers

The results of contact angle were also similar to those of $Cobb_{60}$ value. At lower dose of ASA, the difference in contact angle value with different fillers was observed, which was not reflected at higher dose of ASA. To achieve $100^o$ contact angle, the dose of ASA required without filler, with talc, GCC and PCC was around 0.98, 0.96, 0.97 and 1.16 kg/t respectively. To achieve $110^o$ contact angle, the dose of ASA required without filler, with talc, GCC and PCC was around 1.58, 1.50, 1.32 and 1.56 kg/t respectively, which showed that GCC required lowest dose of ASA to get this contact angle (Figure 35).

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

The $Cobb_{60}$ value vs. contact angle relationship with and without fillers in ASA sizing is shown in Figure 36. The contact angle of paper at higher $Cobb_{60}$ values was different for different fillers. At 30 g/m$^2$ Cobb$_{60}$ value, the contact angle of paper was almost comparable for all the fillers i.e. 108-111$^o$.

## 3.2. Studies with Bleached Mixed Hardwood (MHW) Pulp

### 3.2.1. Optimization of ASA Sizing

#### *3.2.1.1. Without filler*

At 2.0 kg/t dose of ASA, the Cobb$_{60}$ value and contact angle were 25.1g/m$^2$ and 119.6$^0$ respectively. Decreasing ASA dose to 1.0 kg/t increased the Cobb$_{60}$ value to 48.6 g/m$^2$ and decreased the contact angle to 102.3$^0$. Even though the Cobb$_{60}$ value was quite high but the contact angle was still almost constant with respect to time. At the lowest dosage of ASA emulsion, the Cobb$_{60}$ value increased to 74.8 g/m$^2$ and contact angle decreased to 63.4$^0$. This also showed that the contact angle was a better tool to measure the hydrophobicity of paper. The cationic colloidal charge demand of the pulp stock was increased from 4.6 to 7.2 μeq/l with reducing ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry at different ASA dose was in the range of -8.1 to -8.1 mV (Table 48).

#### *3.2.1.2 With talc*

The sizing performance of MHW pulp was slightly improved when talc was used as filler. The reduction in Cobb$_{60}$ value was observed though the contact angle values were almost comparable for without filler and with talc filler at constant dose of ASA. At 2.0 kg/t dose of ASA, the Cobb$_{60}$ value of MHW pulp without filler and with talc were 25.1 and 24.1 g/m$^2$ respectively, whereas the contact angles were comparable. The similar trend was observed at other dose levels of ASA. The cationic colloidal charge demand of the stock suspension was increased from 4.1 to 7.4 μeq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t respectively. The zeta potential of the pulp slurry at different ASA dose was in the range of -8.1 to -8.1 mV (Table 49).

#### *3.2.1.3 With GCC*

The sizing performance of pulp with GCC filler was deteriorated as compared with talc filler. At 2.0 kg/t dose of ASA, the Cobb$_{60}$ value and contact angle with GCC filler were 25.7 g/m$^2$ and 118.6$^0$ whereas those were 24.1 g/m$^2$ and 119.6$^0$ respectively with talc filler. At low dose of ASA (0.8 kg/t), the Cobb$_{60}$ value was very high and contact angle was 83.5$^0$. The cationic charge demand of pulp stock was increased from 9.8 to 12.5 μeq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was -7.9 and -8.0 mV at maximum and minimum ASA dose respectively (Table 50).

#### *3.2.1.4. With PCC*

The sizing performance of PCC filler was slightly improved at lower dose of ASA as compared to that of GCC fillers, though at high dose levels of ASA, it was slightly better or comparable than GCC fillers. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 22.4 $g/m^2$ and $121.1^0$ respectively which were slightly better as compared to those with GCC fillers. At 1.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 58.9 $g/m^2$ and $91.8^0$ respectively which were slightly inferior as compared to those with GCC fillers. The cationic charge demand of pulp stock was increased from 6.2 to 11.2 μeq/l with reduction in ASA dose from 2.0 to 0.8 kg/t. The Zeta potential of the pulp slurry was -7.9 and -8.0 mV at maximum and minimum ASA dose respectively (Table 51).

3.2.2. Comparison of $Cobb_{60}$ Values with Different Fillers

The $Cobb_{60}$ value of paper with talc filler was superior than that without filler followed by PCC and GCC. To achieve around 25 $g/m^2$ $Cobb_{60}$ value, the ASA dose without filler, and with talc and GCC filler was 2 kg/t while with PCC filler the dose of ASA was 1.8 kg/t for getting the same $Cobb_{60}$ value. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the ASA dose required without filler and with talc, GCC and PCC fillers was 1.44, 1.2, 1.45 and 1.3 kg/t respectively (Figure 37) which showed that GCC required higher dose of ASA as compared to PCC and talc.

3.2.3. Comparison of Contact Angle with Different Fillers

At lower dose of ASA, the difference in contact angle value with different fillers was observed, which was not reflected at higher dose of ASA. To achieve $100^o$ contact angle, the dose of ASA required without filler, and with talc, GCC and PCC was around 0.98, 0.99, 0.96 and 1.08 kg/t respectively. To achieve $110^o$ contact angle, the dose of ASA required without filler, and with talc, GCC and PCC was around 1.36, 1.11, 1.37 and 1.19 kg/t respectively, which showed that talc required lowest dose of ASA to get this contact angle (Figure 38).

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

The $Cobb_{60}$ value vs. contact angle relationship with and without fillers in ASA sizing was shown in Figure 39. The contact angle of paper at higher $Cobb_{60}$ values was different for different fillers. At 30 $g/m^2$ $Cobb_{60}$ value, the contact angle of paper was comparable for all the fillers i.e. 112-$115^o$. At 40 $g/m^2$ $Cobb_{60}$ value, the contact angles were more than $100^0$ i.e.104-$107^0$.

### 3.3. Studies with Bleached Bagasse (BBS) Pulp

3.3.1. Optimization of ASA Sizing

*3.3.1.1. Without filler*

The maximum dose of ASA without any filler was 2.0 kg/t which gave the $Cobb_{60}$ value of 25.6 $g/m^2$ and contact angle of 110.7$^o$ whereas the minimum dose of ASA was 0.8 kg/t which gave $Cobb_{60}$ value of 47.0 $g/m^2$ and contact angle of 97.4$^o$. The colloidal charge of the stock suspension was increased from -4.4 to -7.5 $\mu$eq/l with the reduction of ASA dose. The zeta potential of the pulp slurry was in the range of -3.2 to -5.9 mV (Table 52).

*3.3.1.2. With talc*

The sizing performance of BBS pulp was slightly decreased when talc was used as filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value of BBS pulp without filler and with talc were 25.6 and 26.5 $g/m^2$ respectively, whereas the contact angles were comparable. The sizing trend was not similar as observed in case of MHW pulp both with and without filler. The sizing performance of BBS pulp was slightly improved when talc was used as filler. The cationic colloidal charge demand of the stock suspension was increased from 4.3 to 6.2 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t respectively. The zeta potential of the pulp slurry at different ASA dose was in the range of -4.9 to -7.9 mV (Table 53).

*3.3.1.3. With GCC*

At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC filler were 26.2 $g/m^2$ and 111.1$^0$ whereas those were 26.5 $g/m^2$ and 110.8$^0$ respectively with talc filler. At low dosage of ASA (0.8 kg/t), the $Cobb_{60}$ value and contact angle were 48.7 $g/m^2$ and 98.7$^0$ respectively. The cationic charge demand of pulp stock was increased from 4.2 to 6.7 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was in the range of -5.4 to -8.1 mV (Table 54). The sizing performance of BBS pulp was comparatively better than that of MHW pulp.

*3.3.1.4. With PCC*

The sizing performance of PCC filler was comparable to that of GCC at high dosage of ASA, it was slightly better or comparable to GCC filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 26.3 $g/m^2$ and 112.2$^0$ respectively. At 0.8 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 51.1 $g/m^2$ and 98.1$^0$ respectively which were slightly inferior as compared to those with GCC filler. The cationic charge demand of pulp stock was increased from 4.1 to 7.2 $\mu$eq/l with reduction in ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was -5.1 mV at maximum ASA dose and -9.2 mV at minimum ASA dose (Table 55).

3.3.2. Comparison of $Cobb_{60}$ Values with Different Fillers

At higher dose of ASA, the $Cobb_{60}$ values were comparable with all fillers used in this study. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the ASA dose without filler, and with talc, GCC and PCC fillers was 1.9, 1.91, 1.93 and 1.7 kg/t respectively (Figure 40) which showed that GCC required higher dose of ASA as compared to PCC and talc.

3.3.3. Comparison of Contact Angle with Different Fillers

At lower dose of ASA, the difference in contact angle value with different fillers was observed, which was not reflected at higher dose of ASA. To achieve 100$^o$ contact angle, the dose of ASA required without filler, and with GCC and PCC was around 0.94, 0.88 and 1.05 kg/t respectively. Contact angle with talc filler was higher than 100 degree even at lowest dose of ASA. To achieve 110$^o$ contact angle, the dose of ASA required without filler, with talc and GCC was around 1.97 whereas with PCC it was 1.78 kg/t (Figure 41).

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

The contact angle of paper at higher $Cobb_{60}$ values was different for different fillers. At 30 g/m$^2$ $Cobb_{60}$ value, the contact angle of paper was almost comparable for all the fillers i.e. 108-109$^o$. At 40 g/m$^2$ Cobb value the contact angles were more than 100$^0$ i.e. 103-105$^0$ with all fillers (Figure 42).

**3.4. Studies with Bleached Wheat Straw (BWS) Pulp**

3.4.1. Optimization of ASA Sizing

*3.4.1.1. Without filler*

The maximum dose of ASA without any filler was 2.0 kg/t which gave $Cobb_{60}$ value of 25.4 g/m$^2$ and contact angle of 101.1$^o$ where at minimum dose of ASA (0.6 kg/t), the $Cobb_{60}$ and contact angle were 41.4 g/m$^2$ and of 94.2$^o$ respectively. At 0.8 kg/t dosage of ASA emulsion, the $Cobb_{60}$ value and contact angle were 36.5 g/m$^2$ and 96.4$^o$ respectively which was improved in case of BWS pulp as compared to BBS pulp. The colloidal charge of the stock suspension was increased from -4.1 μeq/l to -6.1 μeq/l with the reduction of ASA dose. The Zeta potential of the pulp slurry was in the range of -4.7 to -7.1 mV (Table 56).

*3.4.1.2. With talc*

The sizing performance of BWS pulp was slightly improved when talc was used as filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value of BWS pulp without filler, and with talc were

25.4 and 24.1 g/m$^2$ respectively, whereas the contact angles were comparable. The cationic colloidal charge demand of the stock suspension was increased from 5.6 to 9.1 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.6 kg/t respectively. The zeta potential of the pulp slurry at different ASA dose was in the range of -4.8 to -7.5 mV (Table 57).

*3.4.1.3. With GCC*

The sizing performance of BWS pulp with GCC filler was almost comparable to the case without filler and was comparably inferior to that with talc filler. At 2.0 kg/t dose of ASA, the Cobb$_{60}$ value and contact angle with GCC filler were 25.1g/m$^2$ and 101.2$^0$ whereas those were 24.1 g/m$^2$ and 101.8$^0$ respectively with talc filler. At 0.6 kg/t of ASA, the Cobb$_{60}$ and contact angle were 57.3 g/m$^2$ and 74.4$^0$ respectively. The cationic charge demand of pulp stock was increased from 7.8 to 10.2 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.6 kg/t. The zeta potential of the pulp slurry was in the range of -5.1 to -6.9 mV (Table 58).

*3.4.1.4. With PCC*

The sizing performance of BWS pulp with PCC filler was comparable to that with GCC filler at high dosage of ASA. At 2.0 kg/t dose of ASA, the Cobb$_{60}$ value and contact angle with PCC filler were 23.4 g/m$^2$ and 102.3$^0$ respectively. At 0.6 kg/t dose of ASA, the Cobb$_{60}$ value and contact angle with PCC filler were 68.9 g/m$^2$ and 72.3$^0$ respectively The cationic charge demand of pulp stock was increased from 8.6 to 11.1 $\mu$eq/l with the reduction in ASA dose from 2.0 to 0.8 kg/t. The Zeta potential of the pulp slurry was -4.6 mV at maximum ASA dose and -7.6 mV at minimum ASA dose (Table 59).

3.4.2. Comparison of Cobb$_{60}$ Values with Different Fillers

At higher dosage of ASA, the Cobb$_{60}$ values were comparable with all fillers. To achieve around 30 g/m$^2$ Cobb$_{60}$ value, the ASA dose without filler, and with talc filler was 1.4 and 1.32 kg/t respectively, which was 1.14 kg/t with both GCC and PCC (Figure 31). These results showed that PCC required least dose of ASA as compared to other fillers but this was just because of saturation at higher ASA dose. The actual difference appears at lower ASA dosage which showed that PCC required highest dosage of ASA followed by GCC and talc.

3.4.3. Comparison of Contact Angle with Different Fillers

At lower dose of ASA, the difference in contact angle value with different fillers was observed, which was not reflected at higher dose of ASA. To achieve 100$^o$ contact angle, the dose of ASA required without filler and with GCC was around 1.8 kg/t which was 1.4 kg/t with PCC. The actual difference appeared at lower ASA dosage which showed that

PCC required higher dose of ASA followed by GCC and talc (Figure 32). It was observed that contact angles in case of BWS pulp furnish were not more than 102-104 degree even with quite higher AKD dosage.

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

The $Cobb_{60}$ value vs. contact angle relationships with and without fillers in ASA sizing using BWS pulp was shown in Figure 33. At 30 $g/m^2$ $Cobb_{60}$ value, the contact angle of paper was almost comparable for all the fillers i.e. 98-99$^o$. Opposite to other pulp furnishes, in case of BWS there was no sharp decline in the values of contact angle with the increase in $Cobb_{60}$ value from 30 to 40 $g/m^2$.

**3.5. Studies with Bleached Recycled (BRC) Pulp**

3.5.1. Optimization of ASA Sizing

*3.5.1.1. Without filler*

The ASA dosage of 2.0 kg/t pulp gave the $Cobb_{60}$ value of 22.1 $g/m^2$ and contact angle of 115.8$^o$, whereas minimum dosage of ASA (0.8 kg/t) gave $Cobb_{60}$ value and contact angle of 77.5 $g/m^2$ and 86.9$^o$ respectively. The cationic colloidal charge demand of the stock suspension increased from 9.3 to 16.1 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was -11.1 mV at maximum ASA dose and -18.1 mV at minimum ASA dose (Table 60).

*3.5.1.2. With talc*

The sizing performance of BRC pulp with talc filler was similar to the case without filler. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value without filler and with talc were 22.1 and 22.7 $g/m^2$ respectively, whereas the contact angles were nearly same. This trend was applicable for all dosage of ASA. The cationic colloidal charge demand of the stock suspension increased from 9.4 to 14.1 $\mu$eq/l with the reduction of ASA dosage from 2.0 to 0.8 kg/t respectively. The zeta potential of the pulp slurry at different ASA dose was in the range of -15.7 to -27.4 mV (Table 61).

*3.5.1.3. With GCC*

At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with GCC filler were 24.6 $g/m^2$ and 114.3$^0$ whereas those with talc filler were 22.7 $g/m^2$ and 116.0$^0$ respectively. At 0.8 kg/t dosage of ASA the $Cobb_{60}$ and contact angle were 76.3 $g/m^2$ and 88.8$^0$ respectively which were almost comparable to the case with talc. The cationic charge demand of pulp stock increased from 9.9 to 15.1 $\mu$eq/l with the reduction of ASA dose from 2.0 to 0.8 kg/t. The zeta potential of the pulp slurry was -16.2 mV at maximum ASA dose and -25.3 mV at minimum ASA dose (Table 62).

*3.5.1.4. With PCC*

The sizing performance of PCC filler was comparable to that of GCC at high dose levels of ASA. At 2.0 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 25.4 $g/m^2$ and $113.5^0$ respectively, however at 0.8 kg/t dose of ASA, the $Cobb_{60}$ value and contact angle with PCC filler were 83.7 $g/m^2$ and $66.8^0$ respectively which were nearly similar to the case with GCC filler. The cationic charge demand of pulp stock was in the range of 9.3 to 11.7 μeq/l at all dosage of ASA emulasion. The anionic zeta potential of the pulp slurry was increased -24.3 to -31.6 mV on decreasing the ASA dosage (Table 63)

3.5.2. Comparison of $Cobb_{60}$ Values with Different Fillers

At higher dose of ASA the $Cobb_{60}$ values were comparable with all fillers. To achieve around 30 $g/m^2$ $Cobb_{60}$ value, the ASA dose without filler, and with talc, GCC and PCC fillers was 1.37, 1.25, 1.61 and 1.88 kg/t respectively which showed that PCC required highest dose of ASA followed by GCC and talc. The dose of ASA was reduced by using talc as filler if compared with no filler (Figure 34).

3.5.3. Comparison of Contact Angle with Different Fillers

The trend of contact angle was matching with the results of $Cobb_{60}$ value. To achieve $100^o$ contact angle, the dose of ASA required without filler, and with talc, and GCC was around 0.95, 0.93, 0.94 kg/t respectively whereas with PCC it was on higher side i.e. 1.12 kg/t. The more accurate comparison could be made at lower dosage of ASA which showed that PCC required higher dose of ASA followed by GCC and talc. To achieve $110^o$ contact angle, the dose of ASA required without filler, and with talc, GCC and PCC was around 1.28, 1.2, 1.55 and 1.84 kg/t respectively (Figure 35).

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

The $Cobb_{60}$ value vs. contact angle relationships with and without fillers in ASA sizing using BRC pulp was shown in Figure 36. At 30 $g/m^2$ $Cobb_{60}$ value, the contact angle of paper was almost comparable for all the fillers i.e. 110-$112^o$. The difference in the values of contact angles was observed at higher $Cobb_{60}$ value. At 40 $g/m^2$ $Cobb_{60}$ value, the value of contact angle was more than $100^o$; it was in the range of 106-$107^0$ with GCC and PCC filler and $104^0$ with talc filler.

## 3.6. Sizing Behavior of Different Pulps in ASA Sizing

### 3.6.1. Comparison of $Cobb_{60}$ Value

#### *3.6.1.1. Without Filler*

When $Cobb_{60}$ value of the paper produced with different pulps using ASA emulsion was compared, it was observed that the difference in dose of ASA required to achieve the $Cobb_{60}$ value below 30 g/m$^2$ was not prominent. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the ASA dose required for BBS was highest followed by MHB, MHW, BWS and BRC i.e. around 1.88, 1.6, 1.43, 1.4 and 1.37 kg/t respectively. Among all the pulp furnishes bleached recycled pulp required the least dose of ASA to achieve the 30 Cobb value (Figure 49).

#### *3.6.1.2. With Talc*

Similar to without filler, with talc filler also, the difference in dose of ASA required to achieve the $Cobb_{60}$ value below 30 g/m$^2$ was not prominent. To achieve around 30 g/m$^2$ $Cobb_{60}$ value, the ASA dose required for agro residues such as BBS and BWS and bleached recycled pulp is exactly same as in case of without filler i.e. 1.88, 1.4 and 1.37 kg/t respectively..  The dose of ASA for MHW and MHB, pulp was around 1.21 and 1.4 kg/t respectively which is on lower than that of without filler. The requirement of ASA dose is less just because of the hydrophobic nature of the talc filler (Figure 50).

#### *3.6.1.3. With GCC*

The dose required for different furnishes were also slightly different. To achieve 30 g/m$^2$ $Cobb_{60}$ value, the ASA dose required for MHW, MHB, BBS, BWS and BRC pulp was around 1.45, 1.36, 1.86, 1.18 and 1.61kg/t respectively. This shows that BWS pulp requires lowest ASA and BBS pulp requires highest ASA when GCC is used as filler (Figure 51).

#### *3.6.1.4. With PCC*

Using PCC as filler, to achieve 30 g/m$^2$ $Cobb_{60}$ value, the ASA dose required for MHW, MHB, BBS, BWS and BRC pulp was around 1.30, 1.56, 1.72, 1.18 and 1.89 kg/t respectively. This shows that the BWS pulp require lower ASA dose and bleached recycled pulp required the higher ASA dose to achieve 30 Cobb value (Figure 52).

### 3.6.2. Comparison of Contact Angle

#### *3.6.2.1. Without Filler*

The contact angle behavior of pulps was different with each other. The contact angle of both hardwood pulps i.e. MHW and MHB was more than 110$^0$ whereas it was below 100$^0$

in case of BWS pulp. BBS pulp has shown comparatively better contact angle than BWS pulp. To achieve around $100^0$ contact angle, the ASA dose required for MHW, MHB, BBS and BRC pulps was around 0.96, 0.97, 0.94, 0.96 kg/t respectively. In case of BWS pulp, this contact angle value could not be achieved even with higher dose of ASA. To achieve around $90^0$ contact angle, the ASA dose required for MHW, MHB, and BRC pulps was around 0.92, 0.94 and 0.84 kg/t respectively. The $90^0$ contact angle could not be achieved using wheat straw and bagasse furnish even at higher ASA doses. (Figure 53).

*3.6.2.2. With Talc*

With talc filler also the contact angle of BWS pulp was lowest and below $100^0$. Again, the contact angle of hardwood pulps was above $110^0$. To achieve around $100^0$ contact angle, the ASA dose required for MHW, MHB, and BRC pulps was around 0.99, 0.97and 0.93 and 0.8 kg/t respectively. With BBS pulp the contact angles were more than $100^0$ but the difference at various ASA dose was not significant. In case of BWS pulp to achieve 100 contact angle the ASA dose was very high i.e. 1.83 kg/t but in this case also the difference at various ASA dose was not significant. To achieve around $90^0$ contact angle, the ASA dose required for MHW, MHB and BRC pulps was around 0.88, 0.88, and 0.82 kg/t respectively (Figure 54). In case of talc filler also the $90^0$ contact angle could not be achieved using wheat straw and bagasse furnish even at higher ASA dosage.

*3.6.2.3. With GCC*

Opposite to ASA dose vs. $Cobb_{60}$ value, the trend of ASA dose vs. contact angle is worst in case of BWS pulp. To achieve $100^0$ contact angle, the ASA dose required for MHW, MHB, BBS and BRC pulps was around 0.96, 0.97, 0.89 and 0.84 kg/t respectively. While the ASA dose required to achieve 100 contact angle was higher with wheat straw furnish i.e. 1.76 kg/t though the difference in contact angle even at lower ASA doses was not so prominent. This shows that BBS pulp requires lowest ASA dose as compared with other pulp furnishes. To achieve $90^0$ contact angle, the ASA dose required for MHW, MHB, BWS and BRC pulps was around 0.86, 0.86, 1.94, 0.75 and 0.82 kg/t respectively (Figure 55).

*3.6.2.4. With PCC*

To achieve around $100^0$ contact angle, the ASA dose required for MHW, MHB, BBS and BRC pulps was around 1.08, 1.17, 1.05 and 1.12 kg/t respectively whereas in case of BBS pulp, this contact angle could not be achieved similar to other filler. The doe of ASA required to achieve the same contact angle with PCC filler is slightly higher than that with GCC filler. To achieve $90^0$ contact angle, the ASA dose required for MHW, MHB, BBS, BWS and BRC pulps was around 0.96, 1.08, 0.79, 1.4 and 0.99 kg/t respectively (Figure 56).

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

*3.6.3.1. Without Filler*

The $Cobb_{60}$ value vs. contact angle behavior of MHB pulp was the best among all furnishes. BWS pulp showed the poorest trend. The trend of BBS pulp is better than BWS, and lower than MHW and MHB pulps. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 113, 111, 108, 98 and $111^0$ respectively (Figure 57).

*3.6.3.2. With Talc*

With talc filler the $Cobb_{60}$ value vs. contact angle behavior of MHW and MHB pulps were almost comparable and best among all pulp furnishes. BWS pulp again showed the poorest trend. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 114, 110, 109, 99 and $111^o$ respectively (Figure 58).

*3.6.3.3. With GCC*

Similar to talc filler, with GCC also the $Cobb_{60}$ value vs. contact angle behavior of MHW and MHB pulps were almost similar and best among all pulp furnishes. BWS pulp again showed the poorest trend. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 116, 114, 109, 98 and 110.5 respectively (Figure 59).

*3.6.3.4. With PCC*

With PCC filler, the trend of BWS pulp was again poorest among all furnishes. The contact angle of paper at 30 $g/m^2$ $Cobb_{60}$ value with MHW, MHB, BBS, BWS and BRC pulps was 113, 109.5, 109, 98 and $111^o$ respectively (Figure 60).

## 4. Determination of Bound and Unbound AKD in Paper

### 4.1 Determination of Response Factor (k)

A series of standards were prepared by diluting pure ketone (AKD wax) and internal standard in isooctane. The standards were run through the entire procedure to calculate the response factor. Every standard was analyzed three times.

$$C_s / A_s = k * C_a / A_a$$

$C_s$ = weight of internal standard in sample

$A_s$ = peak area of internal standard

$C_a$ = weight of ketone

$A_a$ = peak area of ketone

Response factor = $\dfrac{Area \quad of \quad IS}{Area \quad of \quad ketone \quad (normalized \quad)}$

The following table shows the values of the response factors calculated for four numbers of sets.

For set no: 1 the response factor is calculated as indicated below:

Response factor = $\dfrac{672726}{56920 \quad \times \dfrac{(0.25)}{(0.1)}}$ = 4.7275

For set no. 2, the response factor is calculated as indicated below:

Response factor = $\dfrac{625260}{143633 \quad \times \dfrac{(0.25)}{(0.2)}}$ = 3.4825

For set no. 3, the response factor will be calculated as indicated below:

Response factor = $\dfrac{688623}{215473 \quad \times \dfrac{(0.25)}{(0.2)}}$ = 3.8350

For set no. 4, the response factor will be calculated as indicated below:

Response factor = $\dfrac{615791}{373471 \quad \times \dfrac{(0.25)}{(0.4)}}$ =3.2977

The average response factor would be the average of set 2, 3 and 4 then the average response factor would be 3.5384.

## 4.2. Determination of Reacted and Unreacted AKD in Commercial Paper Samples

Table 64 shows the calculated values of the reacted and unreacted ketone in commercial paper samples and the calculation for the same is given below:

**Paper Sample 1**

Respons factor = 3.556; $Ketone \quad weight = \dfrac{Ketone \quad area}{\left(\dfrac{IS \quad area}{(IS \quad weight) \quad (\mathrm{Re}\,sponse \quad factor)}\right)}$

*Calculation of unreacted AKD*

Average ketone weight = 0.361 mg;

Paper O.D. = 1g;

$$\therefore \frac{mg \quad ketone}{g \quad paper} = \frac{Y}{X} = \frac{0.361 \quad mg \quad ketone \quad (unreacted)}{g \quad paper}$$

*Calculation of reacted AKD*

Average ktone weight = 0.0614 mg;

Paper O.D. = 1 g;

$$\therefore \frac{mg \quad ketone}{g \quad paper} = \frac{0.0614 \quad mg \quad ketone \quad (reacted)}{g \quad paper}$$

*Total AKD in paper*

Now total retained ketone in paper = (unracted ketone + reacted ketone)

= 0.4224 mg/g paper

Total retained AKD in paper = Total retained ketone in paper $\times$1.05 = 0.4435 mg/g paper

**Paper Sample 2**

Average  unreacted ketone weight = 0.4270 mg

Average  reacted ketone weight = 0.0864 mg

total retained ketone in paper 0.5134 mg/g paper

Total retained AKD in paper is 0.5390 mg/g paper

**Paper Sample 3**

Average  unreacted ketone weight = 0.5536 mg

Average  reacted ketone weight = 0.1340 mg

total retained ketone in paper 0.6876 mg/g paper

Total retained AKD in paper is 0.7219 mg/g paper

**Paper Sample 4**

Average  unreacted ketone weight = 0.3067 mg

Average  reacted ketone weight = 0.0817 mg total retained ketone in paper 0.3884 mg/g paper

Total retained AKD in paper is 0.4078 mg/g paper

# CONCLUSIONS

The average fiber length and width of bleached recycled (BRC) pulp were highest. These properties were comparable for bleached mixed hardwood (MHW), bleached mixed hardwood blended with bamboo (MHB) and bleached wheat straw (BWS) pulps, and were lowest in case of bleached bagasse (BBS) pulp. The coarseness of MHW pulp was highest followed by BRC, BWS, BBS and MHB pulp. The fines were highest in BWS pulp followed by BBS, MHW, BRC and MHB pulp. Cationic charge demand of BBS pulp was highest among all pulp furnishes. The brightness of MHW pulp was highest followed by MHB, BBS, BRC and BWS. The air permanence of handsheets prepared by agro residue furnish was higher than that of hardwood furnishes.

All AKD emulsions were having almost 100% particles less than 2 micron size except AKD-2. All AKD emulsions were cationic in nature. The particle size distribution of the sizing chemicals i.e. AKD and ASA has a significant role in the development of hydrophobicity in paper.

The process parameters mainly colloidal and surface charge of the papermaking system influences the sizing properties of paper. The optimum cationic charge demand for hardwood and agro residue pulps is 10 to 15 µeq/l. The colloidal and surface charge of the papermaking slurry can be controlled with the addition of cationic fixing agents and cationic starch which also help in the development of sizing in paper. The optimized pH for both AKD and ASA was 7.5-8.

The nature and type of filler have an impact on the hydrophobicity of paper which was studied through use of different GCC and PCC fillers. GCC-1 filler was found better than other GCC fillers. PCC-1 filler was found better than PCC-2. Talc filler improved the hydrophobicity of paper due to its own hydrophobic nature. The AKD requirement for PCC was highest followed by GCC and talc.

On increasing the dosage of sizing chemical i.e. AKD or ASA, the $Cobb_{60}$ decrease and contact angle increases. The $Cobb_{60}$ and contact angle has an inverse relationship; on increase of former, latter decreases.

The contact angle of paper was in the range of $102\text{-}107^0$ in case of both mixed hardwood (MHB and MHW) pulp furnishes. It was more than $100^0$ at $Cobb_{60}$ value of 35 g/m$^2$ with all fillers. In case of agro residues the contact angles were slightly lesser than that of hardwood furnishes. They were in the range of $100\text{-}102^0$ with BBS at $Cobb_{60}$ value of 28-30 g/m$^2$ with all fillers. The contact angles were stable but on lower side i.e. in the range of $81\text{-}84^0$ with BWS pulp at $Cobb_{60}$ value of 35 g/m$^2$ with all fillers. In case of recycled furnish, contact angles were more than $100^0$ at $Cobb_{60}$ value of 35 $g/m^2$ with all fillers except GCC; with GCC the AKD requirement was slightly higher to get the contact angle more than $100^0$. When the hydrophobicity of different types of pulp furnishes was compared, it was observed that to achieve around 30 $g/m^2$ $Cobb_{60}$ value, the AKD dose required for MHB pulp was highest followed by BBS, MHW, BWS and BRC pulp. The contact angle of hardwood pulps i.e. MHW and MHB was more than $110^0$ whereas it was below $100^0$ in case of BWS pulp. BBS pulp has shown comparatively better contact angle than BWS pulp.

With talc filler, MHB pulp required highest AKD dose to achieve 30 $g/m^2$ $Cobb_{60}$ value followed by MHW, BBS, BWS and BRC. With GCC filler the dose of AKD required was higher than that of talc and with no filler. To achieve 30 $g/m^2$ $Cobb_{60}$ value with GCC filler, the AKD dose required for MHW, MHB and BBS was almost comparable whereas in case of BWS and BRC it was lower. With PCC filler, the dose of AKD required was higher than that of other fillers. To achieve 30 $g/m^2$ $Cobb_{60}$ value with PCC, the AKD dose required for MHW and MHB pulps was almost comparable but highest amongst five pulp samples. The AKD demand in BBS, BWS and BRC pulp were in the decreasing order.

With talc filler also to achieve around $100^0$ contact angle, the AKD dose required for MHW, MHB and BBS pulps was comparable though it was slightly lesser for BRC pulp. This contact angle could not be achieved with BWS pulp. With GCC filler, AKD dose required for BBS pulp was highest followed by MHB, MHW and BRC. With PCC filler also, AKD dose required for pulp was in similar order as in case of GCC. But AKD demand was more with PCC as compared to GCC

In case of ASA sizing, the demand of ASA emulsion with agro residue based pulps was lesser as compare to hardwood pulps. Sizing properties were more stable using agro residues as compared to hardwood even at lower dosage of ASA with all fillers. Similar to AKD sizing, in case of ASA sizing too, the contact angles with hardwood based pulp were higher (101-$105^0$) as compared with agro residue pulps even at $Cobb_{60}$ value of around 45 $g/m^2$. However in case of BBS pulp also, the contact angle was 100-$102^0$ i.e. more than $100^0$ at $Cobb_{60}$ value of 45 $g/m^2$. In case of BWS pulp, the contact angle was lower but stable. At 30 $g/m^2$ $Cobb_{60}$ value, the contact angle was 96-$98^0$ with all the fillers. A marginal drop in the values of contact angle was observed by increasing the $Cobb_{60}$ value from 30 to 40 $g/m^2$.

The surface roughness of the handsheets prepared with agro residue pulps was lower than that of hardwood pulps which was one of the important parameter responsible for the lower values of contact angles in case of the former.

The method for the determination of bound and unbound forms of AKD sizing agent in paper enables better understanding of sizing mechanisms in different technological environments. The method is suitable for performing routine determinations of AKD distribution in industrial paper samples. Systematic analyses have also confirmed previous assumptions that the most important portion of sizing agent was the one that was chemically bound to cellulosic fibers, though it was not necessarily predominant.

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## REFERENCES


1. Bist BS, Tiwary KN, Verma P, Sharma SK (2005). An experience with alkaline sizing. IPPTA J. 3: 75-77.
2. Hubbe MA (2006). Paper's resistance to wetting – A review of internal sizing chemicals and their effects. Bioresources 2(1): 1-40.
3. Dumas DH (1981). An overview of cellulose-reactive sizes. Tappi J. 64(1): 43-46.
4. Gess JM (1992). A perspective on neutral/alkaline papermaking. Tappi J. 75(4): 79-81.
5. Marton J (1990). Practical aspects of alkaline sizing. Tappi J. 73(11): 139-143.
6. Novak RW, Rende DS (1993). Size reversion in alkaline papermaking. Tappi J. 76(8): 117-120.
7. Jenkins S (2007). Wet-end chemistry with special emphasis on neutral/alkaline sizing', IPPTA J. 19(4): 57-67.
8. Paul SK, Balasubramaniam S, Lakshminarayanan TK (2004). Alkaline sizing for manufacture of coloured papers. IPPTA J. 3: 53-57.
9. Roberts JC, Garner DN (1985). The mechanism of alkyl ketene dimer sizing of paper, part I. Tappi J. 68(4): 118-121.
10. Bajpai PK, Sharma AK, Das S, Varadhan R (2008). Optimization of ASA emulsion and impact of filler on ASA sizing. IPPTA J. 20(3): 99-104.
11. Gess JM, Rende DS (2005). Alkenyl succinic anhydride (ASA). Tappi J. 4(9): 25-30.
12. Farley CE (1987). Principle of ASA sizing. In: Sizing Short Course, Tappi Press, 89-92.
13. Isogai A, Morimoto S (2004). Sizing performance and hydrolysis resistance of alkyl oleate succinic anhydride. Tappi J. 3(7): 8-12.
14. Wasser RB, Brinen JS (1998). Effect of hydrolyzed ASA on sizing in calcium carbonate filler paper. Tappi J. 81(7): 139-144.
15. Fernandes S, Duarte AP (2006). Influence of wet-end variables on the sizing efficiency of ASA on fine papers produced with Eucalyptus globules kraft pulps. Tappi J. 5(12): 17-23.
16. Karademir A (2002). Quantitative determination of alkyl ketene dimer (akd) retention in paper made on a pilot paper machine. Turk J. Agric. For. 26: 253-260.

Table 1: Fiber morphological study of the different pulps

| Particular | MHW | MHB | BBS | BWS | BRC |
|---|---|---|---|---|---|
| Average fiber length, mm | 0.718 | 0.754 | 0.586 | 0.751 | 0.853 |
| Width, $\mu$m | 18.5 | 17.4 | 15.1 | 17.9 | 19.2 |
| Coarseness, $\mu$g/m | 95.4 | 64.5 | 67.5 | 73.1 | 82.3 |
| Fines (Length weighted), % | 9.9 | 6.4 | 16.0 | 21.7 | 9.2 |

Table 2: Pulp characterization

| Particular | MHW | MHB | BBS | BWS | BRC |
|---|---|---|---|---|---|
| Potential, mV | -246 | -222 | -370 | -310 | -552 |
| Charge demand, $\mu$eq/l | -10.5 | -15.4 | -22.3 | -11.2 | -14.3 |
| $^{0}$SR of unbeaten pulp | 21 | 20 | 27 | 27 | 28 |
| Brightness, % ISO | 89.7 | 88.6 | 86.2 | 78.2 | 80.2 |
| Air permeance, Gurley s | 12.5 | 18.1 | 75.3 | 49.0 | 5.6 |
| Bendtsen roughness, ml/min | 120 | 112 | 71 | 43 | 181 |

Table 3: General characteristics of fillers

| Parameter | Talc | GCC-1 | GCC-2 | GCC-3 | PCC-1 | PCC-2 |
|---|---|---|---|---|---|---|
| ISO Brightness, % | 89.7 | 96.9 | 94.4 | 94.0 | 95.8 | 97.2 |
| CIE Whiteness | 83.5 | 97.4 | 88.4 | 93.0 | 94.8 | 93.2 |
| Nature | Anionic | Cationic | Anionic | Cationic | Cationic | Cationic |
| Color | White | White | White | White | White | White |
| pH of 5% slurry | 10.3 | 9.8 | 9.3 | 8.6 | 9.7 | 10.3 |
| Dispersion in water | Poor | Good | Pre-dispersed | Good | Good | Pre-dispersed |
| Moisture, % | 0.2 | 0.1 | 40.0 | 0.1 | - | 75.0 |
| Particle size < 2.2 µm, mass% | 20.9 | 78.4 | 11.3 | - | 19.0 | 29.7 |
| Streaming potential, mV | -370 | +256 | -632 | +257 | +262 | +192 |
| Charge demand, µeq/l | 172 (cationic) | 30 (anionic) | 390 (cationic) | 42 (anionic) | 694 (anionic) | 165 (anionic) |
| Zeta potential, mV | -267 | +294 | -195 | +401 | +159 | +73 |

Table 4: Characterization of AKD emulsions

<table>
<tr><td colspan="2">Parameters</td><td>AKD-1</td><td>AKD-2</td><td>AKD-3</td><td>AKD-4</td><td>AKD-5</td></tr>
<tr><td colspan="2">Solid, % (as such)</td><td>20.8</td><td>20.4</td><td>20.6</td><td>16.1</td><td>15.3</td></tr>
<tr><td colspan="2">pH, 1%</td><td>2.58</td><td>3.71</td><td>3.67</td><td>3.32</td><td>3.99</td></tr>
<tr><td>Potential, mV</td><td rowspan="2">1 % w/v</td><td>+41.4</td><td>+81.2</td><td>+99.2</td><td>+118.9</td><td>+422</td></tr>
<tr><td>Anionic demand, µeq/l</td><td>4600</td><td>5230</td><td>4950</td><td>4780</td><td>6050</td></tr>
</table>

Table 5: Particle size distribution of AKD emulsions

| Particle size distribution | Abundance, % | | | | |
|---|---|---|---|---|---|
| | AKD-1 | AKD-2 | AKD-3 | AKD-4 | AKD-5 |
| < 0.5 μm | 1.5 | 0.4 | 2.3 | 18.2 | 38.9 |
| 0.5 –1.0 μm | 76.0 | 44.5 | 72.7 | 68.0 | 43.6 |
| 1.0 – 2.0 μm | 22.5 | 36.5 | 25.0 | 11.8 | 13.8 |
| 2.0 – 3.0 μm | -- | 16.4 | -- | 2.0 | 3.7 |
| > 3μm | -- | 2.2 | -- | -- | - |

Table 6: Particle size distribution of ASA emulsion

| Particle size distribution | ASA-1 | ASA-2 |
|---|---|---|
| < 0.5 μm | 31 | 39 |
| 0.5 –1.0 μm | 23 | 36 |
| 1.0 – 2.0 μm | 39 | 23 |
| 2.0 – 3.0 μm | 6 | 2 |
| > 3μm | 1 | 0 |

Table 7: Characterization of wet-end chemicals (1% w/v)

| Filler | pH | Viscosity, cp (100 rpm, spindle 2, ambient temperature) | Streaming potential, mV | Charge demand, μeq/l |
|---|---|---|---|---|
| Beaten pulp | 8.2 | - | -257 | 8.8 (cationic) |
| CPF | 4.3* | 11.1*# | +760 | 18000 (anionic) |
| CS | 6.4 | 31 | +135 | 1655 (anionic) |
| AKD | 3.3 | 65.2 | +54 | 2354 (anionic) |
| CPAM | 3.8* | 43* | +1038 | 13978 (anionic) |
| APAM | 7.1* | 39* | -1800 | 8820 (cationic) |
| Process water | 7.7 | - | -333 | 2.8 (cationic) |

* 0.1% w/v
\# Spindle 1

Table 8: pH and charge study of pulp slurry after each stage of chemical addition

| Parameter | pH | Potential, mV | Cationic charge demand, μeq/l |
|---|---|---|---|
| Beaten pulp (1% cy) | 7.8 | -257 | 8.8 |
| Pulp + CPF | 7.8 | -228 | 7.2 |
| Pulp + CPF + CS | 7.7 | -215 | 5.4 |
| Pulp + CPF + CS + AKD-1 | 7.6 | -210 | 4.8 |
| Pulp + CPF + CS + AKD-1 + Talc | 7.8 | -211 | 5.7 |
| Pulp + CPF + CS + AKD-1 + Talc – make-up to 0.33% cy | 7.8 | -275 | 5.9 |
| Pulp + CPF + CS + AKD-1 + Talc + CPAM | 7.7 | -270 | 5.6 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD-1, 1 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 9: Effect of moisture of handsheets on $Cobb_{60}$, $g/m^2$ of paper

| Pressing time, min | Sheet moisture, % | Curing time*, min | | | |
|---|---|---|---|---|---|
| | | 30 | 60 | 120 | 240 |
| 0 | 80.7 | 134 | 122 | 40 | 43 |
| 2 | 66.0 | 26.8 | 26.4 | 25.9 | 24.5 |
| 3 | 64.5 | 26.3 | 26.2 | 25.9 | 24.2 |
| 5 | 63.0 | 25.4 | 24.9 | 24.8 | 24.2 |
| 5 & 2 (standard) | 49.0 | 20.6 | 20.5 | 20.5 | 20.4 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD-1, 1.2 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

* Keeping wet handsheets directly in the oven for above timings

Table 10: Effect of natural curing# on sizing performance

| Day | $Cobb_{60}$, $g/m^2$ | Contact angle, deg | Surface energy, mN/m |
|---|---|---|---|
| On same day | 130 | 27 | 65.9 |
| After one day | 122 | 29 | 65.0 |
| After two days | 120 | 29 | 65.0 |
| After three days | 119 | 32 | 63.7 |
| After four days | 116 | 33 | 62.9 |
| After five days | 116 | 33 | 62.9 |
| On same day (accelerated curing*) | 20.6 | 112.0 | 15.0 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD-1, 1.2 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

# Hand sheets were air-dried and cured in atmosphere

*Accelerated curing: Air dried handsheets were cured in oven at 105 $^0C$ for 30 minutes

Table 11: Effect of pH on sizing performance

| pH | $Cobb_{60}$, $g/m^2$ |
|---|---|
| 7 (maintained by PAC) | 96 |
| 7.8 (as such) | 20.4 |
| 8.0 (maintained by $Na_2CO_3$) | 19.8 |
| 8.5 (maintained by $Na_2CO_3$) | 19.8 |
| 9.0 (maintained by $Na_2CO_3$) | 19.6 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD-1, 1.2 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 12: Effect of CPF on sizing performance

| CPF, g/t | 100 | 100 | 200 | 200 | 300 | 300 |
|---|---|---|---|---|---|---|
| CS, kg/t | - | 5 | - | 5 | - | 5 |
| $Cobb_{60}$, $g/m^2$ | 30.8 | 24.4 | 29.4 | 20.4 | 39.4 | 27.8 |
| pH | 7.8 | 7.8 | 7.9 | 7.8 | 7.9 | 7.8 |
| Charge demand, $\mu$eq/l | -7.2 | -7.0 | -6.4 | -5.4 | -6.4 | -5.8 |

Sequence: MHW pulp + CPF + CS + AKD-1, 1.2 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 13: Optimization of cationic starch dose

| CS, kg/t | $Cobb_{60}$, $g/m^2$ | pH | Cationic charge demand, $\mu$eq/l |
|---|---|---|---|
| 2 | 28.2 | 7.9 | 7.8 |
| 3 | 26.4 | 7.8 | 7.4 |
| 4 | 24.5 | 7.8 | 6.2 |
| 5 | 20.5 | 7.8 | 5.8 |
| 10 | 20.6 | 7.8 | 5.6 |

Sequence: MHW pulp + CPF, 200 g/t + CS + AKD-1, 1.2 kg/t + Talc, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 14: Sizing behavior of MHB pulp with AKD-1 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, µeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 24.0 | 116.0 | 110.4 | 110.3 | 110.1 | 110.0 | 109.8 | 110.0 | 110.8 | 16.98 | -181.5 | 6.2 | 0.472 | -14.7 | 8.0 |
| 1.0 | 34.4 | 108.0 | 105.3 | 105.0 | 105.1 | 104.9 | 104.6 | 104.3 | 105.2 | 21.88 | -191.9 | 7.1 | 0.470 | -15.2 | 8.0 |
| 0.9 | 56.8 | 88.8 | 87.9 | 88.1 | 85.5 | 73.3 | 70.9 | 65.8 | 88.2 | 29.01 | -193.1 | 7.8 | 0.468 | -15.8 | 8.0 |
| 0.8 | 78.3 | 87.9 | 81.8 | 79.9 | 78.2 | 76.4 | 73.5 | 43.0 | 79.9 | 38.21 | -200.2 | 8.1 | 0.461 | -16.9 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 15: Sizing behavior of MHB pulp with AKD-2 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 25.4 | 123.0 | 117.0 | 116.9 | 116.7 | 116.6 | 116.4 | 116.6 | 117.4 | 18.0 | -192.4 | 6.6 | 0.5 | -15.6 | 8.5 |
| 1.0 | 36.5 | 114.5 | 111.6 | 111.3 | 111.4 | 111.2 | 110.9 | 110.6 | 111.5 | 23.2 | -203.4 | 7.5 | 0.5 | -16.1 | 8.5 |
| 0.9 | 60.2 | 94.1 | 93.2 | 93.4 | 90.6 | 77.7 | 75.2 | 69.7 | 93.5 | 30.8 | -204.7 | 8.3 | 0.5 | -16.7 | 8.5 |
| 0.8 | 83.0 | 93.2 | 86.7 | 84.7 | 82.9 | 81.0 | 77.9 | 45.6 | 84.7 | 40.5 | -212.2 | 8.6 | 0.5 | -17.9 | 8.5 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 16: Sizing behavior of MHB pulp with AKD-3 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 23.4 | 112.0 | 112.4 | 112.3 | 112.0 | 111.9 | 111.8 | 111.9 | 112.0 | 16.38 | -204.3 | 8.7 | 0.498 | -16.3 | 8.1 |
| 1.0 | 24.6 | 111.8 | 110.3 | 109.9 | 109.9 | 109.7 | 109.6 | 109.6 | 109.8 | 17.68 | -207.2 | 9.2 | 0.492 | -16.9 | 8.2 |
| 0.9 | 33.8 | 106.0 | 105.2 | 105.1 | 105.3 | 104.9 | 104.7 | 104.7 | 105.2 | 21.88 | -211.2 | 10.2 | 0.488 | -17.2 | 8.0 |
| 0.8 | 52.3 | 89.9 | 88.9 | 88.3 | 84.9 | 76.3 | 73.9 | 63.8 | 87.2 | 29.33 | -219.8 | 11.3 | 0.467 | -17.8 | 8.1 |
| 0.6 | 65.0 | 85.1 | 84.9 | 81.8 | 74.3 | 65.6 | 59.8 | 47.7 | 81.2 | 38.09 | -237.9 | 11.8 | 0.456 | -18.4 | 8.1 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 17: Sizing behavior of MHB pulp with AKD-4 emulsion (without filler)

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 20.1 | 118.2 | 118.6 | 119.4 | 120.1 | 120.9 | 121.8 | 122.1 | 121.5 | 10.87 | -201.3 | -6.7 | 0.461 | -14.4 | 8.1 |
| 1.0 | 21.7 | 117.1 | 117.9 | 118.5 | 118.7 | 120.1 | 120.8 | 121.5 | 120.3 | 11.54 | -213.6 | -7.5 | 0.461 | -15.8 | 8.1 |
| 0.9 | 24.5 | 117.0 | 117.1 | 117.6 | 118.1 | 118.6 | 119.2 | 119.5 | 119.1 | 12.18 | -229.9 | -8.2 | 0.459 | -16.4 | 8.0 |
| 0.8 | 44.8 | 105.8 | 105.1 | 104.9 | 104.2 | 102.3 | 102.1 | 97.2 | 103.1 | 21.18 | -232.6 | -8.4 | 0.465 | -16.8 | 7.9 |
| 0.6 | 62.8 | 95.2 | 95.2 | 95.2 | 92.1 | 91.0 | 90.8 | 89.3 | 92.1 | 26.74 | -238.2 | -8.6 | 0.468 | -17.2 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 18: Sizing behavior of MHB pulp with AKD-5 emulsion (without filler)

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 20.4 | 118.6 | 118.2 | 119.0 | 120.2 | 121.3 | 121.0 | 121.9 | 121.3 | 10.95 | -198.0 | 8.1 | 0.468 | -14.9 | 8.0 |
| 1.0 | 21.2 | 118.2 | 117.9 | 118.2 | 119.1 | 119.7 | 119.9 | 120.1 | 119.6 | 11.71 | -208.2 | 8.6 | 0.471 | -15.4 | 8.0 |
| 0.9 | 23.8 | 117.2 | 117.4 | 118.2 | 118.1 | 118.2 | 119.2 | 120.0 | 118.3 | 12.59 | -215.8 | 8.8 | 0.473 | -16.0 | 8.1 |
| 0.8 | 25.2 | 116.9 | 116.8 | 117.1 | 117.9 | 118.1 | 118.8 | 118.8 | 117.7 | 12.92 | -222.1 | 9.4 | 0.485 | -16.4 | 8.1 |
| 0.6 | 26.8 | 113.1 | 113.9 | 114.8 | 115.2 | 116.0 | 116.3 | 116.2 | 115.5 | 13.98 | -232.2 | 9.8 | 0.483 | -17.2 | 8.0 |
| 0.4 | 34.9 | 105.8 | 105.0 | 104.9 | 104.2 | 104.1 | 103.9 | 103.5 | 104.5 | 22.30 | -238.6 | 10.6 | 0.486 | -17.6 | 8.1 |
| 0.3 | 76.8 | 81.1 | 72.5 | 77.9 | 64.2 | 61.5 | 41.5 | 31.1 | 68.2 | 42.44 | -242.8 | 11.4 | 0.491 | -18.8 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 19: Sizing behavior of MHW pulp with AKD-1 emulsion (without filler)

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ – Time interval, s – 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.2 | 22.5 | 116.0 | 112.0 | 111.9 | 111.2 | 111.1 | 111.3 | 111.0 | 112.2 | 14.99 | -198.2 | 5.6 | 0.463 | -14.0 | 8.0 |
| 1.0 | 29.3 | 114.8 | 111.3 | 110.0 | 110.1 | 110.0 | 109.5 | 109.6 | 109.8 | 17.81 | -191.1 | 5.3 | 0.468 | -13.8 | 8.0 |
| 0.9 | 41.8 | 101.3 | 101.0 | 101.1 | 100.3 | 99.9 | 99.3 | 98.1 | 100.1 | 24.13 | -187.9 | 4.7 | 0.474 | -13.0 | 8.0 |
| 0.8 | 53.5 | 89.9 | 88.4 | 86.5 | 77.5 | 50.1 | 46.5 | 18.5 | 73.5 | 39.54 | -175.5 | 4.2 | 0.461 | -12.6 | 8.0 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 20: Sizing behavior of MHW pulp with AKD-1 emulsion and talc filler

| AKD, kg/t | $Cobb_{60,}$ g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 20.4 | 116.7 | 112.3 | 112.0 | 111.2 | 111.1 | 111.3 | 111.6 | 112.6 | 14.99 | -206.1 | 4.8 | 0.458 | -16.2 | 8.0 |
| 1.0 | 28.5 | 113.7 | 110.3 | 109.2 | 109.6 | 110.9 | 109.3 | 108.6 | 108.7 | 17.96 | -214.6 | 5.2 | 0.452 | -17.2 | 8.0 |
| 0.9 | 40.1 | 101.7 | 101.2 | 101.3 | 101.5 | 99.4 | 99.0 | 98.4 | 100.4 | 24.09 | -222.7 | 5.7 | 0.442 | -17.6 | 8.0 |
| 0.8 | 51.6 | 89.8 | 88.1 | 89.1 | 85.1 | 82.3 | 64.1 | 52.8 | 85.3 | 33.77 | -242.8 | 6.1 | 0.449 | -17.8 | 8.0 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + Talc, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 21: Sizing behavior of MHW pulp with AKD-1 emulsion and GCC-1 filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 5 | 16.2 | 116.2 | 117.2 | 117.3 | 117.9 | 117.9 | 117.8 | 117.9 | 117.8 | 12.88 | -222.8 | 4.0 | 0.459 | -12.9 | 8.2 |
| 3 | 20.8 | 115.1 | 112.8 | 112.4 | 112.5 | 112.2 | 111.9 | 111.9 | 112.2 | 16.37 | -218.3 | 4.1 | 0.488 | -13.0 | 8.1 |
| 2.5 | 21.0 | 115.0 | 113.2 | 112.2 | 112.2 | 112.2 | 112.1 | 111.8 | 112.1 | 16.36 | -218.5 | 4.6 | 0.462 | -13.5 | 8.2 |
| 2.2 | 28.4 | 112.1 | 108.4 | 108.0 | 107.6 | 107.0 | 107.0 | 106.4 | 107.1 | 17.95 | -202.9 | 5.2 | 0.456 | -14.0 | 8.2 |
| 2 | 34.1 | 108.5 | 106.2 | 105.0 | 105.1 | 105.1 | 104.9 | 104.5 | 105.6 | 21.74 | -187.3 | 6.1 | 0.459 | -14.1 | 8.2 |
| 1.8 | 46.8 | 95.8 | 93.1 | 91.2 | 90.1 | 90.0 | 88.1 | 87.2 | 91.2 | 32.12 | -181.6 | 6.5 | 0.477 | -14.5 | 8.3 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 280kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 22: Sizing behavior of MHW pulp with AKD-1 emulsion and GCC-2 filler

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 5 | 16.4 | 116.5 | 116.4 | 117.5 | 117.8 | 117.7 | 117.5 | 117.5 | 117.4 | 12.94 | -261.3 | 4.9 | 0.461 | -15.2 | 8.1 |
| 3 | 26.5 | 114.7 | 108.2 | 108.2 | 107.9 | 107.8 | 107.3 | 107.3 | 108.2 | 17.31 | -255.3 | 5.1 | 0.455 | -15.6 | 8.2 |
| 2.5 | 29.6 | 111.8 | 109.3 | 109.1 | 109.0 | 108.1 | 108.3 | 108.6 | 108.1 | 18.01 | -242.9 | 5.2 | 0.458 | -16.8 | 8.2 |
| 2.2 | 42.4 | 101.2 | 101.1 | 101.1 | 100.9 | 100.1 | 99.2 | 98.3 | 100.1 | 24.01 | -243.3 | 6.3 | 0.462 | -17.0 | 8.2 |
| 2.0 | 52.3 | 89.6 | 88.0 | 87.3 | 85.0 | 82.0 | 74.1 | 50.1 | 84.6 | 33.89 | -217.4 | 6.5 | 0.464 | -17.9 | 8.1 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 270 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 23: Sizing behavior of MHW pulp with AKD-1 emulsion and GCC-3 filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 5.5 | 20.8 | 118.7 | 112.3 | 112.3 | 111.8 | 111.9 | 112.7 | 112.6 | 112.1 | 15.01 | -187.0 | 3.4 | 0.471 | -11.6 | 8.0 |
| 5.0 | 25.7 | 115.9 | 109.4 | 109.3 | 109.1 | 109.0 | 108.8 | 108.9 | 109.2 | 17.12 | -250.3 | 5.3 | 0.468 | -12.8 | 8.0 |
| 4.0 | 41.9 | 101.0 | 101.3 | 101.0 | 101.0 | 99.5 | 99.1 | 98.9 | 100.1 | 24.01 | -265.3 | 6.1 | 0.465 | -12.7 | 8.0 |
| 3.0 | 62.1 | 86.8 | 83.1 | 79.1 | 71.1 | 63.3 | 60.1 | 55.8 | 78.0 | 36.75 | -271.3 | 6.4 | 0.462 | -13.0 | 8.0 |
| 2.5 | 80.6 | 86.9 | 81.0 | 79.1 | 77.2 | 75.4 | 70.5 | 31.0 | 71.7 | 40.66 | -276.9 | 6.9 | 0.457 | -13.4 | 8.0 |
| 2.0 | 91.3 | 82.9 | 82.0 | 81.3 | 76.4 | 65.2 | 58.5 | 49.8 | 69.8 | 42.01 | -277.8 | 7.4 | 0.461 | -14.7 | 8.0 |
| 1.8 | 100.6 | -- | -- | -- | -- | -- | - | -- | -- | -- | -279.2 | 8.1 | 0.452 | -14.2 | 8.0 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 400 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 24: Sizing behavior of MHW pulp with AKD-1 emulsion and PCC-1 filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.8 | 23.1 | 116.9 | 111.2 | 111.0 | 111.1 | 110.0 | 110.2 | 110.3 | 111.2 | 16.62 | -221.6 | 4.9 | 0.469 | -13.0 | 8.2 |
| 2.5 | 33.8 | 108.4 | 106.1 | 105.2 | 105.5 | 105.1 | 105.0 | 104.5 | 105.8 | 21.71 | -228.5 | 5.1 | 0.462 | -13.5 | 8.3 |
| 2.2 | 44.3 | 101.0 | 100.8 | 100.1 | 100.6 | 100.0 | 99.4 | 98.1 | 99.7 | 24.56 | -219.3 | 5.7 | 0.456 | -14.0 | 8.2 |
| 2.0 | 59.3 | 87.9 | 86.8 | 85.1 | 85.0 | 72.3 | 70.1 | 63.1 | 86.8 | 30.22 | -189.3 | 6.6 | 0.459 | -14.1 | 8.2 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 300 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 25: Sizing behavior of MHW pulp with AKD-1 emulsion and PCC-2 filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.8 | 57.2 | 98.3 | 93.8 | 93.5 | 92.9 | 91.1 | 90.0 | 88.8 | 91.2 | 30.01 | -198.2 | 5.1 | 0.384 | -22.3 | 8.1 |
| 2.5 | 86.1 | 96.4 | 78.8 | 69.2 | 58.6 | 46.4 | 33.5 | 33.0 | 76.9 | 39.80 | -219.2 | 5.4 | 0.387 | -22.9 | 8.2 |
| 2.2 | 98.8 | 96.6 | 84.0 | 67.5 | 21.2 | -- | -- | -- | 68.9 | 42.41 | -220.1 | 5.8 | 0.388 | -23.8 | 8.1 |
| 2.0 | >100 | 77.0 | 68.8 | 26.9 | -- | -- | -- | -- | 48.7 | 54.49 | -222.6 | 6.8 | 0.94 | -24.9 | 8.0 |

Sequence: MHW pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 350 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 26: Sizing behavior of MHB pulp with AKD-1 emulsion and talc filler

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 21.2 | 114.9 | 112.1 | 112.0 | 112.1 | 111.9 | 111.8 | 111.1 | 111.9 | 16.41 | -181.7 | 5.5 | 0.442 | -18.6 | 8.0 |
| 1.0 | 29.8 | 108.8 | 106.8 | 105.9 | 105.5 | 105.7 | 105.8 | 105.9 | 106.8 | 21.44 | -231.4 | 7.8 | 0.432 | -20.2 | 8.0 |
| 0.9 | 41.1 | 102.8 | 102.0 | 101.8 | 101.2 | 100.9 | 100.2 | 99.3 | 100.9 | 23.87 | -241.3 | 8.1 | 0.426 | -21.6 | 8.0 |
| 0.8 | 53.8 | 93.8 | 92.9 | 91.1 | 90.5 | 77.3 | 78.9 | 71.8 | 91.2 | 30.01 | -256.3 | 8.6 | 0.412 | -22.8 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + Talc, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 27: Sizing behavior of MHB pulp with AKD-1 emulsion and GCC-1 filler

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.5 | 22.6 | 113.8 | 111.5 | 111.3 | 111.1 | 110.9 | 110.7 | 110.1 | 111.0 | 16.54 | -289.6 | 7.5 | 0.436 | -13.7 | 8.0 |
| 2.2 | 29.7 | 109.8 | 109.4 | 109.5 | 109.2 | 109.1 | 109.0 | 108.8 | 109.3 | 17.47 | -259.4 | 8.4 | 0.439 | -14.5 | 8.0 |
| 2.0 | 41.4 | 95.0 | 94.0 | 93.8 | 93.4 | 91.5 | 90.6 | 89.4 | 92.4 | 27.73 | -242.6 | 9.1 | 0.444 | -14.8 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 28: Sizing behavior of MHB pulp with AKD-1 emulsion and PCC-1 filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.8 | 25.5 | 113.0 | 111.2 | 111.1 | 111.3 | 110.4 | 110.2 | 110.1 | 110.9 | 16.73 | -239.4 | 7.2 | 0.416 | -16.1 | 8.1 |
| 2.5 | 34.6 | 107.9 | 104.9 | 104.1 | 104.1 | 104.0 | 103.8 | 103.3 | 105.0 | 21.90 | -241.1 | 8.7 | 0.414 | -16.2 | 8.0 |
| 2.2 | 47.7 | 95.9 | 93.6 | 91.0 | 90.3 | 90.2 | 88.7 | 87.1 | 91.4 | 32.11 | -253.6 | 8.8 | 0.412 | -17.6 | 7.9 |
| 2.0 | 61.7 | 86.7 | 83.0 | 80.2 | 72.3 | 62.8 | 59.1 | 54.7 | 77.4 | 36.82 | -259.3 | 9.2 | 0.417 | -18.2 | 8.0 |

Sequence: MHB pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 300 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 29: Sizing behavior of BBS pulp with AKD-1 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 24.2 | 102.3 | 102.2 | 101.9 | 101.8 | 101.3 | 100.9 | 100.7 | 101.7 | 23.42 | -172.8 | 5.4 | 0.401 | -8.1 | 8.0 |
| 1.0 | 30.1 | 101.2 | 101.1 | 101.1 | 100.9 | 100.8 | 100.8 | 100.4 | 100.9 | 23.87 | -175.8 | 5.7 | 0.414 | -8.5 | 7.9 |
| 0.9 | 34.5 | 100.2 | 100.1 | 99.3 | 99.5 | 99.4 | 99.0 | 98.1 | 99.8 | 24.01 | -184.3 | 6.9 | 0.412 | -8.9 | 8.0 |
| 0.8 | 38.8 | 94.7 | 94.1 | 93.5 | 92.3 | 91.2 | 90.2 | 89.2 | 91.2 | 27.80 | -185.6 | 8.8 | 0.407 | -9.4 | 8.0 |
| 0.6 | 55.8 | 81.8 | 82.0 | 81.7 | 80.0 | 79.3 | 78.9 | 63.8 | 78.4 | 39.67 | -188.3 | 8.9 | 0.401 | -9.7 | 8.1 |

Sequence: BBS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 30: Sizing behavior of BBS pulp with AKD-1 emulsion and talc filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 22.1 | 104.2 | 104.3 | 104.9 | 104.7 | 104.2 | 104.5 | 104.7 | 104.6 | 21.92 | -215.8 | 6.0 | 0.399 | -11.4 | 8.1 |
| 1.0 | 26.9 | 102.9 | 102.7 | 102.3 | 102.9 | 102.8 | 102.9 | 102.4 | 102.7 | 23.22 | -264.8 | 6.7 | 0.397 | -16.7 | 8.1 |
| 0.9 | 32.1 | 101.9 | 100.7 | 99.9 | 99.2 | 99.0 | 98.9 | 98.9 | 100.2 | 23.99 | -238.1 | 7.9 | 0.399 | -17.3 | 8.0 |
| 0.8 | 34.9 | 96.8 | 96.1 | 95.7 | 93.3 | 92.3 | 90.5 | 89.9 | 92.9 | 26.76 | -280.0 | 13.3 | 0.401 | -18.8 | 7.9 |
| 0.6 | 51.8 | 83.7 | 82.3 | 81.4 | 81.0 | 73.3 | 71.6 | 67.8 | 82.9 | 38.6 | -288.2 | 8.5 | 0.406 | -19.1 | 8.0 |

Sequence: BBS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + Talc, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 31: Sizing behavior of BBS pulp with AKD-1 emulsion and GCC-1 filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.5 | 23.8 | 102.2 | 102.1 | 102.3 | 101.9 | 101.8 | 100.9 | 100.6 | 101.9 | 23.38 | -217.6 | 5.8 | 0.343 | -7.3 | 8.2 |
| 2.2 | 31.1 | 101.9 | 101.7 | 100.9 | 100.2 | 99.9 | 99.6 | 99.3 | 100.8 | 23.84 | -223.6 | 6.2 | 0.349 | -7.6 | 8.1 |
| 2.0 | 37.9 | 95.5 | 95.2 | 94.8 | 93.6 | 92.2 | 90.9 | 90.5 | 93.6 | 26.61 | -240.7 | 6.8 | 0.350 | -7.9 | 8.0 |
| 1.8 | 45.1 | 88.9 | 85.9 | 84.3 | 78.3 | 72.7 | 69.1 | 61.7 | 77.4 | 36.82 | -248.0 | 7.2 | 0.356 | -8.2 | 8.1 |
| 1.7 | 68.2 | 71.3 | 69.9 | 68.2 | 65.3 | 63.8 | 61.0 | 54.7 | 65.3 | 44.01 | -253.6 | 7.6 | 0.365 | -8.8 | 8.0 |

Sequence: BBS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 280 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 32: Sizing behavior of BBS pulp with AKD-1 emulsion and PCC-1 filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.8 | 24.9 | 102.6 | 102.5 | 102.0 | 101.7 | 101.1 | 100.4 | 100.4 | 101.9 | 23.39 | -191.7 | 5.9 | 0.388 | -10.5 | 8.1 |
| 2.5 | 27.9 | 101.5 | 101.4 | 101.5 | 101.4 | 101.4 | 101.6 | 100.2 | 101.1 | 23.76 | -204.6 | 5.6 | 0.387 | -11.0 | 8.0 |
| 2.2 | 33.3 | 97.3 | 97.2 | 96.1 | 94.1 | 94.0 | 92.5 | 91.9 | 94.8 | 26.40 | -221.7 | 6.4 | 0.370 | -11.2 | 8.1 |
| 2.0 | 44.5 | 89.1 | 86.6 | 84.5 | 79.3 | 75.7 | 70.2 | 66.7 | 78.9 | 35.99 | -229.9 | 6.9 | -0.387 | -11.5 | 8.1 |
| 1.8 | 52.4 | 83.8 | 82.9 | 81.1 | 80.5 | 71.3 | 70.9 | 66.5 | 74.5 | 37.01 | -234.1 | 7.2 | 0.398 | -12.1 | 8.0 |

Sequence: BBS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 300kg/t – make-up to 0.33% cy + APAM, 200 g/t

Table 33: Sizing behavior of BWS pulp with AKD-3 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, µeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 23.5 | 97.9 | 97.8 | 97.6 | 97.5 | 97.3 | 97.3 | 97.0 | 97.5 | 24.60 | -156.9 | 7.2 | 0.495 | -9.0 | 8.0 |
| 1.5 | 24.4 | 94.2 | 94.4 | 93.9 | 93.7 | 93.9 | 93.7 | 93.6 | 93.9 | 26.83 | -174.8 | 7.8 | 0.493 | -9.4 | 8.1 |
| 1.2 | 25.5 | 94.0 | 93.7 | 93.6 | 93.3 | 93.1 | 93.1 | 92.4 | 93.2 | 26.91 | -187.9 | 8.2 | 0.493 | -9.8 | 8.1 |
| 1.0 | 28.8 | 87.1 | 87.0 | 86.9 | 86.6 | 86.4 | 86.1 | 85.8 | 86.8 | 31.37 | -192.6 | 8.4 | 0.482 | -10.2 | 8.0 |
| 0.9 | 32.2 | 83.0 | 82.7 | 82.6 | 82.3 | 81.9 | 81. 7 | 81.4 | 81.7 | 34.43 | -198.2 | 8.7 | 0.480 | -11.8 | 8.1 |
| 0.8 | 50.2 | 83.3 | 83.1 | 81.0 | 81.2 | 78.3 | 77.4 | 72.6 | 80.4 | 35.42 | -221.9 | 9.4 | 0.477 | -13.0 | 8.1 |
| 0.6 | 66.9 | 91.2 | 87.9 | 82.5 | 75.2 | 62.4 | 47.4 | 38.8 | 75.4 | 40.82 | -237.8 | 12.8 | 0.468 | -13.6 | 8.0 |

Sequence: BWS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 34: Sizing behavior of BWS pulp with AKD-3 emulsion and talc filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 22.8 | 98.1 | 97.9 | 97.8 | 97.8 | 97.5 | 97.3 | 97.2 | 97.8 | 24.36 | -212.9 | 8.4 | 0.486 | -11.0 | 8.2 |
| 1.0 | 28.0 | 87.7 | 87.7 | 87.9 | 87.3 | 87.2 | 87.1 | 87.0 | 87.4 | 31.11 | -201.2 | 8.8 | 0.476 | -11.8 | 8.1 |
| 0.9 | 29.4 | 87.2 | 87.2 | 87.0 | 86.7 | 86.2 | 86.0 | 85.7 | 86.6 | 31.23 | -197.0 | 9.2 | 0.475 | -12.6 | 8.1 |
| 0.8 | 48.7 | 84.5 | 84.0 | 83.2 | 83.0 | 82.7 | 82.4 | 82.1 | 82.8 | 33.36 | -196.0 | 9.6 | 0.471 | -13.2 | 8.0 |
| 0.6 | 63.8 | 82.3 | 81.0 | 77.3 | 72.9 | 65.3 | 59.4 | 50.2 | 63.9 | 44.21 | -192.1 | 10.2 | 0.468 | -13.8 | 8.1 |

Sequence: BWS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + Talc, 190 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 35: Sizing behavior of BWS pulp with AKD-3 emulsion and GCC-1 filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.5 | 23.5 | 98.0 | 97.7 | 97.3 | 97.6 | 97.4 | 97.2 | 97.2 | 97.7 | 24.37 | -171.4 | 8.1 | 0.487 | -11.0 | 8.2 |
| 2.2 | 25.6 | 91.9 | 91.4 | 91.2 | 89.7 | 89.6 | 88.5 | 88.0 | 89.7 | 29.49 | -183.1 | 9.2 | 0.483 | -11.9 | 8.2 |
| 2.0 | 28.2 | 87.5 | 87.4 | 87.5 | 87.2 | 87.3 | 87.5 | 87.0 | 87.2 | 31.06 | -190.2 | 11.3 | 0.480 | -12.3 | 8.1 |
| 1.7 | 33.5 | 83.0 | 82.4 | 82.2 | 82.0 | 81.5 | 81.3 | 81.0 | 82.1 | 34.58 | -192.6 | 11.6 | 0.477 | -12.6 | 8.1 |
| 1.5 | 40.5 | 84.2 | 84.2 | 84.0 | 81.8 | 81.4 | 81.2 | 80.2 | 81.1 | 35.96 | -196.2 | 12.2 | 0.470 | -12.9 | 8.2 |
| 1.3 | 55.9 | 83.0 | 83.3 | 81.4 | 81.6 | 79.0 | 77.8 | 72.1 | 78.5 | 36.37 | -201.3 | 12.6 | 0.467 | -13.2 | 8.0 |
| 1.2 | 71.1 | 80.4 | 77.0 | 74.1 | 67.9 | 58.3 | 47.0 | 41.3 | 61.7 | 46.12 | -221.0 | 13.2 | 0.461 | -13.8 | 8.1 |
| 1.0 | 86.0 | 72.6 | 65.8 | 57.4 | 50.8 | 45.8 | 49.3 | 12.0 | 51.1 | 53.13 | -237.3 | 13.7 | 0.453 | -14.2 | 8.1 |

Sequence: BWS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 220 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 36: Sizing behavior of BWS pulp with AKD-3 emulsion and PCC-1 filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.5 | 23.7 | 98.2 | 97.4 | 97.7 | 97.9 | 98.1 | 97.6 | 97.7 | 97.9 | 24.31 | -176.2 | 8.4 | 0.491 | -11.6 | 8.2 |
| 2.2 | 26.3 | 92.1 | 91.7 | 91.2 | 88.3 | 88.4 | 89.1 | 88.6 | 89.3 | 29.57 | -186.2 | 9.6 | 0.494 | -12.7 | 8.2 |
| 2.0 | 30.2 | 87.2 | 87.2 | 87.0 | 86.7 | 86.2 | 86.0 | 85.7 | 86.6 | 31.23 | -194.2 | 11.7 | 0.499 | -13.2 | 8.1 |
| 1.7 | 35.4 | 82.7 | 81.6 | 81.3 | 80.3 | 80.5 | 79.9 | 79.2 | 80.2 | 34.69 | -201.3 | 12.1 | 0.502 | -13.8 | 8.1 |
| 1.5 | 42.8 | 83.2 | 83.0 | 82.1 | 79.3 | 79.0 | 79.1 | 78.6 | 79.1 | 37.02 | -214.6 | 12.3 | 0.506 | -14.3 | 8.2 |
| 1.3 | 58.3 | 81.2 | 81.3 | 80.4 | 78.6 | 76.0 | 75.2 | 70.1 | 76.1 | 37.89 | -221.3 | 12.9 | 0.515 | -16.3 | 8.1 |
| 1.2 | 76.3 | 79.2 | 77.0 | 72.1 | 63.9 | 56.6 | 42.5 | 38.2 | 57.4 | 48.01 | -232.6 | 13.6 | 0.521 | -17.2 | 8.1 |

Sequence: BWS pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 230 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 37: Sizing behavior of BRC pulp with AKD-3 emulsion (without filler)

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.5 | 22.3 | 111.2 | 111.0 | 111.0 | 110.8 | 110.7 | 110.6 | 110.4 | 110.8 | 16.63 | -207.4 | 7.0 | 0.491 | -18.9 | 8.1 |
| 1.2 | 24.4 | 106.6 | 106.6 | 106.5 | 106.4 | 106.3 | 106.2 | 106.1 | 106.4 | 19.22 | -208.5 | 9.9 | 0.475 | -21.3 | 8.0 |
| 1.0 | 26.6 | 102.0 | 102.6 | 102.9 | 103.0 | 102.9 | 103.0 | 103.2 | 102.8 | 21.37 | 219.2 | 8.9 | 0.483 | -22.1 | 7.9 |
| 0.9 | 29.4 | 101.2 | 101.2 | 101.4 | 101.3 | 101.0 | 101.2 | 101.1 | 101.2 | 23.27 | -230.5 | 10.2 | 0.482 | -24.1 | 8.0 |
| 0.8 | 36.2 | 99.2 | 99.5 | 99.8 | 99.7 | 99.8 | 99.7 | 99.7 | 99.5 | 23.35 | -233.6 | 10.4 | 0.472 | -24.2 | 8.0 |
| 0.7 | 52.7 | 97.3 | 95.0 | 92.5 | 88.1 | 81.7 | 82.8 | 81.3 | 84.6 | 33.89 | -238.7 | 10.7 | 0.470 | -24.6 | 8.1 |
| 0.6 | 65.6 | 87.3 | 85.0 | 82.5 | 80.1 | 79.7 | 78.8 | 78.3 | 81.5 | 34.56 | -242.8 | 11.1 | 0.485 | -25.1 | 8.1 |

Sequence: BRC pulp + CPF, 200 g/t + CS, 5 kg/t + AKD – make-up to 0.33% cy + CPAM, 200 g/t

Table 38: Sizing behavior of BRC pulp with AKD-3 emulsion and talc filler

| AKD, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 1.2 | 23.3 | 107.8 | 108.1 | 108.0 | 108.4 | 108.4 | 108.2 | 108.3 | 107.9 | 18.31 | -191.0 | 10.9 | 0.471 | -22.9 | 8.1 |
| 1.0 | 25.2 | 104.0 | 102.2 | 104.5 | 104.7 | 104.6 | 104.5 | 104.7 | 104.5 | 20.32 | -199.9 | 9.8 | 0.480 | -23.1 | 8.1 |
| 0.9 | 28.3 | 103.4 | 103.6 | 103.3 | 103.4 | 103.3 | 103.3 | 103.4 | 103.4 | 20.99 | -202.8 | 9.2 | 0.482 | -23.9 | 8.0 |
| 0.8 | 34.9 | 99.8 | 99.6 | 99.9 | 100.1 | 100.1 | 100.2 | 100.1 | 100.2 | 23.22 | -207.1 | 8.4 | 0.476 | -24.4 | 8.1 |
| 0.7 | 50.3 | 98.3 | 97.6 | 97.5 | 89.3 | 85.3 | 84.2 | 83.6 | 86.4 | 30.33 | -211.1 | 7.9 | 0.476 | -25.1 | 7.9 |
| 0.6 | 62.8 | 87.3 | 85.0 | 82.5 | 80.1 | 79.7 | 78.8 | 78.3 | 81.5 | 34.56 | -217.8 | 7.1 | 0.478 | -25.5 | 8.0 |

Sequence: BRC pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + Talc, 210 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 39: Sizing behavior of BRC pulp with AKD-3 emulsion and GCC-1 filler

| AKD, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.5 | 21.5 | 112.0 | 112.1 | 112.2 | 112.2 | 112.2 | 112.3 | 112.3 | 112.2 | 16.01 | -249.8 | 6.4 | 0.477 | -15.4 | 8.2 |
| 2.2 | 22.4 | 108.0 | 108.4 | 108.7 | 109.2 | 109.2 | 109.2 | 109.3 | 108.4 | 18.02 | -251.6 | 7.2 | 0.479 | -16.2 | 8.1 |
| 2.0 | 27.5 | 104.9 | 105.3 | 105.4 | 105.5 | 105.5 | 105.5 | 105.1 | 105.2 | 19.94 | -259.0 | 8.2 | 0.481 | -18.8 | 8.0 |
| 1.8 | 38.2 | 97.3 | 96.4 | 96.2 | 95.6 | 95.1 | 94.7 | 94.3 | 95.2 | 25.99 | -266.5 | 8.4 | 0.482 | -22.1 | 8.1 |
| 1.7 | 43.8 | 96.3 | 95.8 | 94.3 | 93.8 | 92.8 | 92.1 | 89.3 | 92.1 | 27.70 | -268.3 | 8.7 | 0.486 | -23.8 | 8.0 |
| 1.5 | 58.3 | 87.2 | 85.7 | 84.7 | 85.0 | 73.8 | 71.1 | 64.2 | 86.8 | 30.22 | -277.4 | 9.1 | 0.487 | -24.9 | 8.1 |
| 1.2 | 87.3 | 78.2 | 72.3 | 61.3 | 35.0 | -- | -- | .. | .. | .. | -281.2 | 9.3 | 0.485 | -25.8 | 8.2 |

Sequence: BRC pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + GCC, 200 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 40: Sizing behavior of BRC pulp with AKD-3 emulsion and PCC-1 filler

| AKD, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Cationic charge demand, µeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.8 | 24.2 | 107.2 | 108.1 | 108.0 | 107.8 | 107.9 | 107.8 | 107.6 | 107.2 | 18.37 | -193.4 | 7.4 | 0.467 | -22.1 | 8.1 |
| 2.5 | 27.2 | 104.9 | 105.0 | 105.3 | 105.3 | 105.3 | 105.4 | 105.2 | 105.1 | 19.94 | -198.2 | 8.4 | 0.484 | -23.8 | 8.0 |
| 2.2 | 42.6 | 102.4 | 101.9 | 101.5 | 101.5 | 101.5 | 101.2 | 100.5 | 101.5 | 22.11 | -200.0 | 9.3 | 0.477 | -24.5 | 8.1 |
| 2.0 | 52.3 | 97.3 | 96.2 | 96.2 | 83.3 | 82.4 | 81.6 | 81.0 | 83.4 | 30.61 | -228.3 | 8.6 | 0.483 | -26.2 | 8.1 |
| 1.8 | 65.7 | 87.1 | 86.2 | 82.5 | 80.2 | 81.2 | 79.3 | 79.2 | 81.4 | 34.55 | -231.8 | 10.0 | 0.477 | -27.8 | 8.0 |

Sequence: BRC pulp + CPF, 200 g/t + CS, 5 kg/t + AKD + PCC, 300 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 41: Sizing behavior of MHB pulp with ASA emulsion (without filler)

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.2 | 116.9 | 117.4 | 120.0 | 120.7 | 120.9 | 120.8 | 121.3 | 120.3 | 11.49 | -214.3 | -6.8 | 0.481 | -4.1 | 7.9 |
| 1.8 | 27.2 | 114.6 | 114.3 | 114.2 | 114.5 | 115.0 | 114.9 | 114.8 | 114.5 | 14.54 | -220.0 | -7.1 | 0.499 | -4.7 | 7.9 |
| 1.5 | 32.3 | 108.3 | 108.4 | 108.2 | 108.2 | 108.1 | 108.0 | 108.0 | 108.2 | 17.78 | -235.5 | -7.3 | 0.501 | -5.8 | 7.9 |
| 1.2 | 42.3 | 102.6 | 102.5 | 102.2 | 103.2 | 103.3 | 102.3 | 103.4 | 102.6 | 21.48 | -239.1 | -7.5 | 0.494 | -7.3 | 8.0 |
| 1.0 | 50.3 | 97.8 | 102.2 | 102.7 | 102.8 | 102.2 | 102.5 | 102.1 | 102.2 | 21.69 | -260.3 | -7.8 | 0.502 | -7.5 | 7.9 |
| 0.8 | 82.5 | 72.2 | 65.4 | 58.2 | 52.8 | 49.3 | 48.2 | 14.8 | 53.1 | 52.62 | -268.3 | -8.4 | 0.518 | -8.0 | 8.0 |

Sequence: MHB pulp + CFA, 1 kg/t + PAC, 4 kg/t + CS, 3 kg/t + ASA – make-up to 0.33% cy + CPAM, 200 g/t

Table 42: Sizing behavior of MHB pulp with ASA emulsion and talc filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, $\mu eq/l$ | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 23.4 | 118.2 | 119.8 | 120.8 | 120.9 | 120.6 | 120.7 | 120.8 | 120.2 | 11.63 | -206.3 | -3.9 | 0.490 | -4.1 | 7.9 |
| 1.8 | 26.4 | 117.6 | 118.6 | 118.8 | 119.1 | 119.2 | 119.3 | 119.7 | 119.5 | 12.01 | -209.8 | -4.1 | 0.494 | -4.6 | 7.9 |
| 1.5 | 29.0 | 110.7 | 110.3 | 110.2 | 109.9 | 109.9 | 109.7 | 109.7 | 110.0 | 17.22 | -210.1 | -4.9 | 0.488 | -4.9 | 7.9 |
| 1.2 | 33.1 | 108.8 | 108.9 | 109.1 | 108.3 | 107.1 | 107.0 | 106.9 | 108.0 | 18.28 | -211.2 | -5.6 | 0.491 | -5.0 | 8.0 |
| 1.0 | 45.6 | 106.0 | 105.3 | 104.7 | 103.1 | 102.9 | 102.6 | 98.6 | 102.9 | 21.29 | -216.5 | -6.0 | 0.496 | -5.3 | 7.9 |
| 0.8 | 75.2 | 97.5 | 96.4 | 88.9 | 78.4 | 71.6 | 70.8 | 70.6 | 79.8 | 35.63 | -219.3 | -6.2 | 0.501 | -6.2 | 8.0 |

Sequence: MHB pulp + CFA, 1 kg/t + PAC, 4 kg/t + CS, 3 kg/t + ASA + Talc, 225 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 43: Sizing behavior of MHB pulp with ASA emulsion and GCC-1 filler

| ASA, kg/t | $Cobb_{60,}$ $g/m^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 27.2 | 114.4 | 114.6 | 114.5 | 114.3 | 114.9 | 114.7 | 114.4 | 114.8 | 14.49 | -169.4 | -4.7 | 0.496 | -1.8 | 7.9 |
| 1.8 | 30.2 | 109.2 | 109.1 | 109.0 | 108.9 | 108.6 | 108.2 | 108.1 | 108.5 | 17.43 | -179.0 | -5.4 | 0.464 | -5.0 | 7.9 |
| 1.5 | 35.6 | 105.5 | 105.4 | 105.1 | 104.9 | 104.2 | 103.9 | 104.2 | 105.1 | 20.87 | -182.1 | -5.8 | 0.471 | -6.2 | 7.9 |
| 1.2 | 45.6 | 106.7 | 104.35 | 104.2 | 103.7 | 103.1 | 102.8 | 99.2 | 102.3 | 21.37 | -206.1 | -6.2 | 0.476 | -7.5 | 8.0 |
| 1.0 | 59.5 | 97.7 | 96.8 | 96.3 | 94.6 | 93.2 | 92.2 | 90.1 | 94.5 | 27.01 | -211.4 | -7.3 | 0.482 | -7.9 | 7.9 |

Sequence: MHB pulp + CFA, 1 kg/t + PAC, 4 kg/t + CS, 3 kg/t + ASA + GCC-1, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 44: Sizing behavior of MHB pulp with ASA emulsion and GCC-2 filler

| ASA, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, $\mu$eq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 24.8 | 118.9 | 119.9 | 119.9 | 120.2 | 120.2 | 119.9 | 120.1 | 120.1 | 11.57 | -177.7 | -5.4 | 0.483 | -9.0 | 7.9 |
| 1.8 | 25.2 | 118.6 | 119.6 | 119.5 | 119.8 | 119.7 | 119.7 | 119.8 | 119.9 | 11.96 | --180.1 | -5.7 | 0.495 | -10.3 | 7.9 |
| 1.5 | 27.8 | 114.2 | 114.1 | 113.5 | 113.8 | 114.1 | 114.0 | 113.9 | 114.1 | 14.58 | 201.5 | -6.1 | 0.499 | -15.1 | 7.9 |
| 1.2 | 33.5 | 109.1 | 108.6 | 108.1 | 109.3 | 108.3 | 108.1 | 107.0 | 108.3 | 18.33 | -173.8 | -6.7 | 0.491 | -16.2 | 8.0 |
| 1.0 | 44.6 | 106.9 | 105.5 | 104.2 | 103.2 | 102.2 | 101.7 | 100.1 | 102.0 | 21.29 | -186.1 | -7.4 | 0.494 | -16.4 | 8.0 |
| 0.8 | 86.3 | 93.5 | 92.4 | 87.8 | 86.3 | 85.6 | 77.3 | 65.5 | 84.7 | 32.2 | -190.2 | -7.7 | 0.502 | -16.6 | 8.0 |

Sequence: MHB pulp + CFA, 1 kg/t + PAC, 4 kg/t + CS, 3 kg/t + ASA + GCC-2, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 45: Sizing behavior of MHB pulp with ASA emulsion and GCC-3 filler

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 26.5 | 118.2 | 118.7 | 118.7 | 118.9 | 119.1 | 119.3 | 119.5 | 119.3 | 12.11 | -155.8 | -5.4 | 0.486 | -4.3 | 7.9 |
| 1.8 | 28.5 | 114.0 | 113.9 | 113.7 | 113.7 | 113.9 | 113.5 | 113.0 | 113.5 | 14.71 | -164.6 | -5.8 | 0.492 | -4.9 | 7.9 |
| 1.5 | 33.2 | 110.1 | 109.3 | 108.2 | 108.9 | 108.2 | 108.0 | 107.3 | 108.5 | 18.29 | -174.9 | -6.7 | 0.497 | -5.3 | 7.9 |
| 1.2 | 46.6 | 105.7 | 105.5 | 103.9 | 103.2 | 103.0 | 102.2 | 99.9 | 101.4 | 21.52 | -182.5 | -7.3 | 0.499 | -5.9 | 8.0 |
| 1.0 | 61.7 | 95.7 | 95.8 | 96.3 | 92.6 | 91.2 | 91.2 | 89.7 | 92.5 | 26.52 | -191.8 | -7.7 | 0.499 | -6.2 | 7.9 |

Sequence: MHB pulp + CFA, 1 kg/t + PAC, 4 kg/t + CS, 3 kg/t + ASA + GCC-3, 300 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 46: Sizing behavior of MHB pulp with ASA emulsion and PCC-1 filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, µeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 22.4 | 119.6 | 119.8 | 120.8 | 120.9 | 121.2 | 121.1 | 121.7 | 121.1 | 11.09 | -181.2 | -5.1 | 0.489 | -7.8 | 7.9 |
| 1.8 | 24.1 | 118.9 | 119.2 | 120.1 | 120.3 | 120.4 | 120.5 | 120.7 | 120.5 | 11.32 | -198.1 | -5.8 | 0.505 | -8.5 | 7.9 |
| 1.5 | 31.2 | 109.1 | 109.0 | 108.8 | 108.7 | 108.2 | 108.0 | 107.6 | 108.1 | 17.67 | -204.6 | -6.2 | 0.504 | -9.4 | 7.9 |
| 1.2 | 45.1 | 106.5 | 105.1 | 105.2 | 104.1 | 103.6 | 102.1 | 98.3 | 102.5 | 21.25 | -211.3 | -7.4 | 0.507 | -10.2 | 8.0 |
| 1.0 | 68.4 | 89.1 | 87.2 | 85.5 | 82.2 | 83.2 | 81.3 | 79.2 | 83.4 | 33.35 | -217.2 | -7.8 | 0.512 | -10.6 | 7.9 |
| 0.8 | 88.2 | 77.4 | 74.3 | 72.1 | 68.4 | 64.2 | 62.1 | 62.0 | 67.2 | 48.15 | -219.3 | -8.1 | 0.518 | -10.9 | 8.0 |

Sequence: MHB pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + PCC,250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 47: Sizing behavior of MHB pulp with ASA emulsion and PCC-2 filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge demand, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 22.0 | 120.1 | 120.0 | 119.9 | 120.7 | 121.4 | 121.5 | 121.6 | 120.7 | 10.84 | -106 | -5.8 | 0.481 | -8.2 | 7.9 |
| 1.8 | 27.1 | 115.1 | 114.6 | 114.6 | 114.8 | 114.5 | 114.5 | 113.7 | 114.3 | 14.46 | -110 | -6.1 | 0.492 | -11.8 | 7.9 |
| 1.5 | 30.9 | 109.0 | 108.7 | 108.1 | 108.0 | 107.6 | 107.8 | 107.6 | 108.0 | 17.72 | -113 | -6.4 | 0.485 | -12.6 | 7.9 |
| 1.2 | 42.4 | 105.0 | 104.2 | 103.2 | 102.6 | 102.2 | 101.6 | 100.5 | 102.1 | 21.76 | -220 | -6.8 | 0.482 | -13.7 | 8.0 |
| 1.0 | 65.3 | 87.0 | 86.0 | 82.1 | 80.0 | 79.9 | 79.0 | 78.1 | 81.0 | 34.77 | -224 | -7.2 | 0.480 | -14.1 | 7.9 |
| 0.8 | 86.8 | 79.4 | 76.3 | 72.1 | 70.2 | 66.8 | 64.8 | 61.8 | 67.9 | 47.76 | -229 | -7.6 | 0.486 | -14.3 | 8.0 |

Sequence: MHB pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + PCC,240 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 48: Sizing performance of emulsion without filler

| ASA, kg/t | $Cobb_{60,}$ g/$m^2$ | Contact angle, °<br>Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.1 | 118.5 | 119.2 | 119.7 | 119.7 | 119.9 | 119.9 | 120.0 | 119.6 | 12.11 | -83.5 | -4.6 | 0.441 | -3.4 | 8.1 |
| 1.8 | 26.5 | 117.4 | 117.6 | 117.9 | 1181 | 117.9 | 117.8 | 117.4 | 117.7 | 12.81 | -143.2 | -5.4 | 0.447 | -3.8 | .8.1 |
| 1.5 | 28.4 | 115.2 | 115.1 | 114.8 | 114.2 | 115.0 | 114.8 | 114.6 | 114.8 | 14.23 | -196.9 | -5.8 | 0.451 | -4.8 | 8.0 |
| 1.2 | 39.0 | 104.2 | 104.3 | 103.9 | 103.8 | 104.2 | 103.5 | 103.1 | 103.8 | 21.53 | -228.2 | -6.1 | 0.459 | -6.6 | 8.0 |
| 1.0 | 48.6 | 104.1 | 104.2 | 103.3 | 103.1 | 102.2 | 101.2 | 98.2 | 102.3 | 21.40 | -238.8 | -6.4 | 0.462 | -6.8 | 8.0 |
| 0.8 | 74.8 | 83.1 | 77.5 | 74.9 | 65.8 | 60.5 | 47.3 | 35.1 | 63.4 | 44.84 | -242.6 | -7.2 | 0.478 | -7.0 | 8.1 |

Sequence: MHW pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA – make-up to 0.33% cy + CPAM, 200 g/t

Table 49 Sizing performance of emulsion with talc as filler

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 24.1 | 118.8 | 119.1 | 120.2 | 120.5 | 120.8 | 119.9 | 120.0 | 119.6 | 12.11 | -299 | -4.1 | 0.436 | -7.8 | 8.1 |
| 1.8 | 25.9 | 117.7 | 117.9 | 118.1 | 118.5 | 119.0 | 118.8 | 118.2 | 118.3 | 13.13 | -279 | -5.7 | 0.433 | -8.1 | .8.1 |
| 1.5 | 28.0 | 115.7 | 115.8 | 115.2 | 115.3 | 115.7 | 115.6 | 115.2 | 115.5 | 14.58 | -258 | -6.2 | 0.422 | -9.8 | 8.0 |
| 1.2 | 30.5 | 114.7 | 114.3 | 114.0 | 113.9 | 114.2 | 114.6 | 114.2 | 114.2 | 15.23 | -247 | -6.8 | 0.417 | -10.5 | 8.0 |
| 1.0 | 44.9 | 103.2 | 102.2 | 102.1 | 101.9 | 101.2 | 100.2 | 96.2 | 101.0 | 22.05 | -224 | -7.0 | 0.411 | -12.9 | 8.0 |
| 0.8 | 68.8 | 89.2 | 86.3 | 84.3 | 82.3 | 80.2 | 78.3 | 70.2 | 81.5 | 35.70 | -208 | -7.4 | 0.408 | -14.5 | 8.1 |

Sequence: MHW pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + talc, 225 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 50: Sizing performance of ASA emulsion With GCC-2 as filler (At 15% Ash level) 15.4/33

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.7 | 117.9 | 118.1 | 118.0 | 118.7 | 118.9 | 119.5 | 119.2 | 118.6 | 12.32 | -299.8 | -9.8 | 0.451 | -6.7 | 7.9 |
| 1.8 | 27.4 | 115.9 | 115.9 | 116.2 | 116.0 | 116.1 | 116.2 | 115.9 | 116.0 | 14.84 | -293.4 | -11.4 | 0.439 | -8.0 | 7.9 |
| 1.5 | 29.2 | 114.9 | 115.2 | 114.9 | 115.0 | 114.9 | 114.9 | 115.2 | 115.0 | 15.63 | -291.6 | -11.7 | 0.425 | -9.5 | 7.9 |
| 1.2 | 36.8 | 105.2 | 104.9 | 103.9 | 104.2 | 104.0 | 103.8 | 103.2 | 104.1 | 21.37 | -294.6 | -12.0 | 0.417 | -10.8 | 8.0 |
| 1.0 | 46.8 | 105.1 | 104.9 | 104.6 | 103.8 | 103.2 | 101.2 | 96.2 | 102.7 | 21.60 | -265.3 | -12.3 | 0.411 | -11.7 | 8.0 |
| 0.8 | 84.6 | 95.5 | 93.8 | 88.9 | 85.2 | 82.3 | 76.3 | 62.5 | 83.5 | 41.61 | -299.1 | -12.5 | 0.402 | -13.5 | 8.0 |

Sequence: MHW pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + GCC,250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 51: Sizing performance of ASA emulsion With PCC-1 as filler (At 15% Ash level)

| ASA, kg/t | $Cobb_{60}$, g/$m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 21.0 | 119.2 | 119.4 | 120.1 | 120.9 | 121.2 | 120.9 | 121.0 | 119.6 | 11.51 | -209.0 | -6.2 | 0.438 | -7.9 | 7.9 |
| 1.8 | 24.7 | 117.1 | 118.1 | 118.2 | 119.0 | 119.3 | 118.7 | 119.1 | 118.6 | 12.32 | -217.5 | -6.8 | 0.433 | -8.3 | 7.9 |
| 1.5 | 27.0 | 114.1 | 115.5 | 115.8 | 115.9 | 115.6 | 115.7 | 115.3 | 115.5 | 13.99 | -249.0 | -7.4 | 0.429 | -9.8 | 7.9 |
| 1.2 | 34.1 | 108.0 | 110.3 | 111.0 | 110.9 | 110.9 | 110.8 | 110.6 | 110.7 | 16.66 | -261.0 | -9.8 | 0.422 | -10.7 | 8.0 |
| 1.0 | 58.9 | 96.3 | 95.9 | 95.5 | 92.3 | 91.1 | 88.3 | 85.5 | 91.8 | 28.08 | -272.0 | -10.7 | 0.403 | -11.9 | 8.0 |
| 0.8 | 75.2 | 97.5 | 93.2 | 91.9 | 88.2 | 85.3 | 79.8 | 68.5 | 86.3 | 39.93 | -278.1 | -11.2 | 0.388 | -12.2 | 8.0 |

Sequence: MHW pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + PCC,250 kg/t – make-up to 0.33% cy +APAM,80g/t

Table 52: Sizing performance of emulsion without filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, °<br>Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.6 | 108.0 | 110.3 | 111.0 | 110.9 | 110.9 | 110.8 | 110.8 | 110.7 | 16.66 | -193.2 | -4.4 | 0.398 | -3.2 | 8.0 |
| 1.8 | 32.6 | 106.8 | 106.0 | 107.0 | 107.6 | 108.0 | 107.8 | 108.0 | 107.0 | 18.85 | -198.9 | -5.1 | 0.397 | -3.9 | 8.1 |
| 1.5 | 36.0 | 108.7 | 107.7 | 107.1 | 106.9 | 105.5 | 104.2 | 103.7 | 106.1 | 19.37 | -202.9 | -5.6 | 0.394 | -4.1 | 8.0 |
| 1.2 | 39.5 | 106.3 | 106.0 | 105.2 | 104.9 | 103.1 | 102.6 | 100.4 | 103.8 | 20.72 | -212.9 | -5.9 | 0.393 | -5.1 | 7.9 |
| 1.0 | 43.2 | 105.8 | 106.2 | 104.5 | 103.2 | 102.8 | 100.2 | 98.2 | 101.2 | 22.32 | -218.2 | -6.5 | 0.391 | -5.4 | 8.1 |
| 0.8 | 47.0 | 101.3 | 101.1 | 100.5 | 100.1 | 100.3 | 99.1 | 94.3 | 97.4 | 24.65 | -239.8 | -7.5 | 0.388 | -5.9 | 8.1 |

Sequence: BBS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA – make-up to 0.33% cy + CPAM, 200 g/t

Table 53: Sizing performance of emulsion with talc as filler

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 26.5 | 110.4 | 110.8 | 111.3 | 110.9 | 111.0 | 110.6 | 110.6 | 110.8 | 16.65 | -141.0 | -4.3 | 0.391 | -4.9 | 8.1 |
| 1.8 | 33.0 | 106.5 | 107.0 | 106.8 | 106.6 | 107.5 | 107.2 | 107.1 | 107.1 | 18.84 | .146.6 | -4.5 | 0.390 | -5.7 | 8.0 |
| 1.5 | 34.5 | 106.7 | 107.0 | 106.8 | 106.4 | 106.2 | 105.9 | 104.9 | 106.5 | 19.34 | -169.3 | -5.1 | 0.382 | -6.8 | 8.0 |
| 1.2 | 38.1 | 106.8 | 106.2 | 106.5 | 105.9 | 105.1 | 103.6 | 101.4 | 105.1 | 19.96 | -219.9 | -5.4 | 0.374 | -7.0 | 8.1 |
| 1.0 | 40.8 | 104.1 | 103.0 | 103.1 | 102.7 | 102.4 | 102.0 | 100.1 | 102.4 | 21.21 | -201.1 | -5.5 | 0.372 | -7.7 | 7.9 |
| 0.8 | 42.5 | 104.2 | 103.2 | 104.1 | 103.2 | 102.1 | 100.2 | 96.2 | 101.8 | 22.28 | -220.0 | -6.2 | 0.368 | -7.9 | 8.0 |

Sequence: BBS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + talc, 225 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 54: Sizing performance of emulsion with GCC-2 as filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | |
| 2.0 | 26.2 | 112.2 | 111.2 | 110.8 | 111.3 | 110.9 | 111.0 | 110.6 | 111.1 | 16.63 | -154.5 | -4.2 | 0.370 | -5.4 |
| 1.8 | 34.7 | 109.9 | 107.4 | 107.1 | 106.9 | 105.8 | 106.1 | 105.8 | 107.0 | 19.31 | -187.5 | -6.7 | 0.371 | -7.5 |
| 1.5 | 36.5 | 108.7 | 108.0 | 107.2 | 106.1 | 106.0 | 105.1 | 104.2 | 106.3 | 19.35 | -201.4 | -6.9 | 0.375 | -7.9 |
| 1.2 | 38.8 | 107.9 | 107.2 | 106.8 | 105.5 | 105.1 | 102.5 | 99.4 | 104.9 | 19.97 | 196.6 | -6.1 | 0.374 | -6.8 |
| 1.0 | 43.5 | 105.1 | 104.1 | 103.2 | 102.8 | 101.1 | 100.2 | 97.8 | 102.0 | 22.27 | -201.1 | -6.4 | 0.378 | 7.9 |
| 0.8 | 48.7 | 102.2 | 100.3 | 99.4 | 99.0 | 98.4 | 96.2 | 95.5 | 98.7 | 23.72 | -209.7 | -6.7 | 0.381 | -8.1 |

Sequence: BBS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + GCC, 250 kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 55: Sizing performance of emulsion with PCC-1 as filler

| ASA, kg/t | Cobb 60, g/m² | Contact angle, °<br>Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 26.3 | 113.4 | 112.8 | 112.4 | 111.5 | 111.9 | 111.5 | 111.9 | 112.2 | 15.97 | -151.2 | -4.1 | 0.377 | -5.1 | 8.1 |
| 1.8 | 28.9 | 111.7 | 110.8 | 111.1 | 110.9 | 109.8 | 109.1 | 108.8 | 110.3 | 16.67 | -153.0 | -4.6 | 0.379 | -5.5 | 8.1 |
| 1.5 | 32.7 | 106.6 | 107.2 | 106.9 | 106.8 | 106.2 | 107.2 | 106.9 | 106.8 | 18.87 | -173.4 | -5.7 | 0.382 | -5.9 | 7.9 |
| 1.2 | 34.8 | 107.2 | 106.4 | 105.9 | 106.1 | 104.2 | 104.2 | 104.0 | 105.4 | 19.71 | -194.3 | -6.6 | 0.387 | -7.5 | 8.0 |
| 1.0 | 51.1 | 103.1 | 101.1 | 98.4 | 98.0 | 97.4 | 95.2 | 93.5 | 98.1 | 23.75 | -199.2 | -6.9 | 0.391 | 7.7 | 8.1 |
| 0.8 | 69.9 | 98.3 | 95.2 | 93.1 | 92.3 | 91.4 | 90.0 | 84.5 | 91.8 | 28.08 | -211.3 | -7.2 | 0.395 | -9.2 | 8.0 |

Sequence:. BBS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA + PCC, 250 kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 56: Sizing performance of emulsion without filler

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.4 | 101.0 | 101.5 | 101.4 | 101.1 | 101.2 | 101.3 | 101.3 | 101.1 | 22.36 | -121.1 | -4.1 | 0.371 | -4.7 | 8.0 |
| 1.8 | 26.5 | 99.1 | 99.0 | 99.4 | 99.5 | 98.8 | 98.6 | 99.0 | 99.1 | 23.60 | -147.9 | -4.5 | 0.381 | -5.4 | 8.1 |
| 1.5 | 29.2 | 99.1 | 98.7 | 98.8 | 98.8 | 98.5 | 98.2 | 98.0 | 98.5 | 23.94 | -151.8 | -4.9 | 0.387 | -6.1 | 8.1 |
| 1.2 | 32.0 | 99.4 | 98.8 | 98.4 | 98.3 | 98.4 | 98.0 | 97.1 | 98.1 | 24.18 | -157.6 | -5.1 | 0.389 | -6.3 | 8.0 |
| 1.0 | 34.1 | 99.6 | 98.2 | 97.5 | 97.1 | 96.9 | 96.2 | 96.1 | 97.0 | 24.86 | -160.9 | -5.7 | 0.392 | -6.5 | 8.1 |
| 0.8 | 36.5 | 98.1 | 97.2 | 96.6 | 96.4 | 96.6 | 96.2 | 95.7 | 96.4 | 25.24 | -169.1 | -5.9 | 0.558 | -6.9 | 8.0 |
| 0.6 | 41.4 | 96.2 | 96.3 | 95.2 | 94.1 | 94.0 | 93.8 | 92.3 | 94.2 | 26.60 | -178.5 | -6.1 | 0.563 | -7.1 | 8.0 |

Sequence: BWS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA – make-up to 0.33% cy + CPAM, 200 g/t

Table 57: Sizing performance of emulsion with Talc

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, °<br>Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, µeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 24.1 | 101.5 | 101.8 | 101.8 | 101.9 | 102.1 | 101.9 | 101.9 | 101.8 | 21.94 | -179.4 | -5.6 | 0.511 | -4.8 | 8.0 |
| 1.8 | 26.0 | 99.5 | 99.5 | 99.4 | 99.3 | 99.1 | 98.9 | 99.2 | 99.6 | 23.30 | -183.1 | -6.8 | 0.529 | -5.1 | 8.1 |
| 1.5 | 28.9 | 99.6 | 99.1 | 99.0 | 98.9 | 98.8 | 98.5 | 98.2 | 98.8 | 23.76 | -187.3 | -7.3 | 0.548 | -5.9 | 8.0 |
| 1.2 | 30.6 | 99.4 | 98.6 | 99.0 | 98.9 | 98.5 | 98.5 | 97.8 | 98.9 | 23.70 | -191.6 | -7.8 | 0.555 | -6.4 | 8.0 |
| 1.0 | 34.0 | 99.0 | 99.2 | 98.0 | 97.8 | 97.2 | 96.5 | 95.8 | 97.1 | 24.80 | -208.2 | -8.1 | 0.559 | -6.8 | 8.0 |
| 0.8 | 36.4 | 98.8 | 98.1 | 97.1 | 96.3 | 96.5 | 96.1 | 95.8 | 96.4 | 25.24 | -217.1 | -8.6 | 0.563 | -7.2 | 8.1 |
| 0.6 | 39.5 | 97.1 | 96.8 | 96.0 | 95.2 | 94.2 | 93.8 | 93.5 | 94.8 | 26.24 | -212.2 | -9.1 | 0.569 | -7.5 | 8.1 |

Sequence: BWS pulp+ Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ talc, 190kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 58: Sizing performance of emulsion with GCC-2

| ASA, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.1 | 101.4 | 101.4 | 101.4 | 101.3 | 101.1 | 101.9 | 100.8 | 101.2 | 22.32 | -222.2 | -7.8 | 0.538 | -5.1 | 8.1 |
| 1.8 | 26.0 | 99.6 | 99.6 | 99.3 | 99.2 | 99.4 | 98.6 | 99.5 | 99.9 | 23.12 | -221.4 | -8.2 | 0.560 | -5.3 | 8.1 |
| 1.5 | 28.1 | 99.8 | 99.8 | 99.8 | 99.1 | 99.0 | 98.9 | 98.6 | 99.2 | 23.52 | 215.2 | -9.0 | 0.555 | -5.7 | 8.1 |
| 1.2 | 29.4 | 99.2 | 99.0 | 98.6 | 98.2 | 98.3 | 98.1 | 97.2 | 98.1 | 24.18 | -231.4 | -9.5 | 0.542 | -6.3 | 8.0 |
| 1.0 | 33.8 | 99.6 | 99.1 | 98.5 | 98.0 | 97.3 | 96.1 | 95.2 | 97.6 | 24.50 | -183.2 | -9.8 | 0.531 | -6.5 | 8.1 |
| 0.8 | 42.6 | 95.4 | 93.6 | 93.4 | 93.4 | 93.2 | 93.1 | 92.3 | 93.3 | 27.20 | -189.4 | -10.2 | 0.537 | -6.9 | 8.0 |
| 0.6 | 57.3 | 83.1 | 81.1 | 78.0 | 85.4 | 73.8 | 67.4 | 65.0 | 74.4 | 39.00 | -191.8 | -10.4 | 0.566 | -7.1 | 8.1 |

Sequence: BWS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ GCC, 200kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 59: Sizing performance of emulsion with PCC-1

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 23.4 | 102.9 | 102.5 | 102.5 | 102.4 | 102.6 | 102.7 | 102.6 | 102.3 | 21.64 | -173.8 | -8.6 | 0.366 | -4.6 | 8.1 |
| 1.8 | 24.1 | 102.1 | 101.9 | 101.9 | 102.0 | 101.8 | 101.5 | 101.7 | 101.8 | 21.94 | -178.9 | -9.0 | 0.371 | -4.8 | 8.0 |
| 1.5 | 24.9 | 100.5 | 100.5 | 100.4 | 100.2 | 100.0 | 100.7 | 100.2 | 100.4 | 22.80 | -189.1 | -9.4 | 0.379 | -5.6 | 8.1 |
| 1.2 | 28.8 | 99.6 | 99.5 | 98.2 | 98.1 | 98.0 | 97.8 | 97.9 | 98.3 | 24.06 | -198.2 | -9.8 | 0.382 | -5.9 | 8.0 |
| 1.0 | 34.6 | 99.1 | 98.8 | 98.1 | 97.8 | 971 | 95.3 | 94.5 | 96.7 | 25.04 | -201.2 | -10.2 | 0.399 | -6.4 | 8.0 |
| 0.8 | 47.9 | 94.6 | 93.4 | 92.8 | 91.6 | 91.0 | 90.5 | 89.9 | 91.1 | 28.55 | -211.8 | -10.6 | 0.423 | -7.1 | 8.1 |
| 0.6 | 68.9 | 80.8 | 76.8 | 74.9 | 68.9 | 57.4 | 47.0 | 72.3 | 61.7 | 46.12 | -237.4 | -11.1 | 0.436 | -7.6 | 8.0 |

Sequence: BWS pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ PCC, 190kg/t – make-up to 0.33% cy + APAM, 80 g/t

Table 60: Sizing performance of emulsion without filler

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° |  |  |  |  |  |  |  | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Time interval, s |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. |  |  |  |  |  |  |
| 2.0 | 22.1 | 115.4 | 115.2 | 115.3 | 115.6 | 115.6 | 115.7 | 115.6 | 115.8 | 14.07 | -119.2 | -9.3 | 0.360 | -11.1 | 8.0 |
| 1.8 | 23.1 | 114.6 | 114.0 | 114.4 | 114.3 | 114.2 | 114.1 | 114.0 | 114.0 | 14.71 | -143.2 | -12.9 | 0.363 | -11.6 | 8.1 |
| 1.5 | 27.1 | 111.0 | 111.0 | 111.4 | 111.3 | 111.2 | 111.1 | 111.0 | 111.1 | 16.85 | -159.5 | -13.3 | 0.365 | -12.3 | 8.0 |
| 1.2 | 35.7 | 109.2 | 109.0 | 108.9 | 109.3 | 109.1 | 108.6 | 108.4 | 108.9 | 16.34 | -190.4 | -14.3 | 0.369 | -16.8 | 8.1 |
| 1.0 | 49.8 | 105.2 | 104.1 | 103.9 | 103.4 | 102.1 | 101.8 | 100.9 | 103.1 | 21.15 | -194.9 | -15.8 | 0.379 | -17.2 | 8.1 |
| 0.8 | 77.5 | 91.0 | 91.7 | 93.2 | 90.9 | 86.9 | 81.2 | 72.8 | 86.9 | 31.16 | -199.3 | -16.1 | 0.382 | -18.1 | 8.1 |

Sequence: BRC pulp + Cartaflex  IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA – make-up to 0.33% cy + CPAM, 200 g/t

Table 61: Sizing performance of emulsion with Talc

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Contact angle, ° Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 22.7 | 115.9 | 115.9 | 116.1 | 116.0 | 115.8 | 115.8 | 116.1 | 116.0 | 13.95 | -114.1 | -9.4 | 0.366 | -15.7 | 8.1 |
| 1.8 | 24.0 | 115.0 | 115.1 | 114.9 | 114.8 | 114.8 | 114.7 | 114.4 | 114.8 | 14.22 | -169.9 | -9.6 | 0.367 | -16.9 | 8.1 |
| 1.5 | 25.2 | 111.9 | 112.0 | 111.9 | 111.5 | 111.5 | 111.6 | 111.7 | 111.7 | 16.49 | -174.8 | -11.4 | 0.373 | -18.9 | 8.0 |
| 1.2 | 31.8 | 109.9 | 110.1 | 110.9 | 110.3 | 110.2 | 109.8 | 109.3 | 110.1 | 15.50 | -193.4 | -11.7 | 0.376 | -20.8 | 8.1 |
| 1.0 | 38.5 | 106.2 | 106.1 | 105.8 | 105.1 | 103.3 | 102.2 | 101.9 | 104.4 | 20.38 | -204.8 | 12.1 | 0.379 | -24.5 | 8.0 |
| 0.8 | 70.0 | 94.5 | 93.9 | 93.2 | 92.8 | 88.9 | 82.2 | 76.4 | 88.8 | 29.99 | -207.0 | -14.1 | 0.380 | -27.4 | 8.0 |

Sequence: BRC pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ talc, 185kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 62: Sizing performance of emulsion with GCC-2

| ASA, kg/t | Cobb$_{60}$, g/m$^2$ | Contact angle, $^o$ | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time interval, s | | | | | | | | | | | | | |
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 24.6 | 114.8 | 114.4 | 114.1 | 113.8 | 114.1 | 114.4 | 114.8 | 114.3 | 14.94 | -142.7 | -9.9 | 0.383 | -16.2 | 8.1 |
| 1.8 | 26.9 | 113.6 | 113.2 | 113.1 | 113.0 | 113.1 | 112.7 | 112.4 | 113.0 | 15.28 | -153.7 | -10.0 | 0.390 | -17.7 | 8.0 |
| 1.5 | 32.3 | 110.8 | 110.2 | 110.1 | 109.5 | 109.1 | 108.6 | 107.7 | 109.4 | 17.85 | -167.1 | -12.7 | 0.394 | -20.4 | 8.0 |
| 1.2 | 40.7 | 109.9 | 108.7 | 108.1 | 107.6 | 107.1 | 106.9 | 106.2 | 107.8 | 16.88 | -189.3 | -13.4 | 0.399 | -22.8 | 8.1 |
| 1.0 | 51.8 | 104.9 | 104.5 | 104.1 | 103.9 | 103.3 | 101.1 | 100.9 | 103.2 | 21.07 | -208.2 | -14.2 | 0.408 | -24.8 | 8.0 |
| 0.8 | 76.3 | 93.4 | 93.1 | 91.2 | 90.4 | 85.4 | 80.1 | 75.2 | 88.8 | 30.99 | -215.3 | -15.1 | 0.412 | -25.3 | 8.1 |

Sequence: BRC pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ GCC, 190kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 63: Sizing performance of emulsion with PCC

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Contact angle, $^o$ Time interval, s | | | | | | | | Surface energy, mN/m | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 40 | 50 | 60 | Avg. | | | | | | |
| 2.0 | 25.4 | 114.8 | 114.0 | 113.3 | 113.2 | 113.0. | 113.2 | 113.2 | 113.5 | 15.71 | -199.4 | -9.3 | 0.385 | -24.3 | 8.1 |
| 1.8 | 33.4 | 110.9 | 110.4 | 110.0 | 109.1 | 109.0 | 108.8 | 107.1 | 109.3 | 17.91 | -201.8 | -9.5 | 0.392 | -26.8 | 8.1 |
| 1.5 | 41.2 | 109.1 | 108.4 | 108.0 | 107.8 | 107.4 | 107.1 | 106.4 | 107.6 | 17.00 | -203.7 | -9.9 | 0.395 | -27.2 | 8.1 |
| 1.2 | 51.2 | 105.2 | 104.2 | 104.0 | 103.4 | 103.0 | 101.5 | 100.0 | 103.0 | 21.19 | -210.6 | -10.8 | 0.398 | -29.2 | 8.1 |
| 1.0 | 62.9 | 95.2 | 93.1 | 92.1 | 90.2 | 90.1 | 89.2 | 86.2 | 90.8 | 28.68 | -218.4 | -11.5 | 0.401 | -32.1 | 8.0 |
| 0.8 | 83.7 | 85.8 | 81.8 | 76.9 | 70.8 | 64.4 | 51.0 | 37.2 | 66.8 | 43.03 | -221.4 | -11.7 | 0.407 | -31.6 | 8.1 |

Sequence: BRC pulp + Cartaflex IGS, 1kg/t + PAC,4 kg/t + CS, 3 kg/t + ASA+ PCC, 220kg/t – make-up to 0.33% cy + CPAM, 200 g/t

Table 64: Reacted and unreacted AKD in different commercial paper samples

| Sample | Unreacted Ketene | | | | Reacted Ketene | | | | Total AKD (mg/g of paper) |
|---|---|---|---|---|---|---|---|---|---|
| | Internal Standard | | Ketene / g of paper | | Internal Standard | | Ketene / g of paper | | |
| | Weight (mg) | Peak area | Weight (mg) | Peak area | Weight (mg) | Peak area | Weight (mg) | Peak area | |
| Paper sample-1 | 0.5 | 703872 | 0.4270 | 180905 | 0.5 | 703872 | 0.0864 | 34203 | 0.5390 |
| Paper sample-2 | 0.5 | 866271 | 0.5536 | 269723 | 0.5 | 697382 | 0.1340 | 52558 | 0.7219 |
| Sappi Art 130 | 0.5 | 763278 | 0.3067 | 131663 | 0.5 | 762104 | 0.0817 | 35019 | 0.4078 |

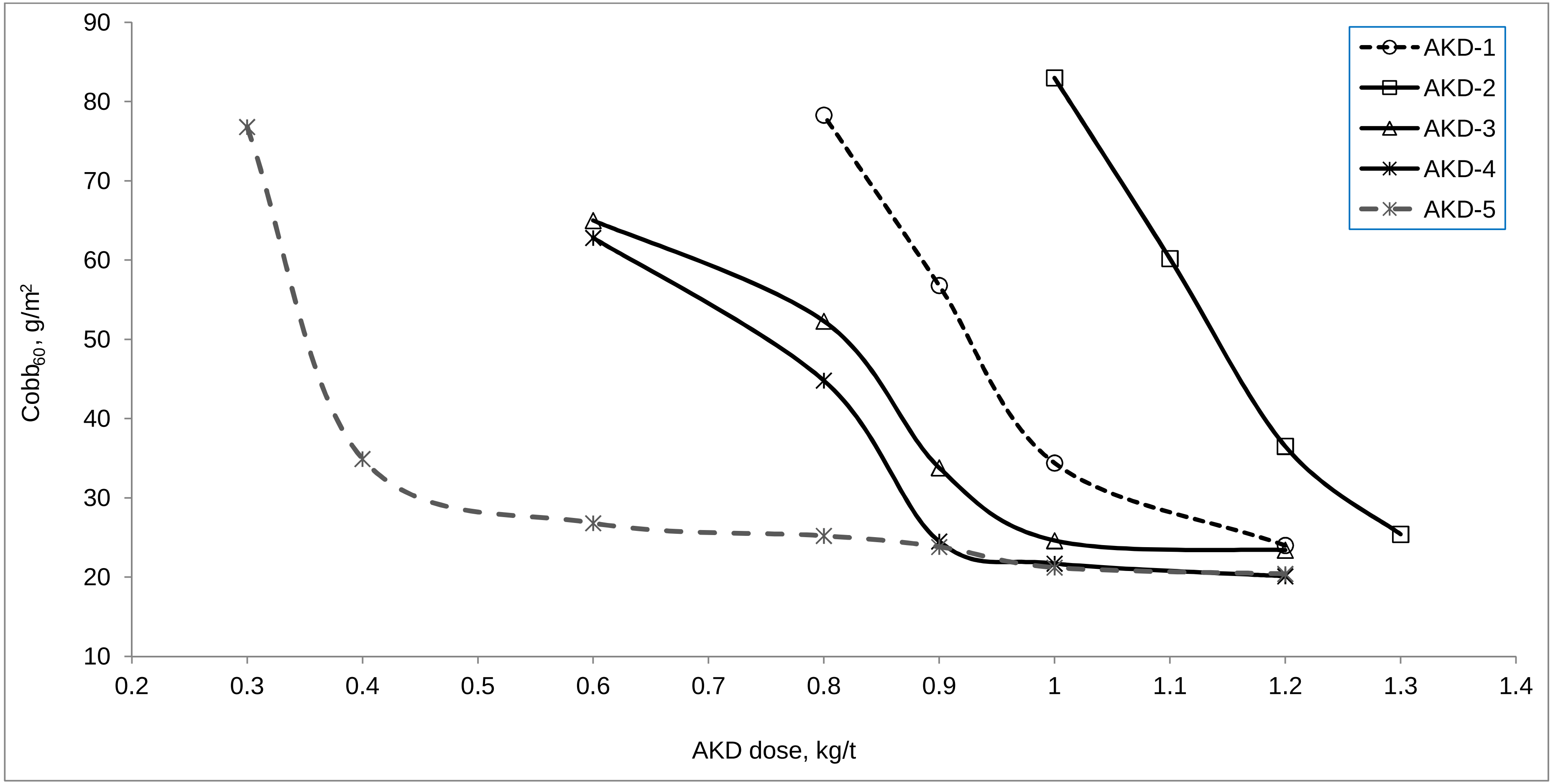


Figure 1: Comparison of $Cobb_{60}$ of paper prepared from MHB pulp with different AKD emulsions

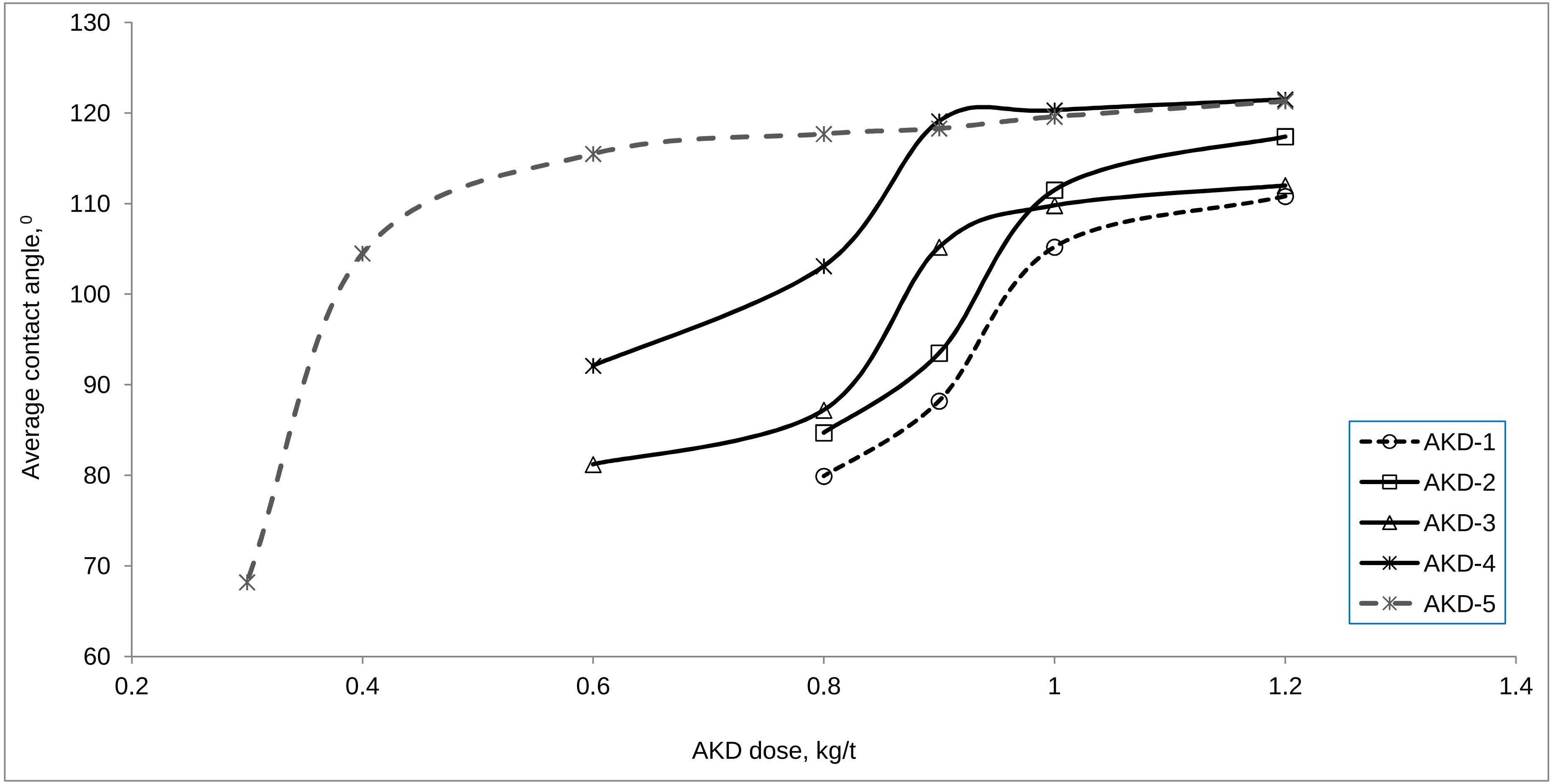


Figure 2: Comparison of contact angle of paper prepared from MHB pulp with different AKD emulsions

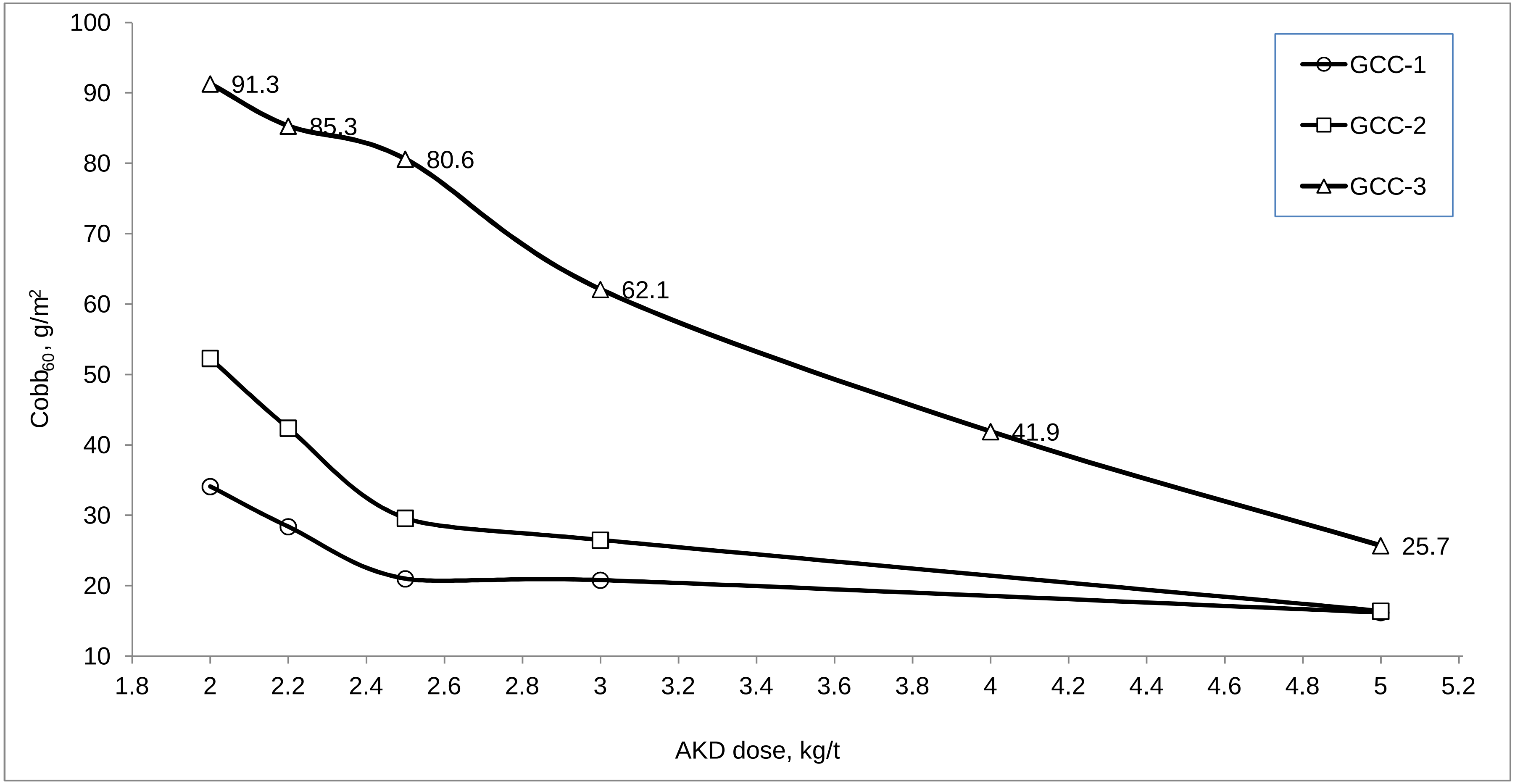


Figure 3: Effect of GCC filler on $Cobb_{60}$ value of paper made with MHW pulp in AKD sizing

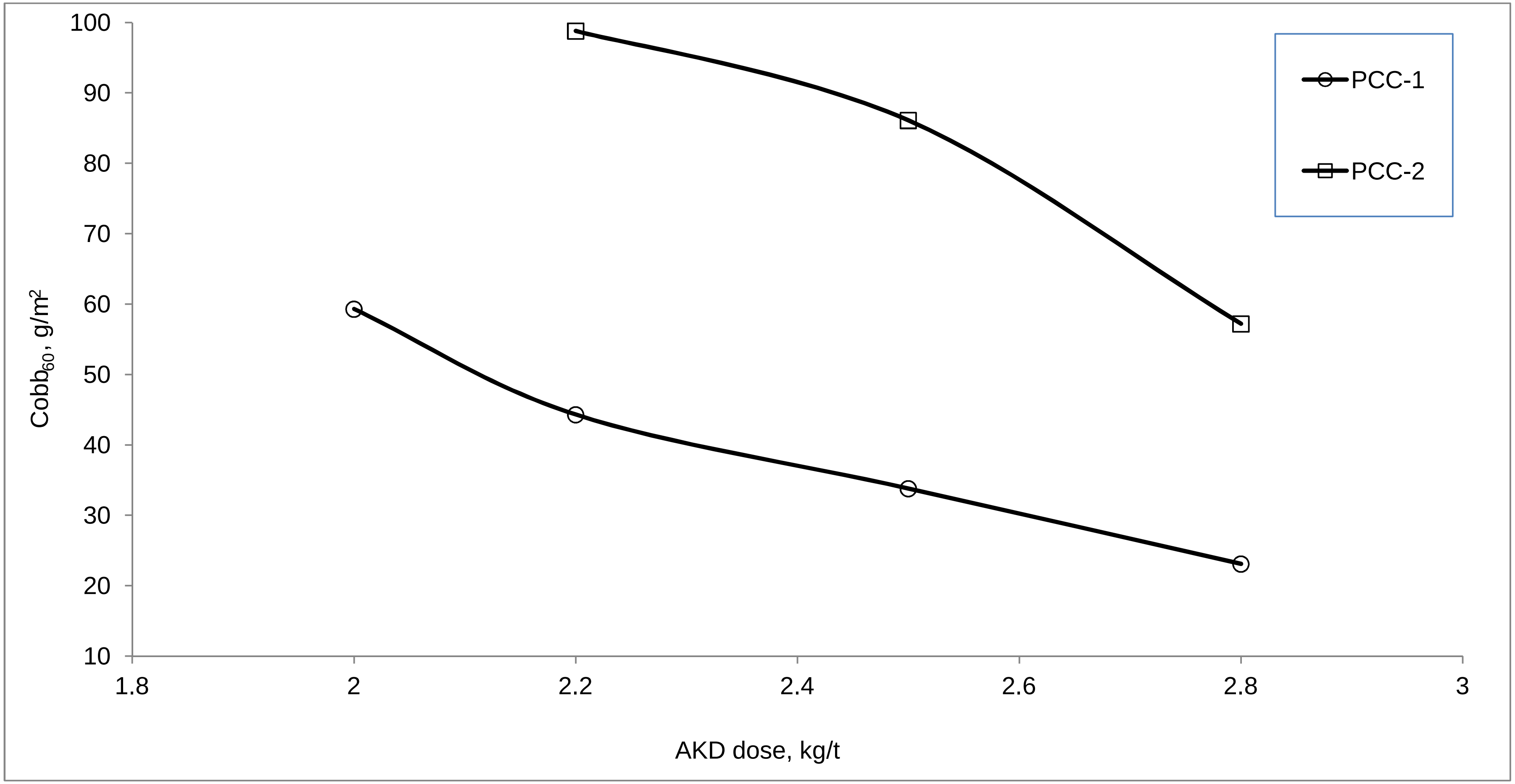


Figure 4: Effect of PCC filler on $Cobb_{60}$ value of paper made with MHW pulp in AKD sizing

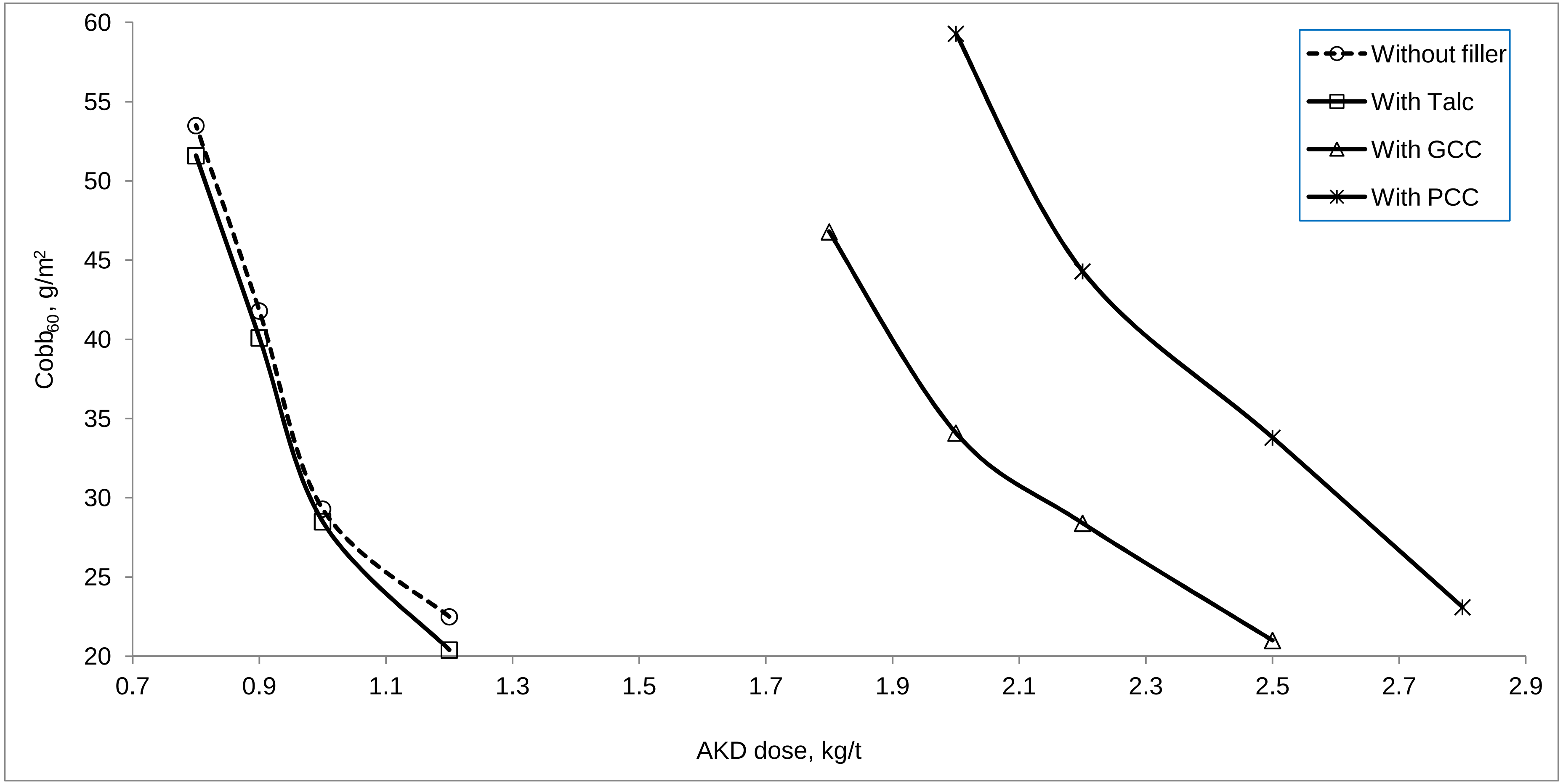


Figure 5: Effect of filler on $Cobb_{60}$ value with MHW pulp in AKD sizing

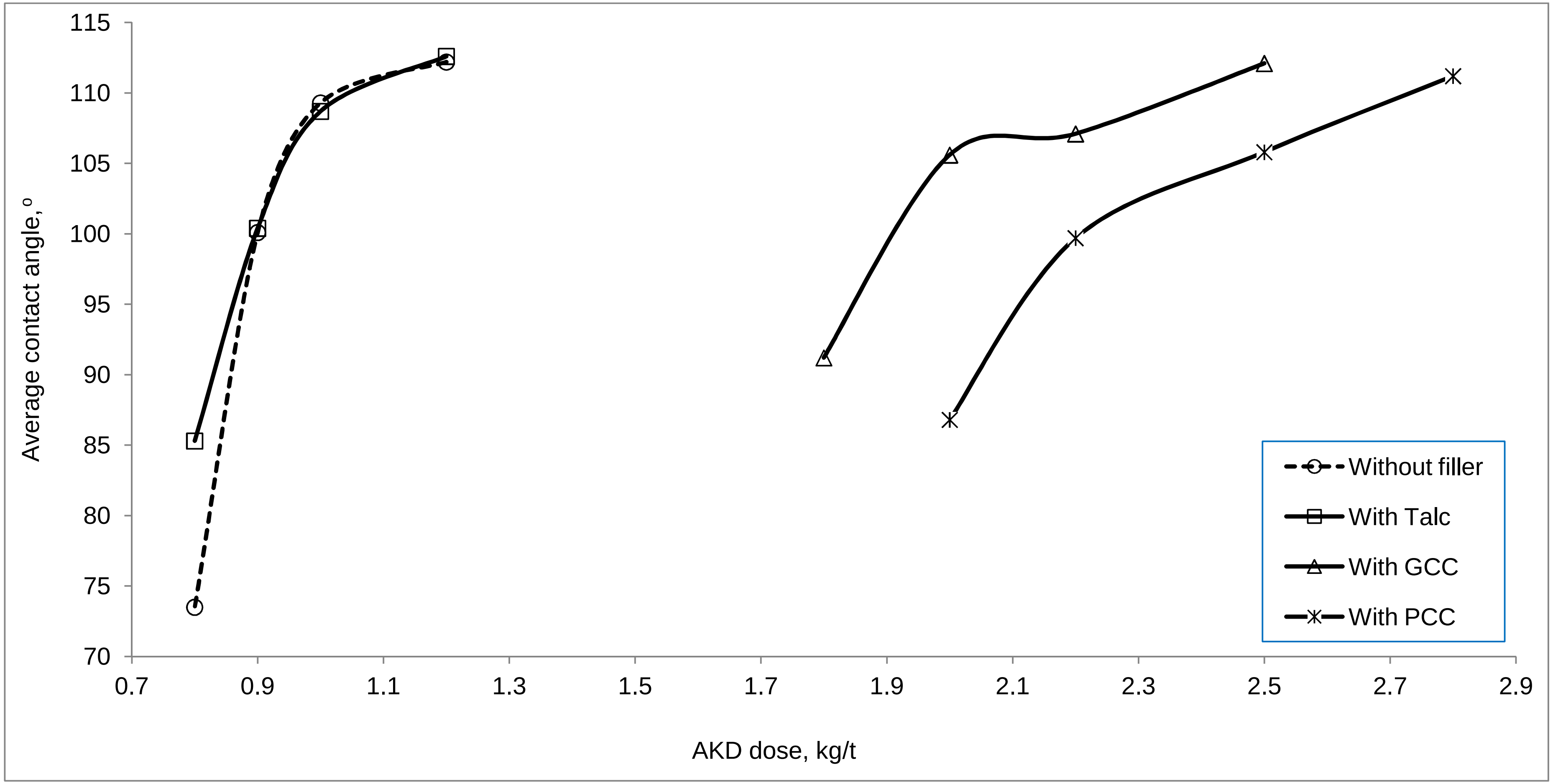


Figure 6: Effect of filler on contact angle with MHW pulp in AKD sizing

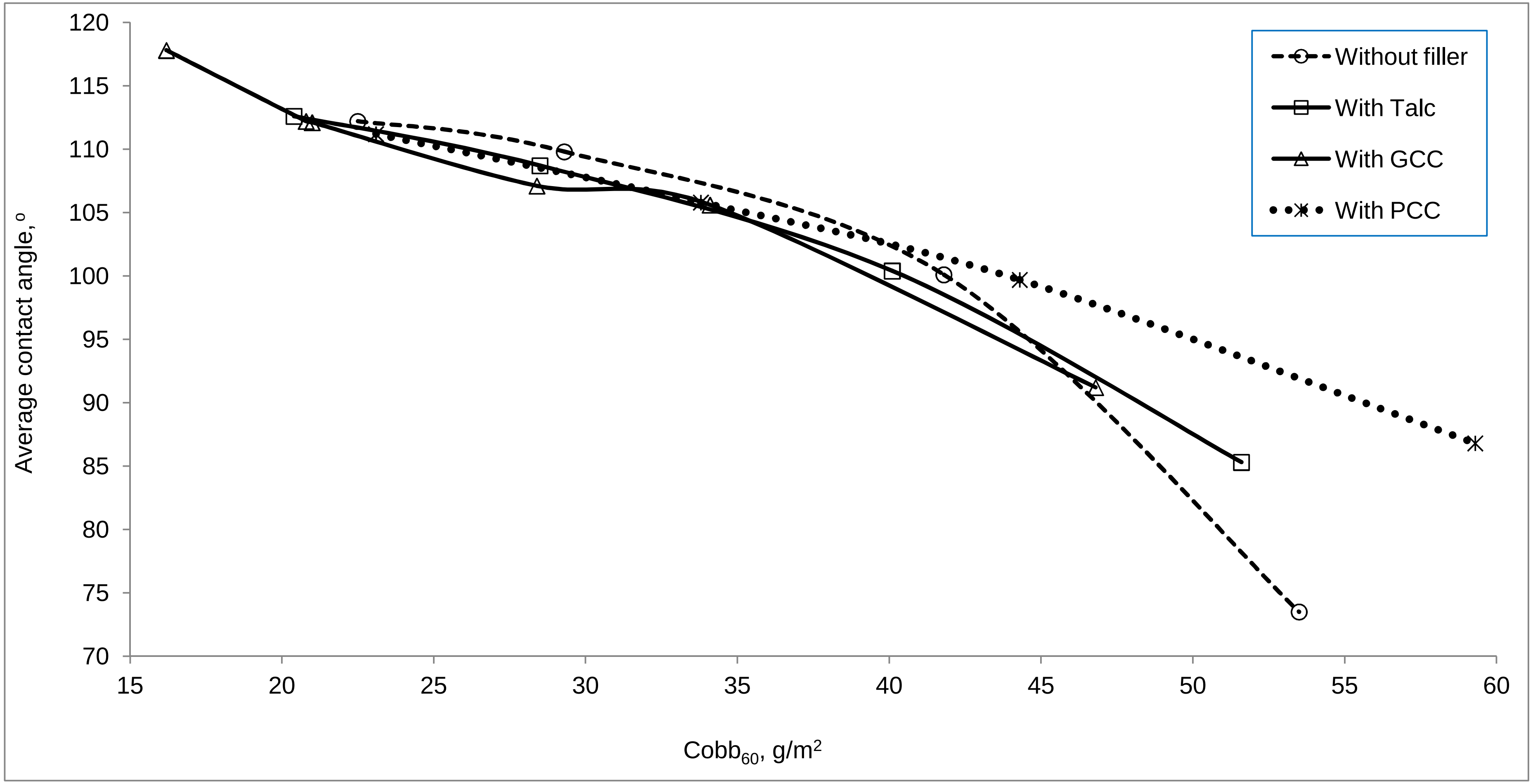


Figure 7: $Cobb_{60}$ vs. contact angle relationship for MHW pulp in AKD sizing

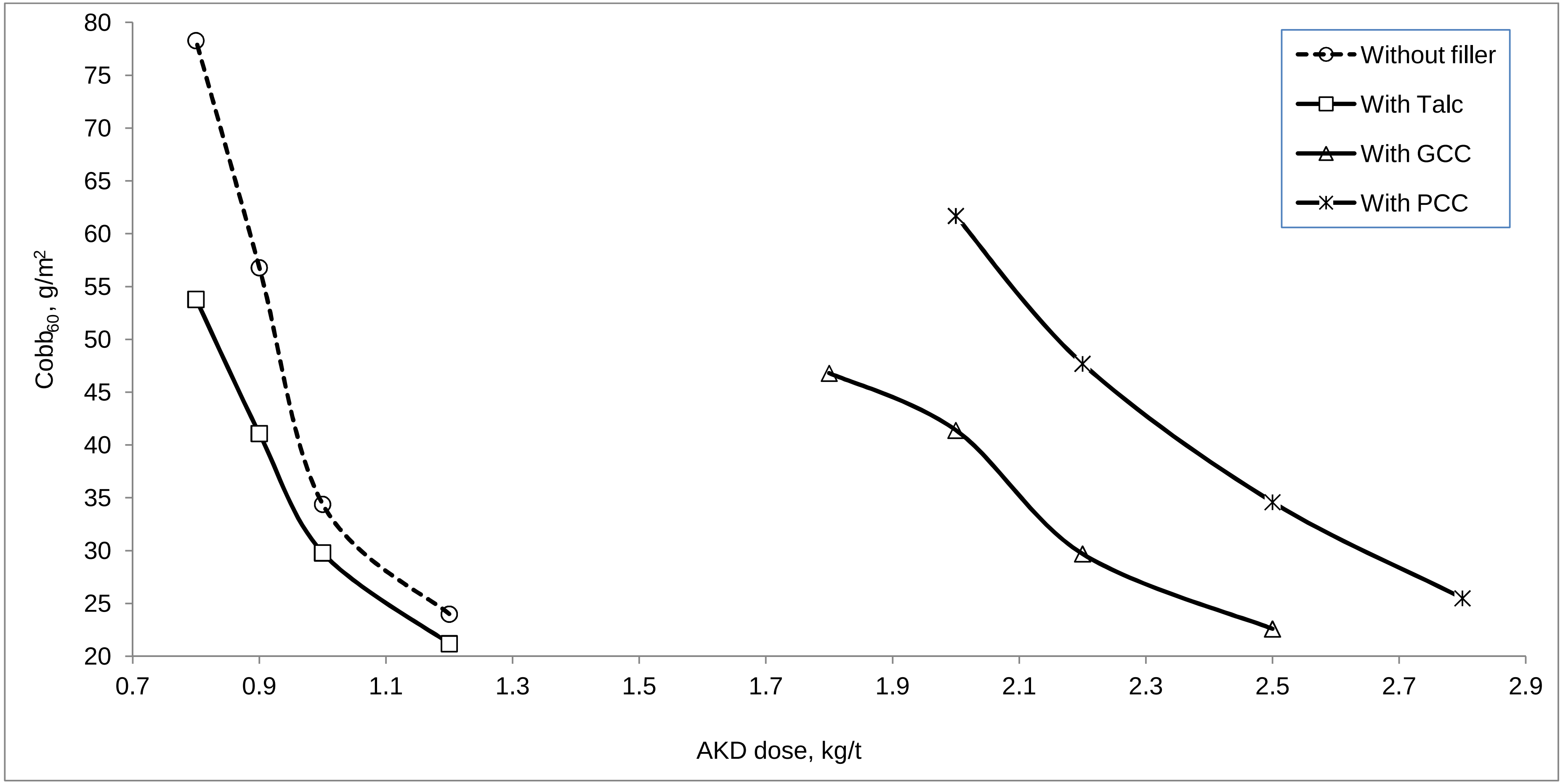


Figure 8: Effect of filler on $Cobb_{60}$ value with MHB pulp in AKD sizing

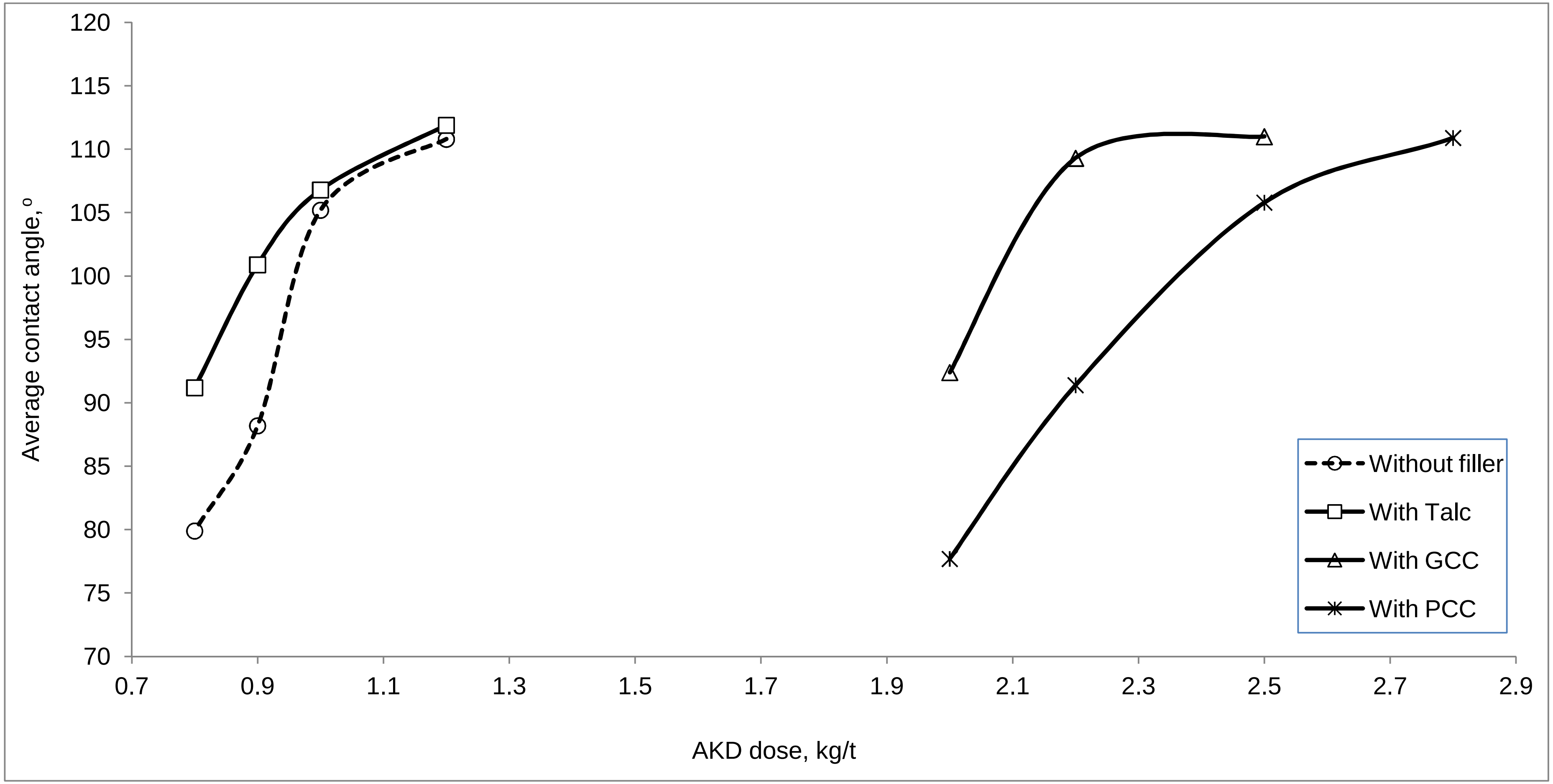


Figure 9: Effect of filler on contact angle with MHB pulp in AKD sizing

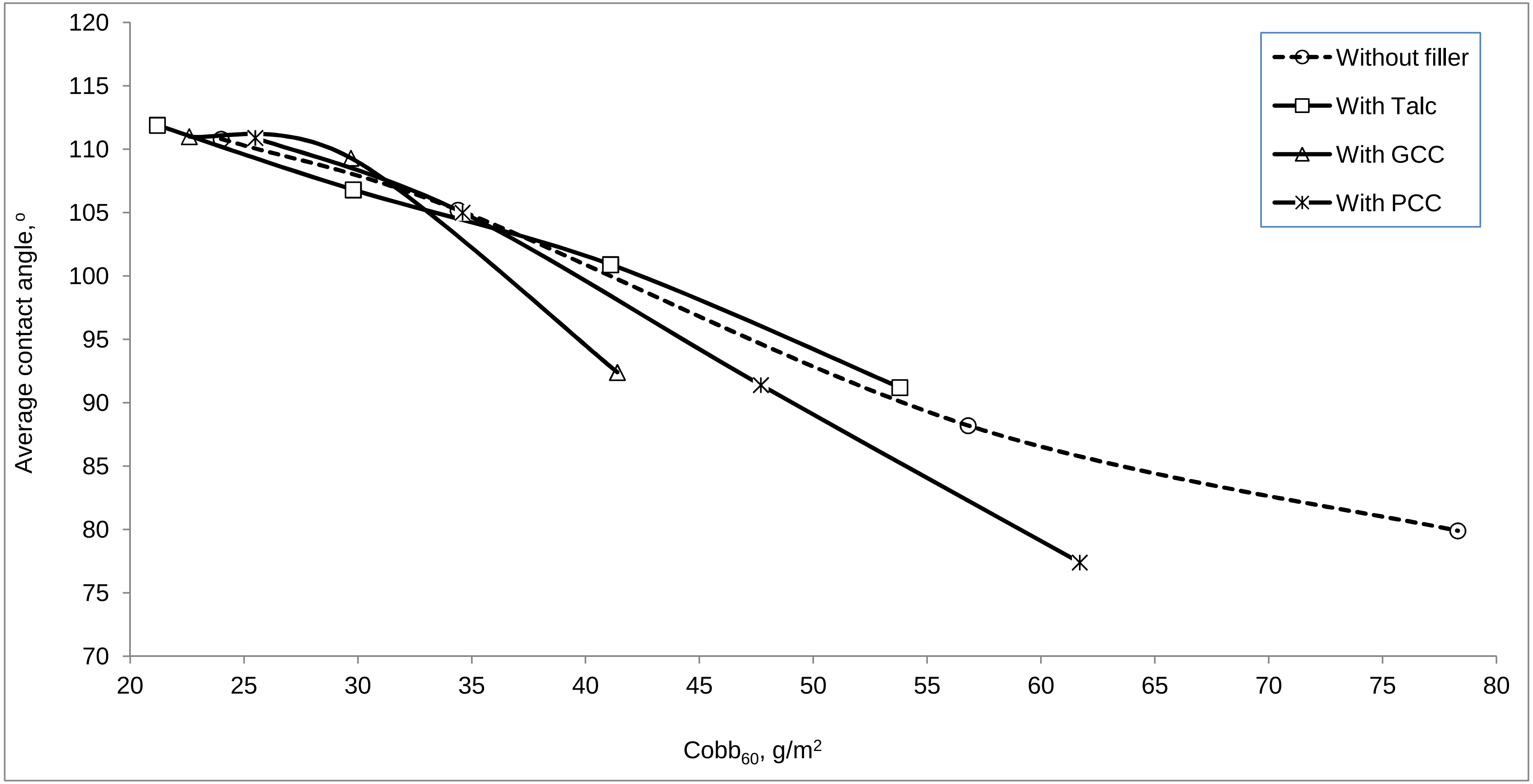


Figure 10: $Cobb_{60}$ vs. contact angle relationship for MHB pulp in AKD sizing

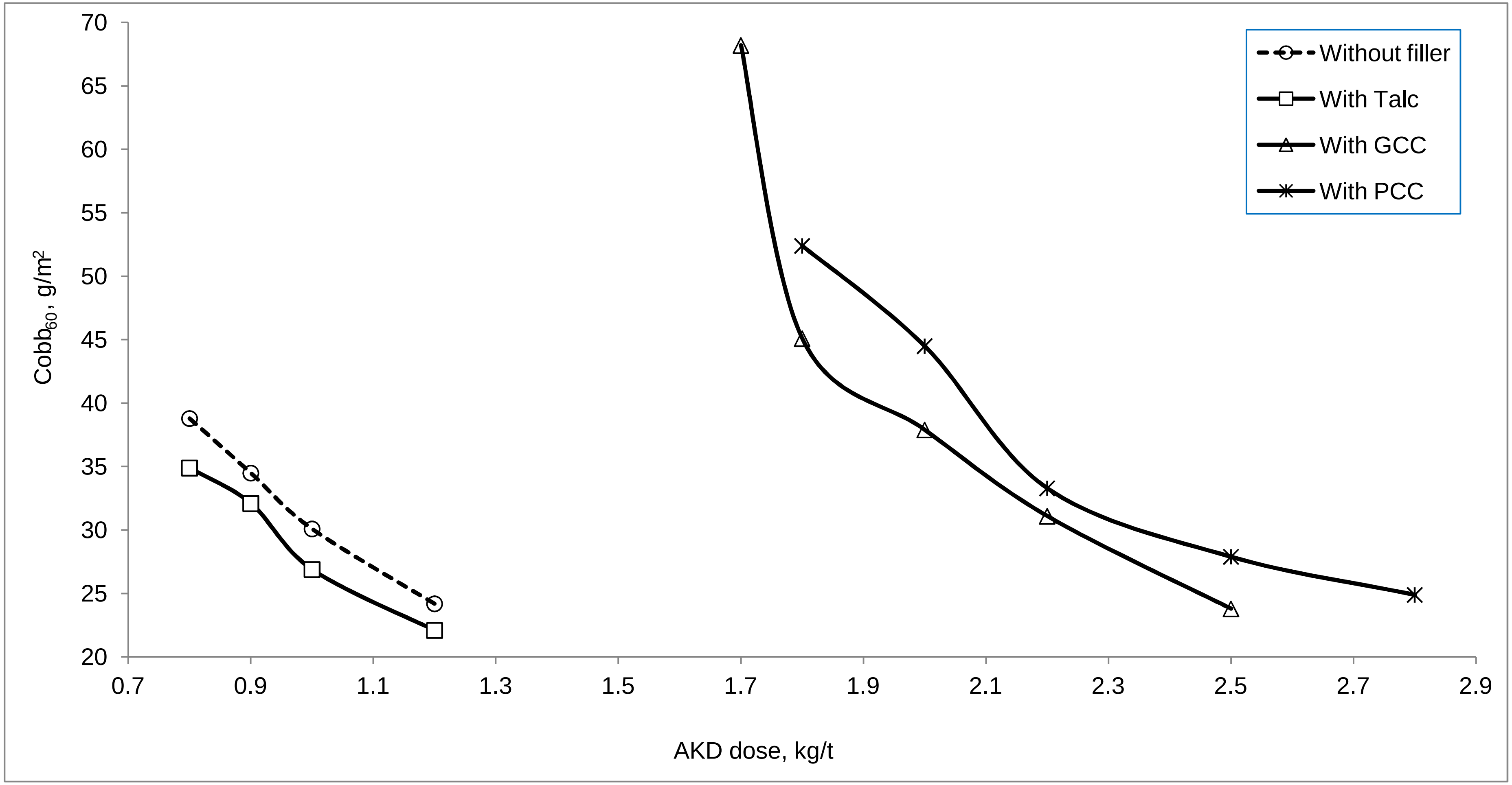


Figure 11: Effect of filler on $Cobb_{60}$ value with BBS pulp in AKD sizing

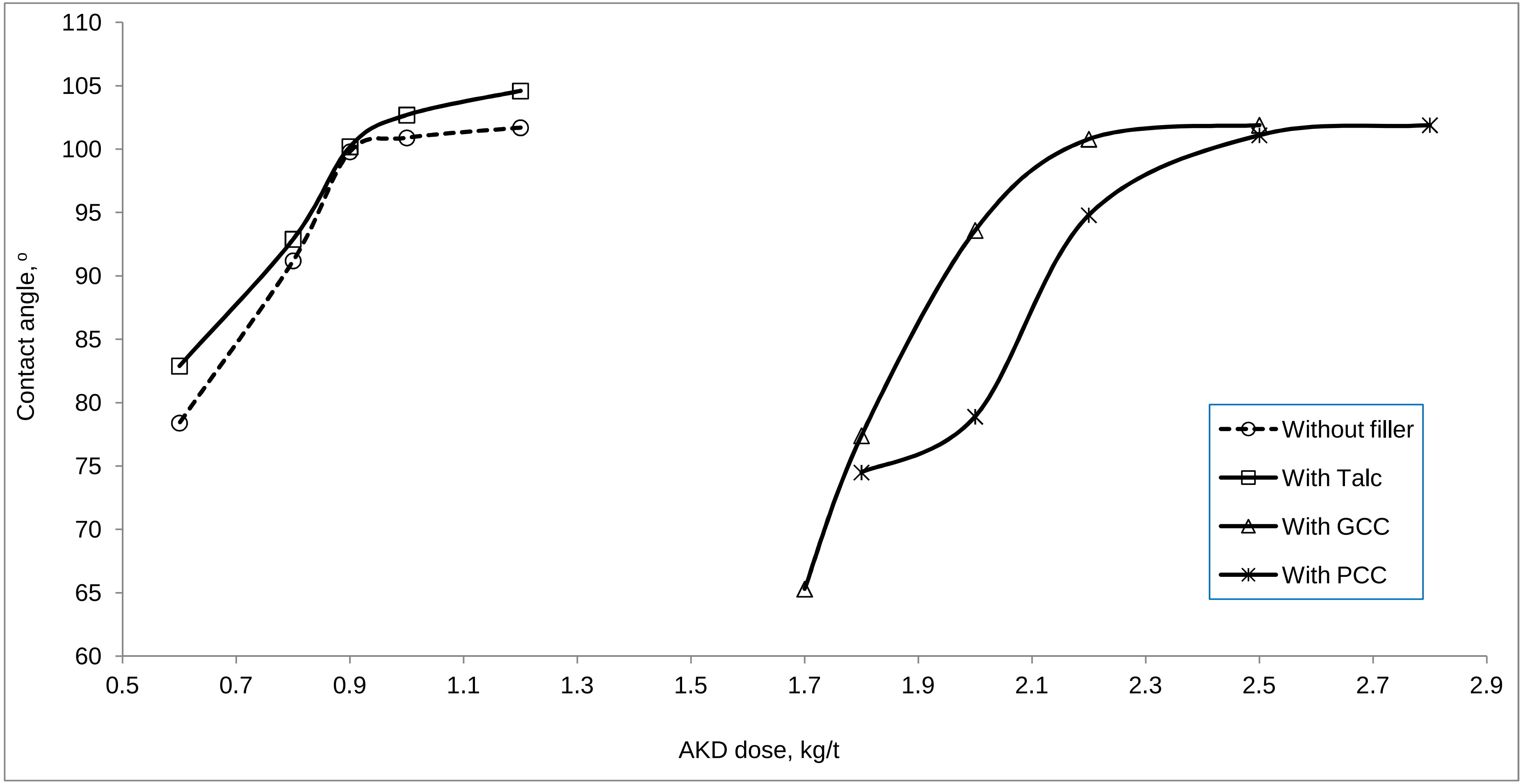


Figure 12: Effect of filler on contact angle with BBS pulp in AKD sizing

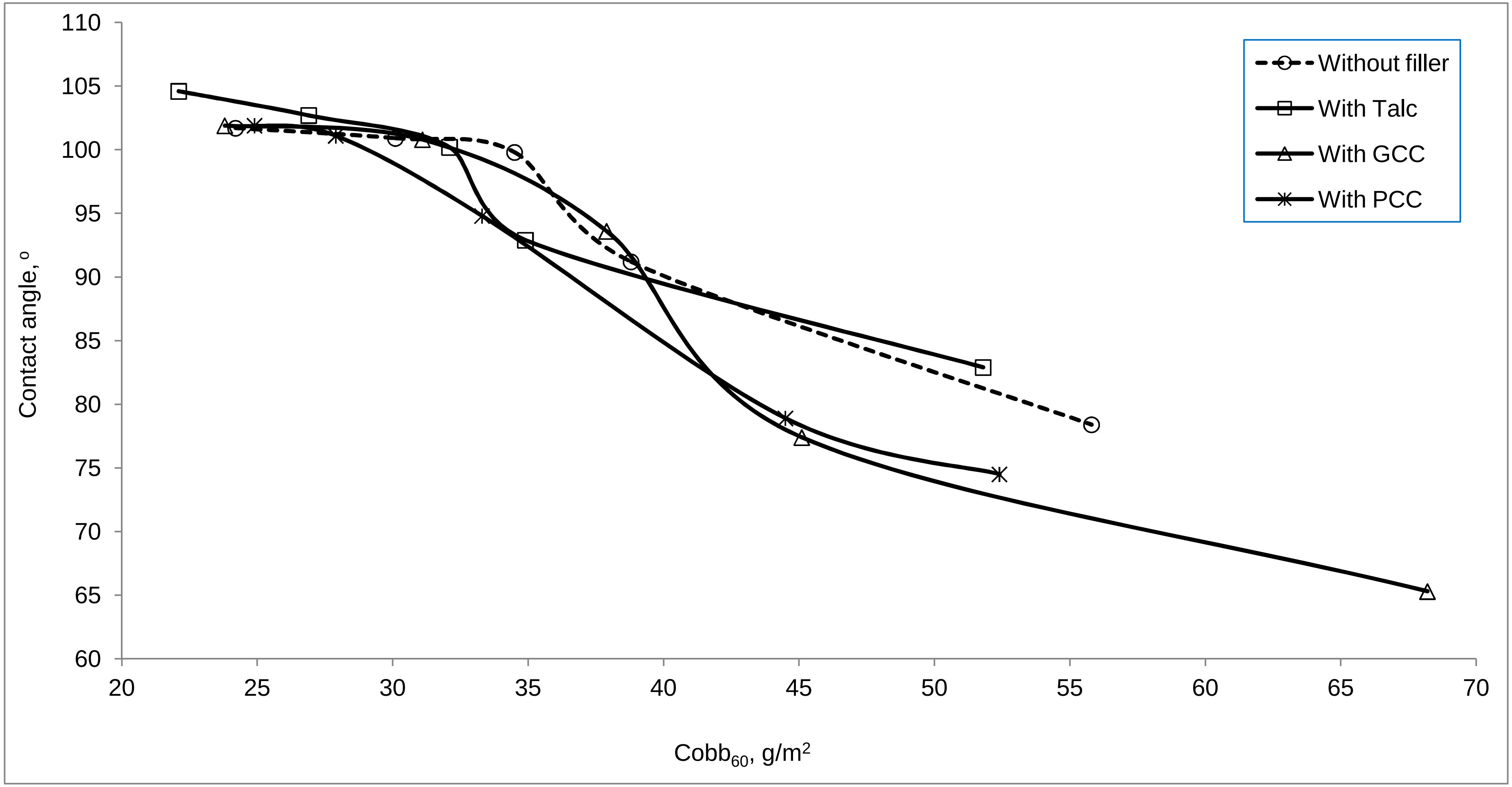


Figure 13: $Cobb_{60}$ vs. contact angle relationship for BBS pulp in AKD sizing

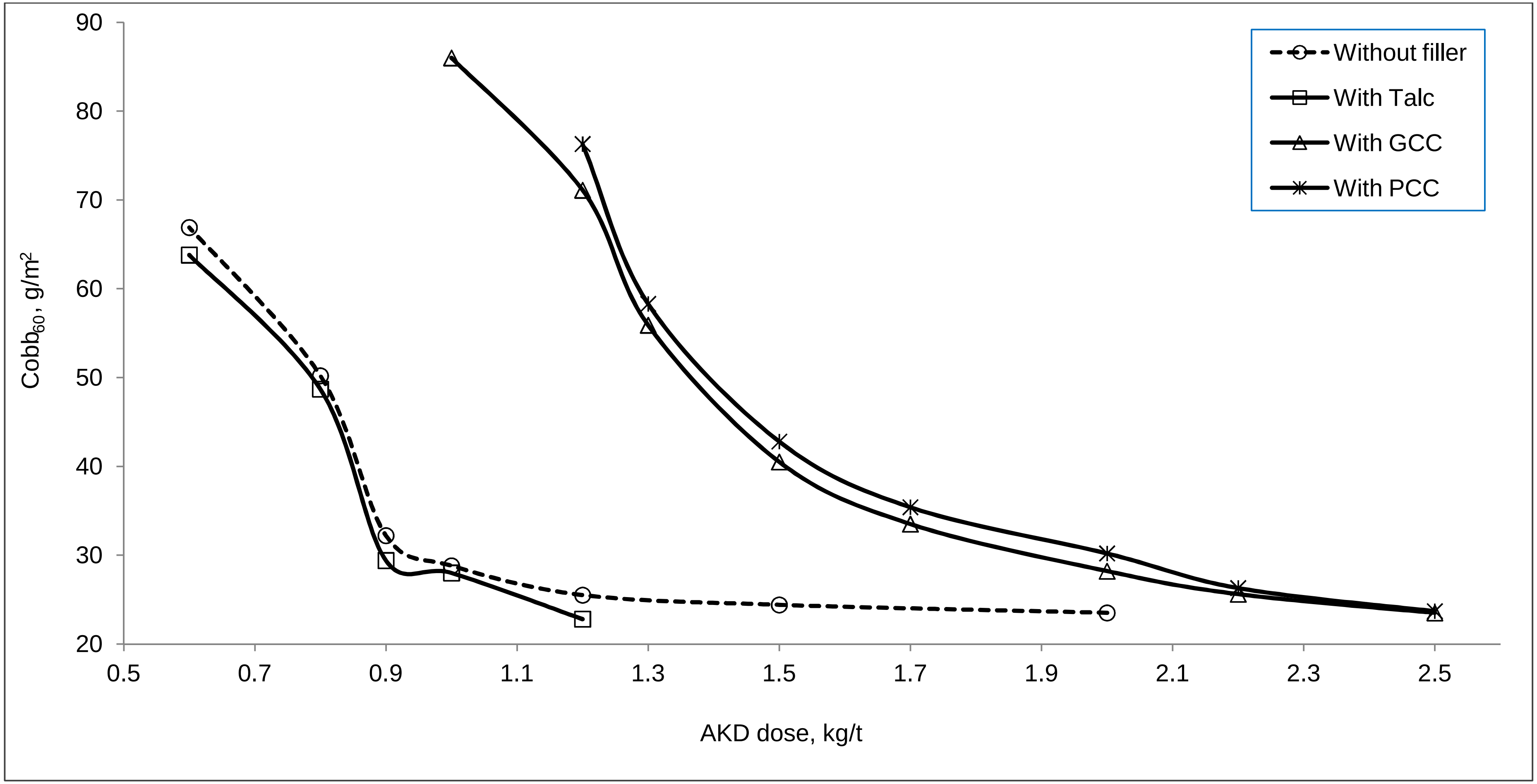


Figure 14: Effect of filler on $Cobb_{60}$ value with BWS pulp in AKD sizing

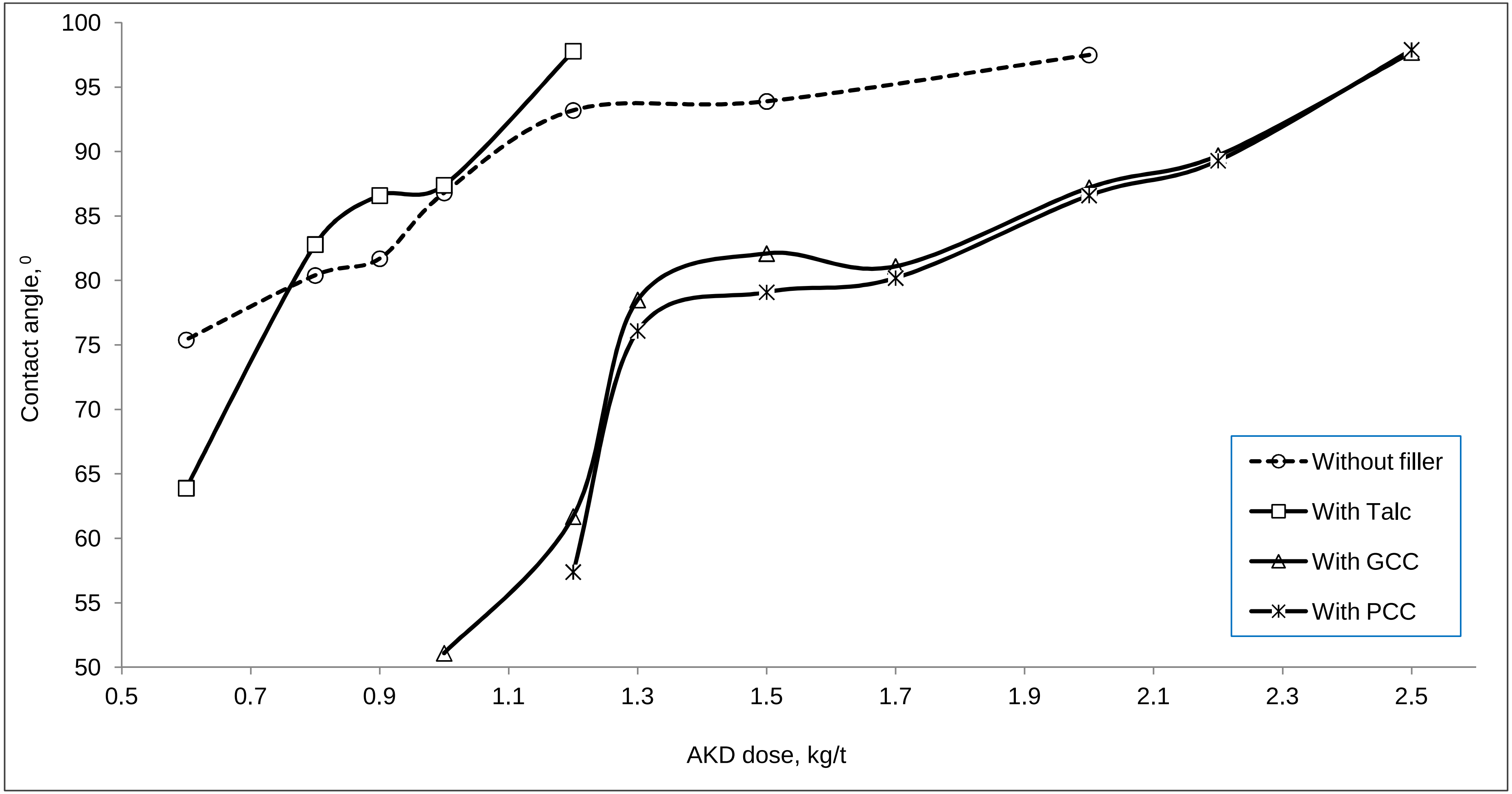


Figure 15: Effect of filler on contact angle with BWS pulp in AKD sizing

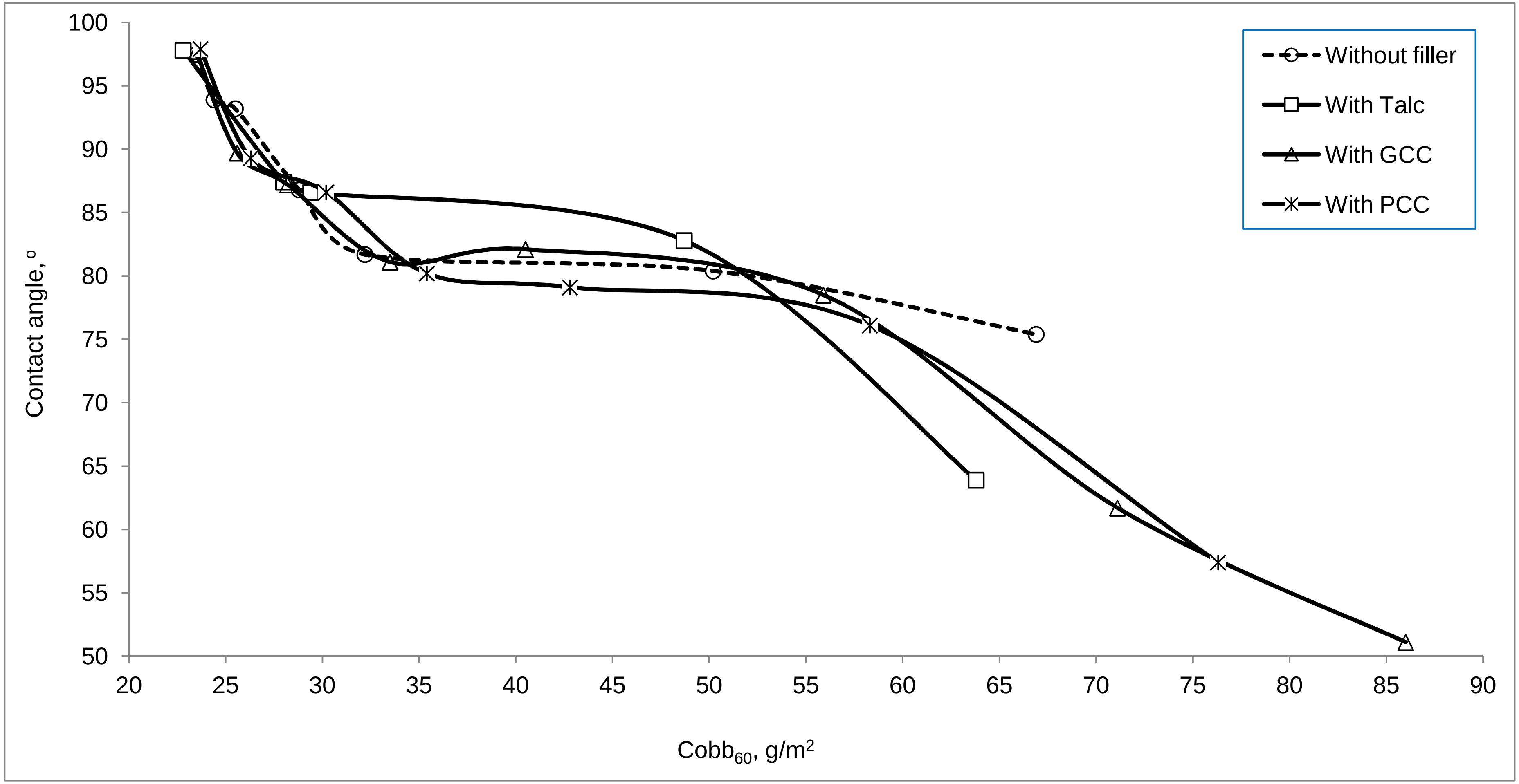


Figure 16: $Cobb_{60}$ vs. contact angle relationship for BWS pulp in AKD sizing

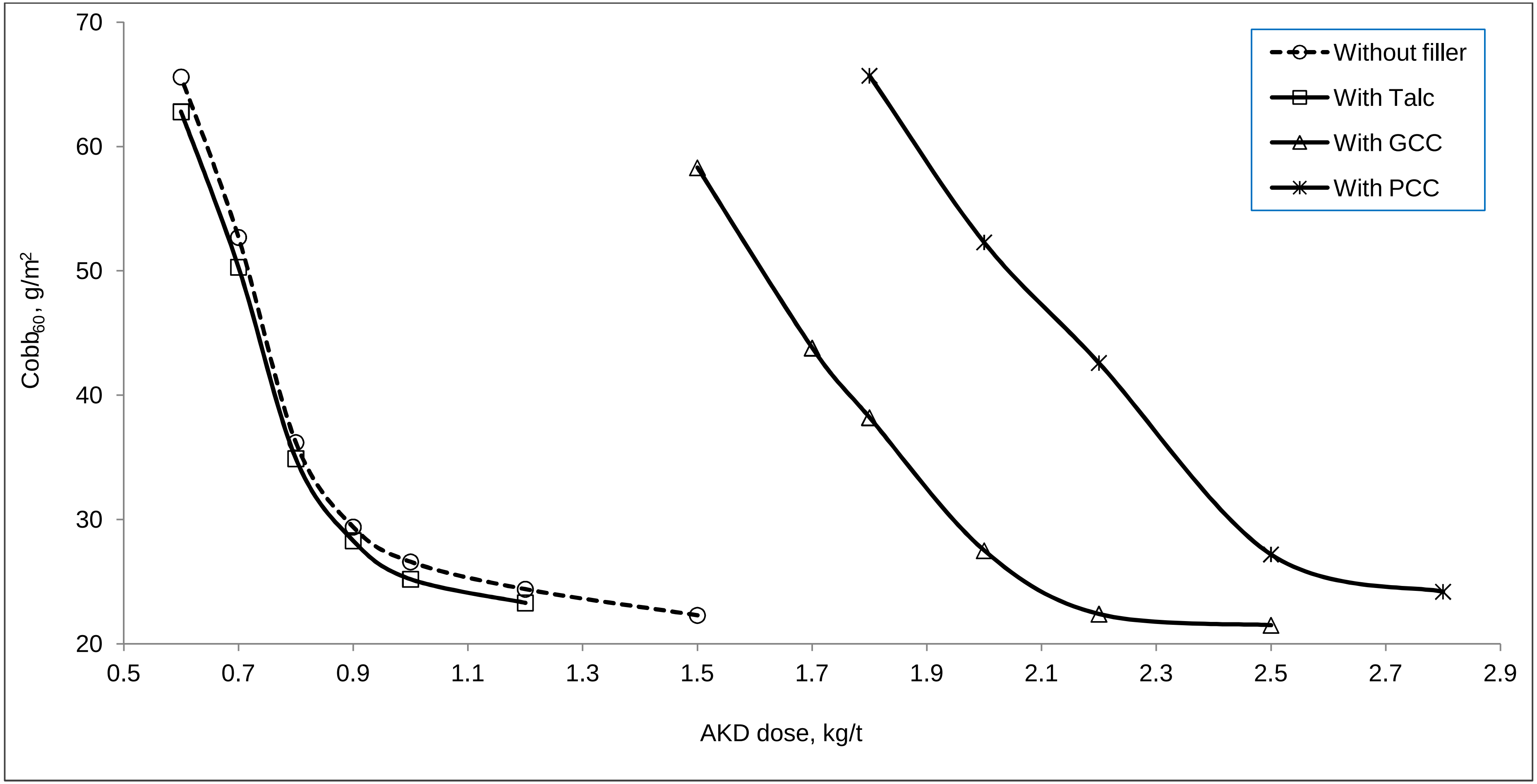


Figure 17: Effect of filler on $Cobb_{60}$ value with BRC pulp in AKD sizing

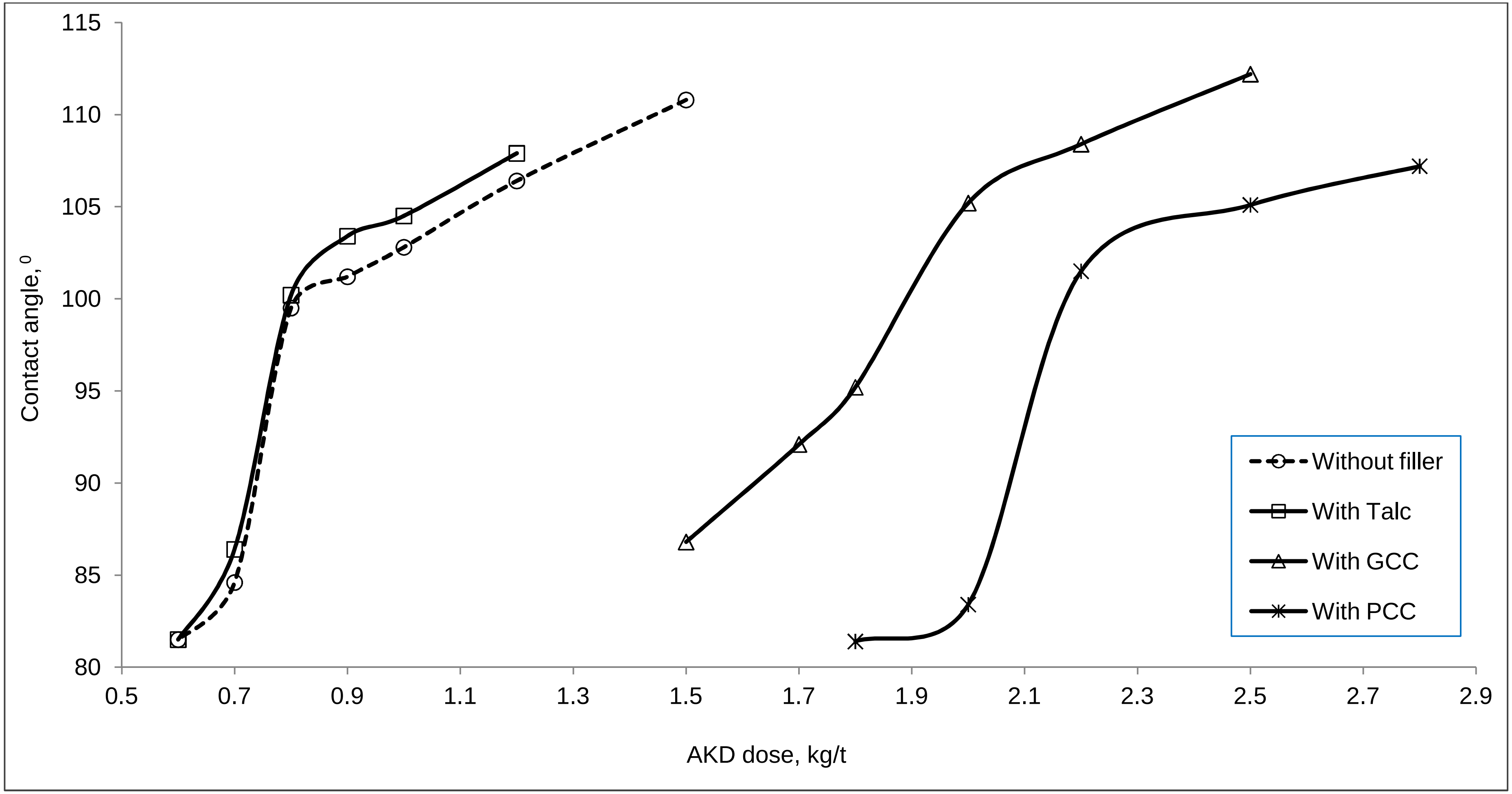


Figure 18: Effect of filler on contact angle with BRC pulp in AKD sizing

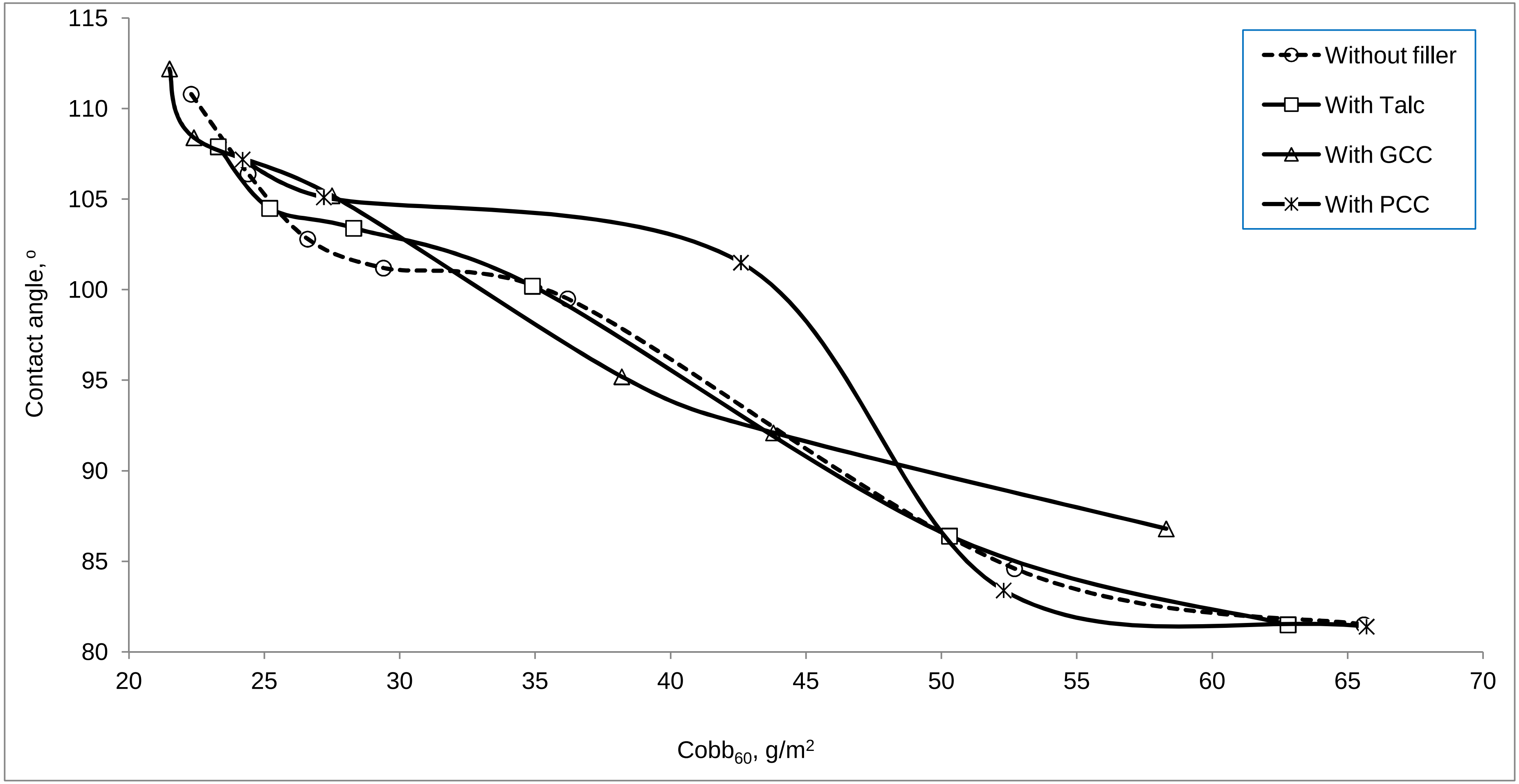


Figure 19: $Cobb_{60}$ vs. contact angle relationship for BRC pulp in AKD sizing

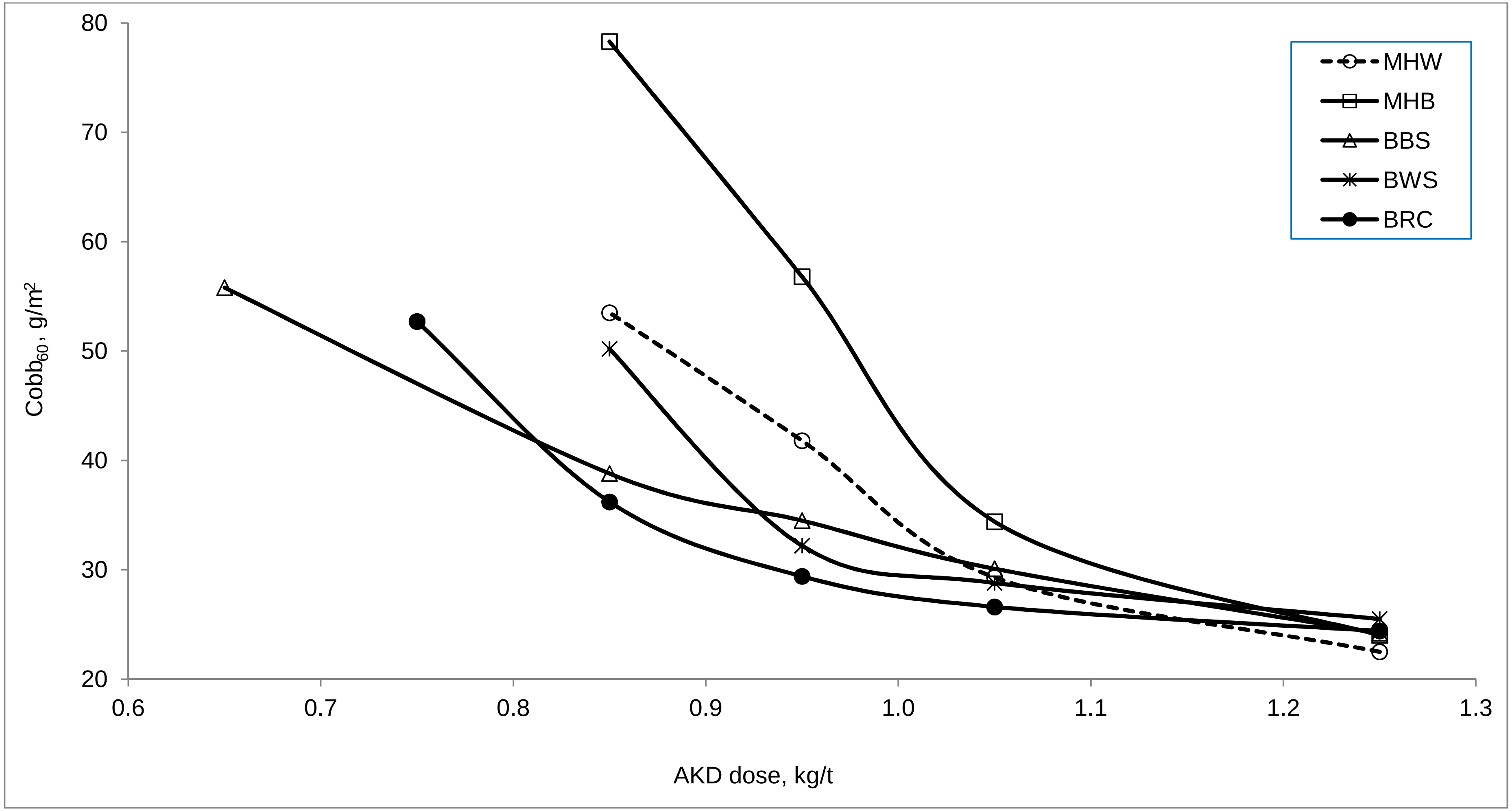


Figure 20: Comparison of $Cobb_{60}$ value of different pulp furnishes in AKD sizing (without filler)

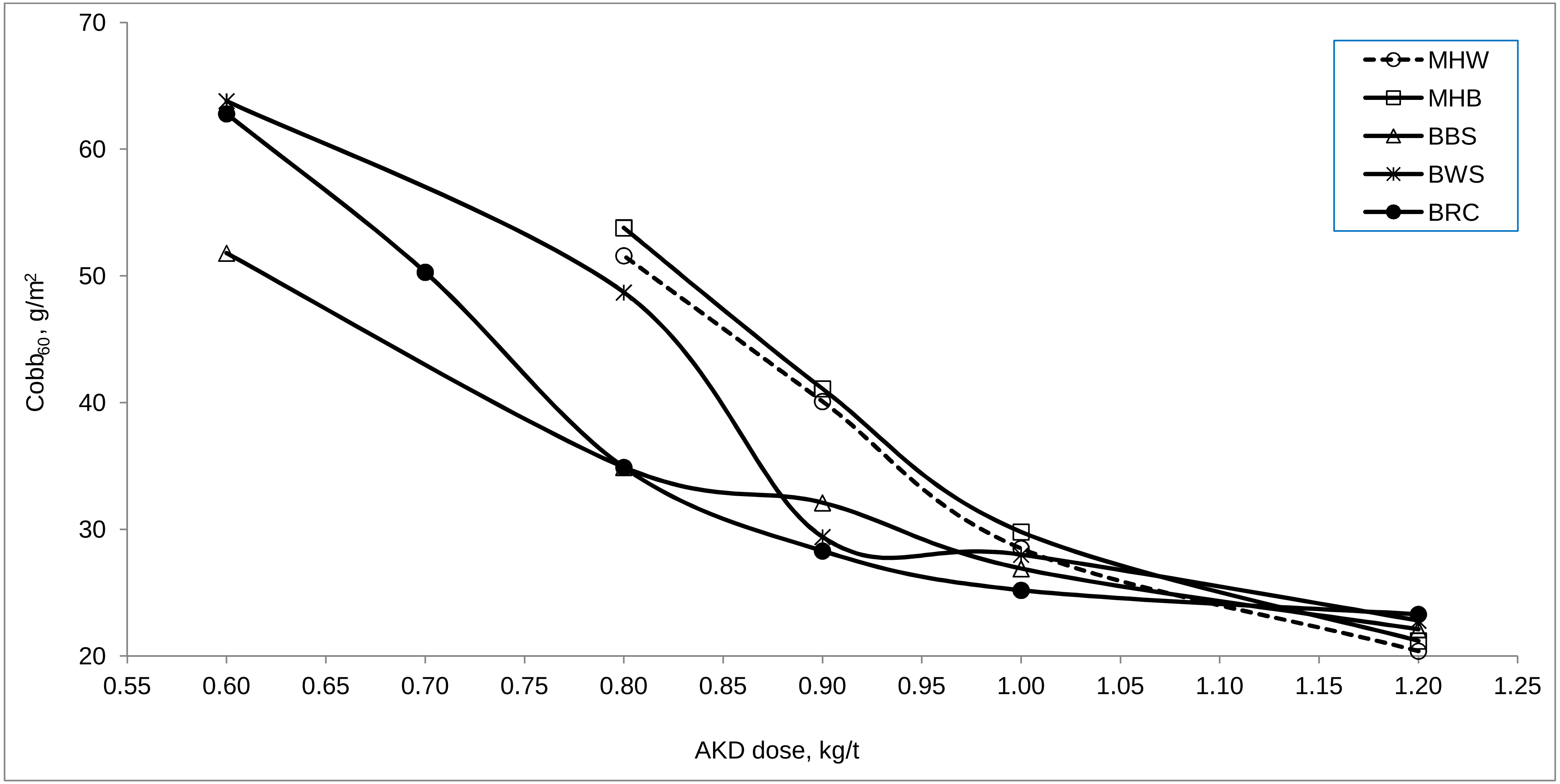


Figure 21: Comparison of $Cobb_{60}$ value of different pulp furnishes in AKD sizing with talc filler

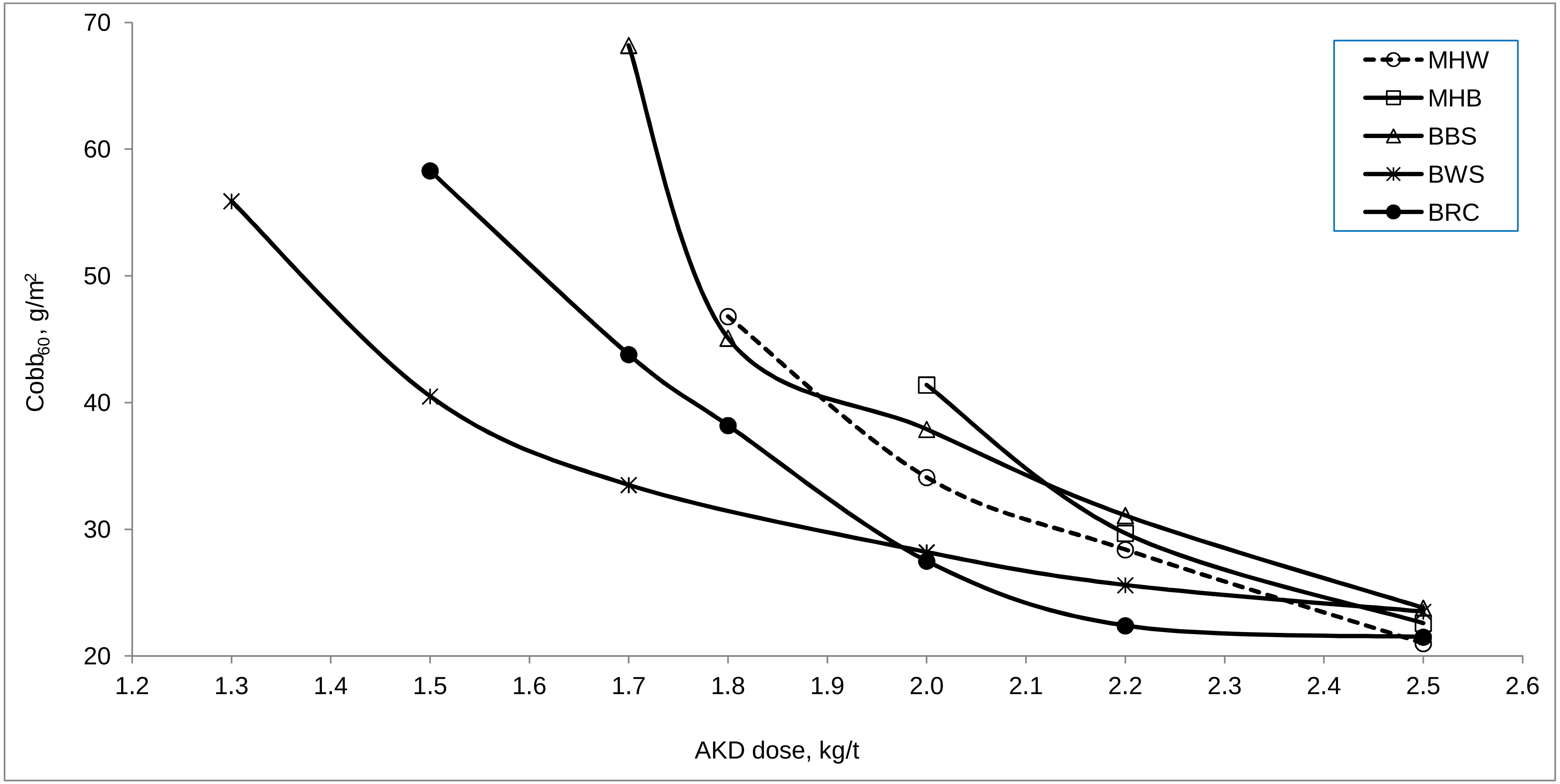


Figure 22: Comparison of $Cobb_{60}$ value of different pulp furnishes in AKD sizing with GCC filler

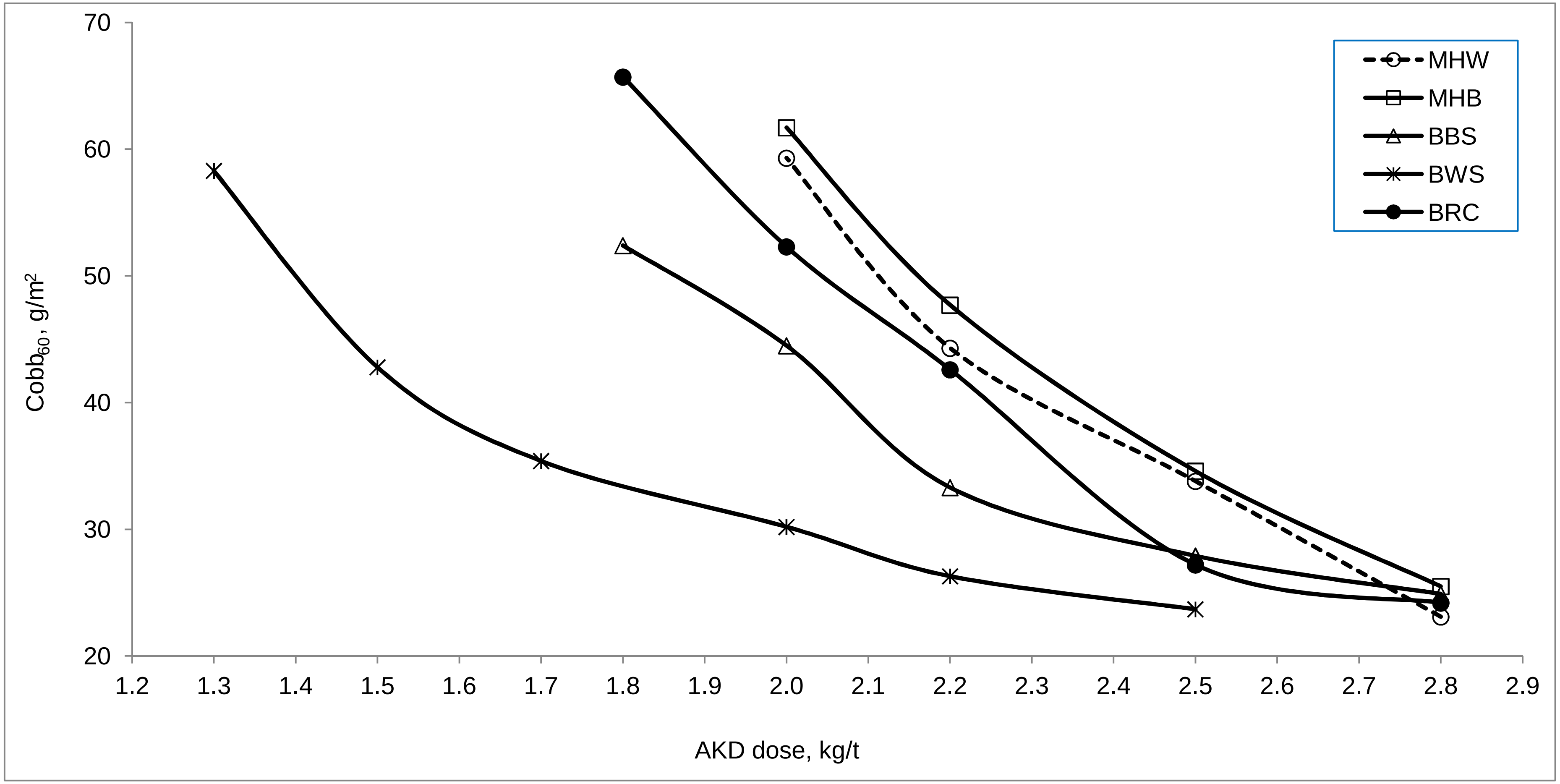


Figure 23: Comparison of $Cobb_{60}$ value of different pulp furnishes in AKD sizing with PCC filler

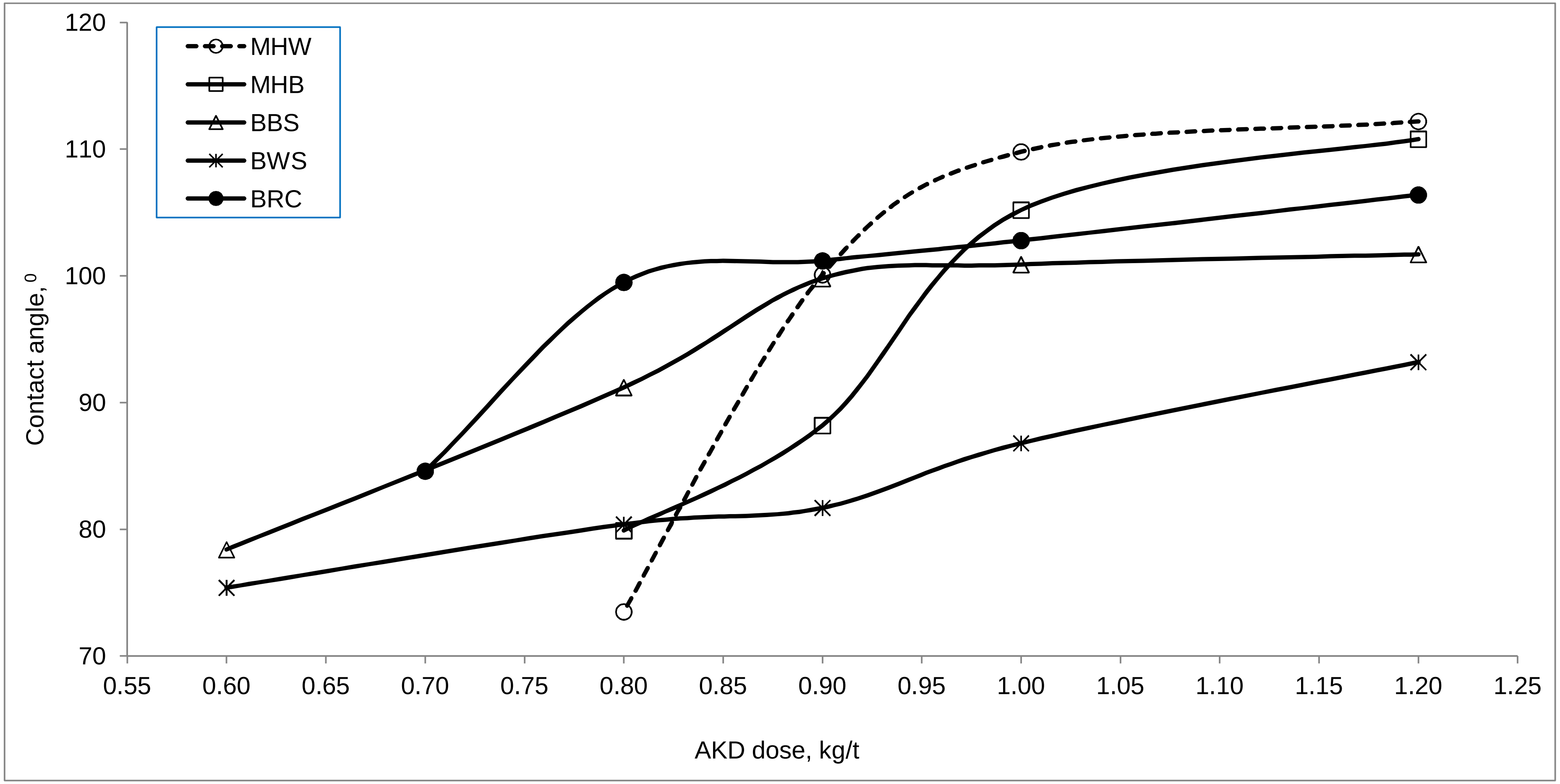


Figure 24: Comparison of contact angle of different pulp furnishes in AKD sizing (without filler)

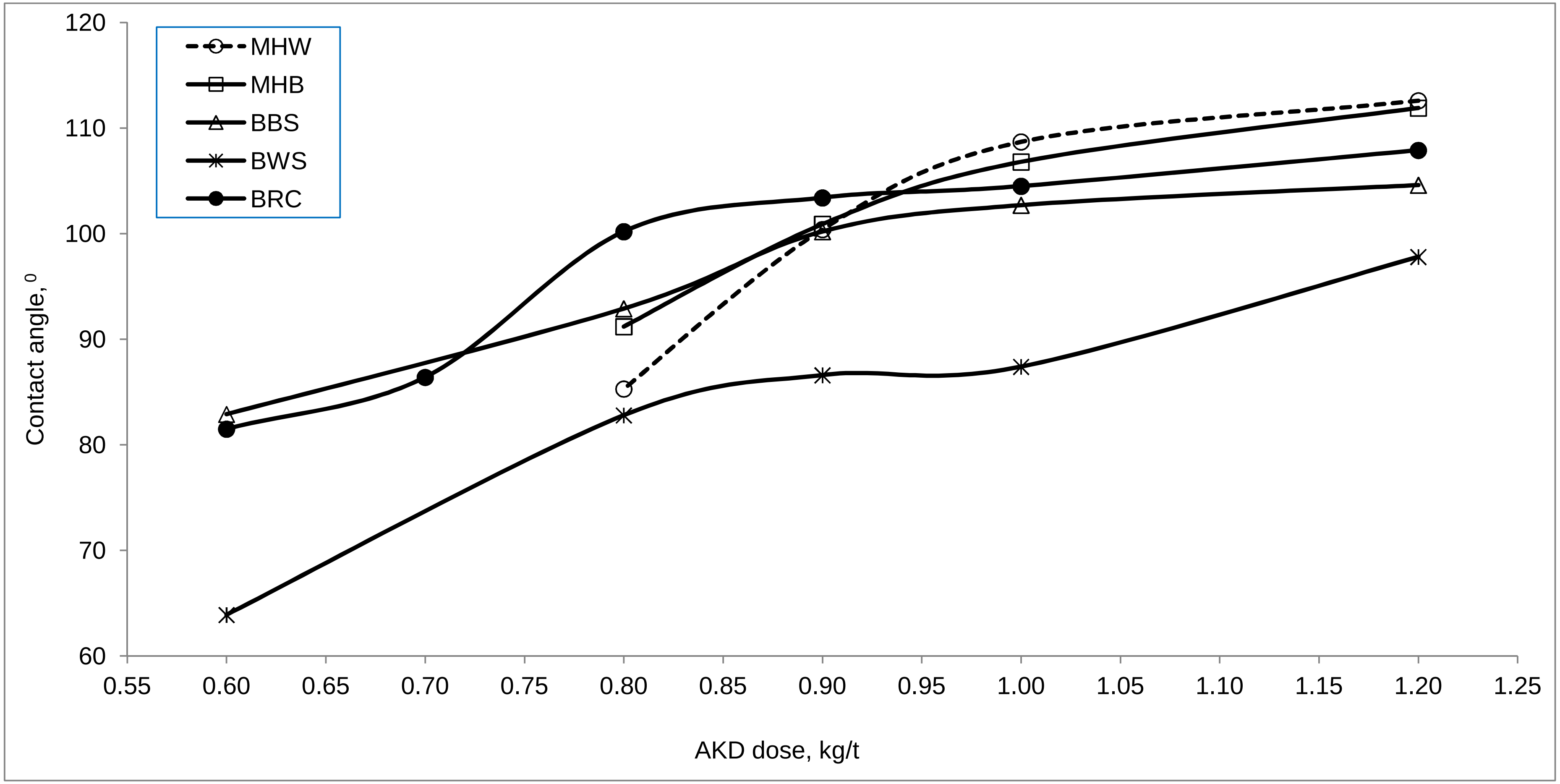


Figure 25: Comparison of contact angle of different pulp furnishes in AKD sizing with talc filler

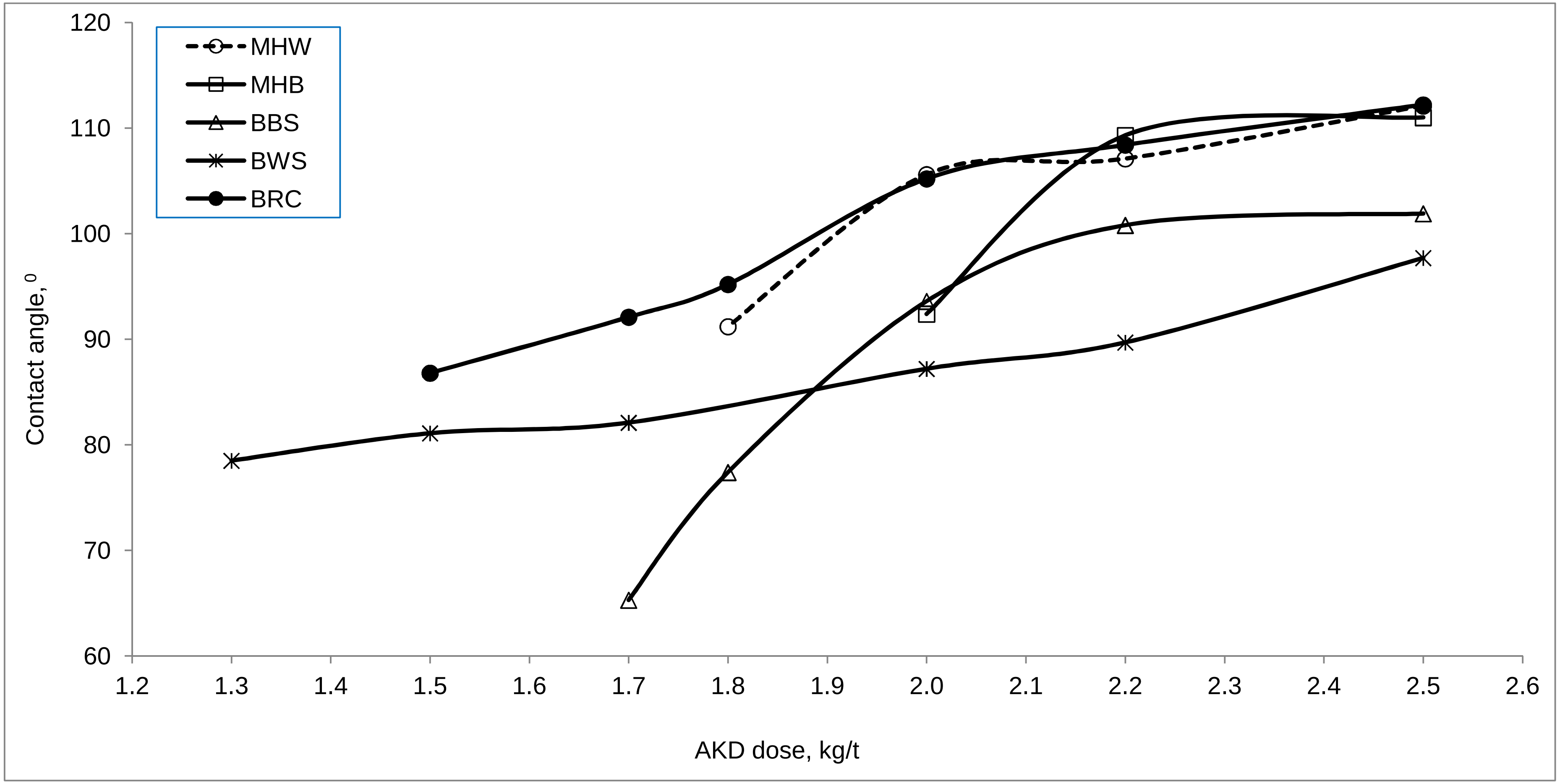


Figure 26: Comparison of contact angle of different pulp furnishes in AKD sizing with GCC filler

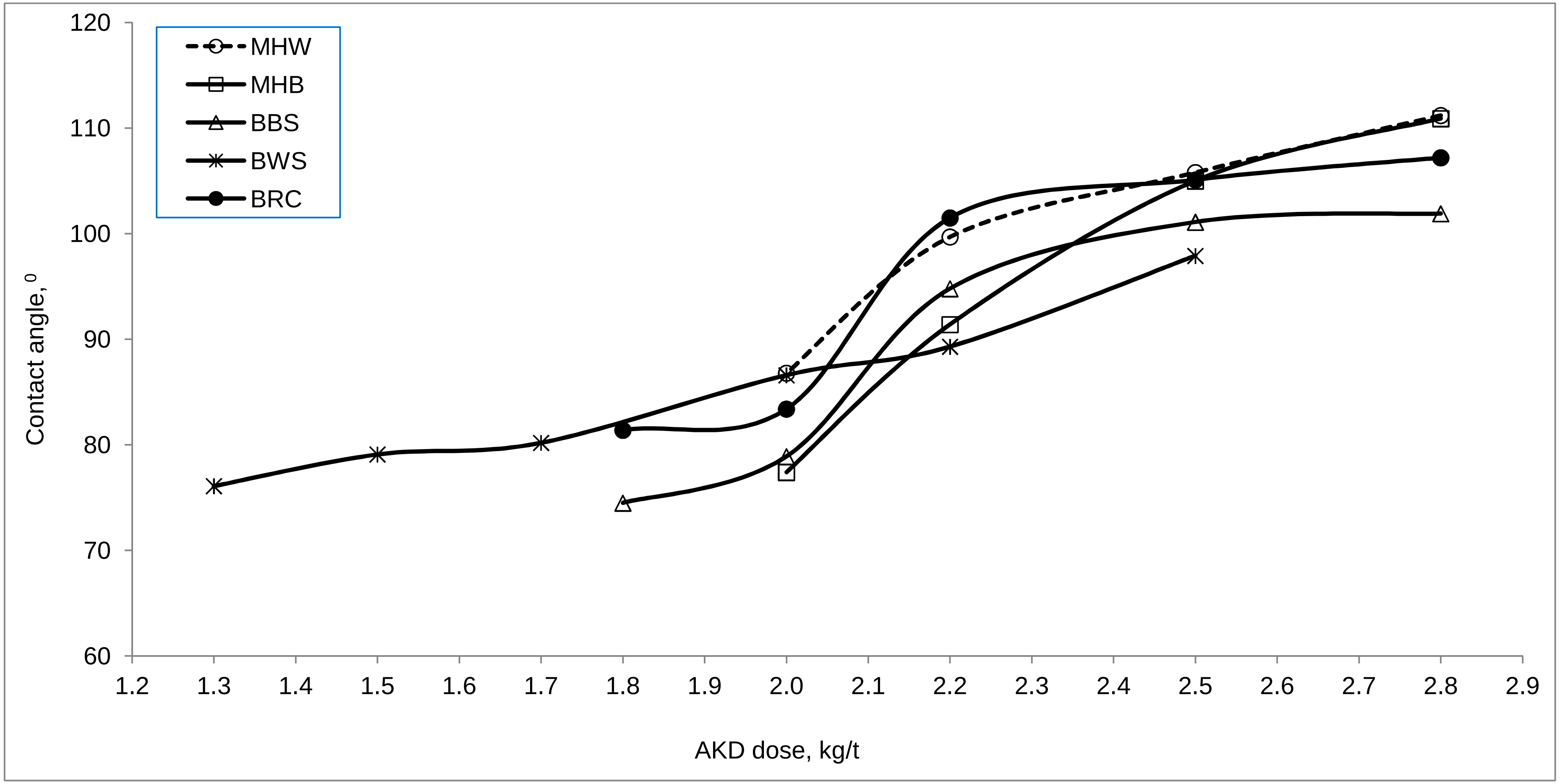


Figure 27: Comparison of contact angle of different pulp furnishes in AKD sizing with PCC filler

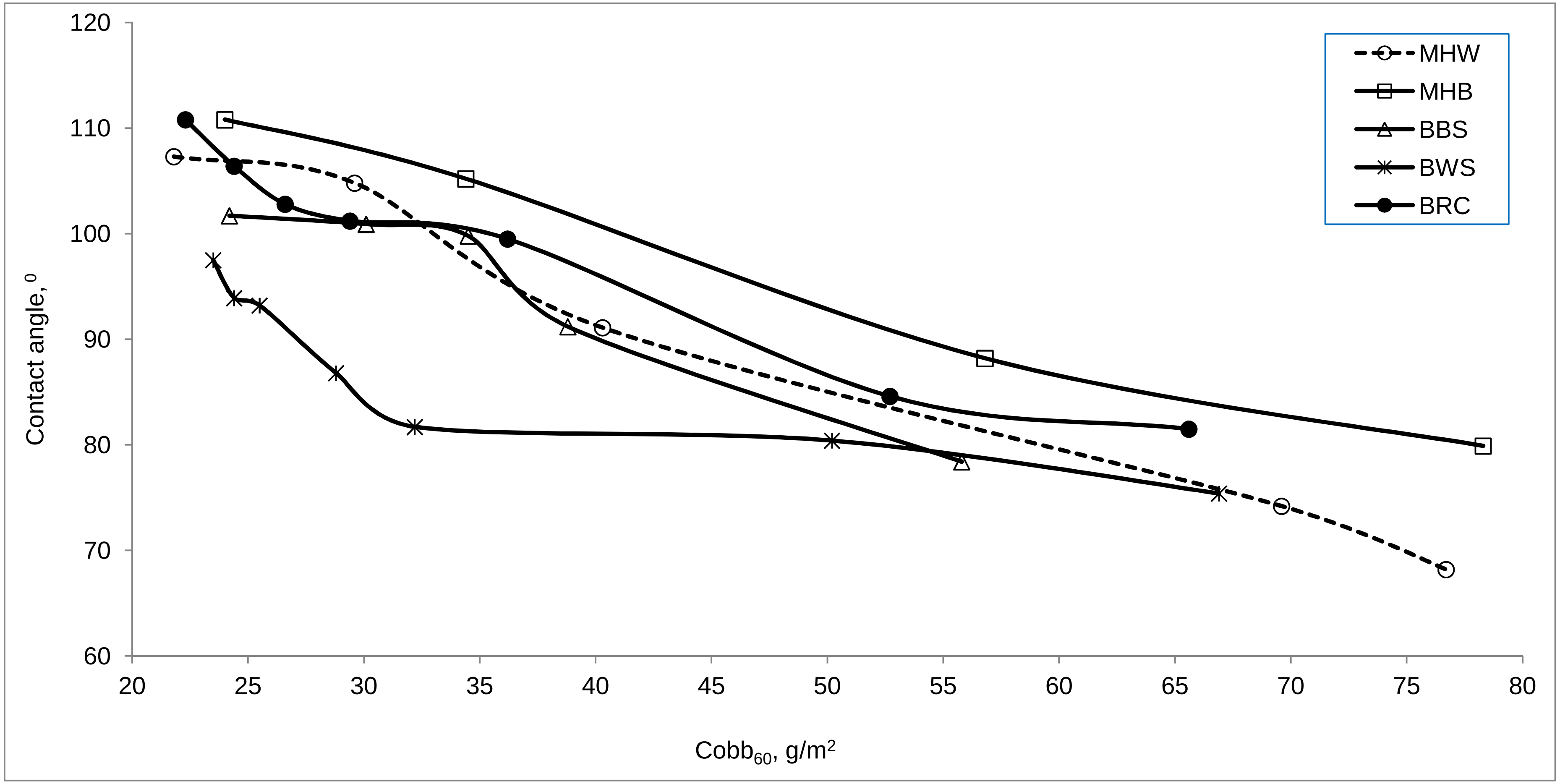


Figure 28: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in AKD sizing (without Filler)

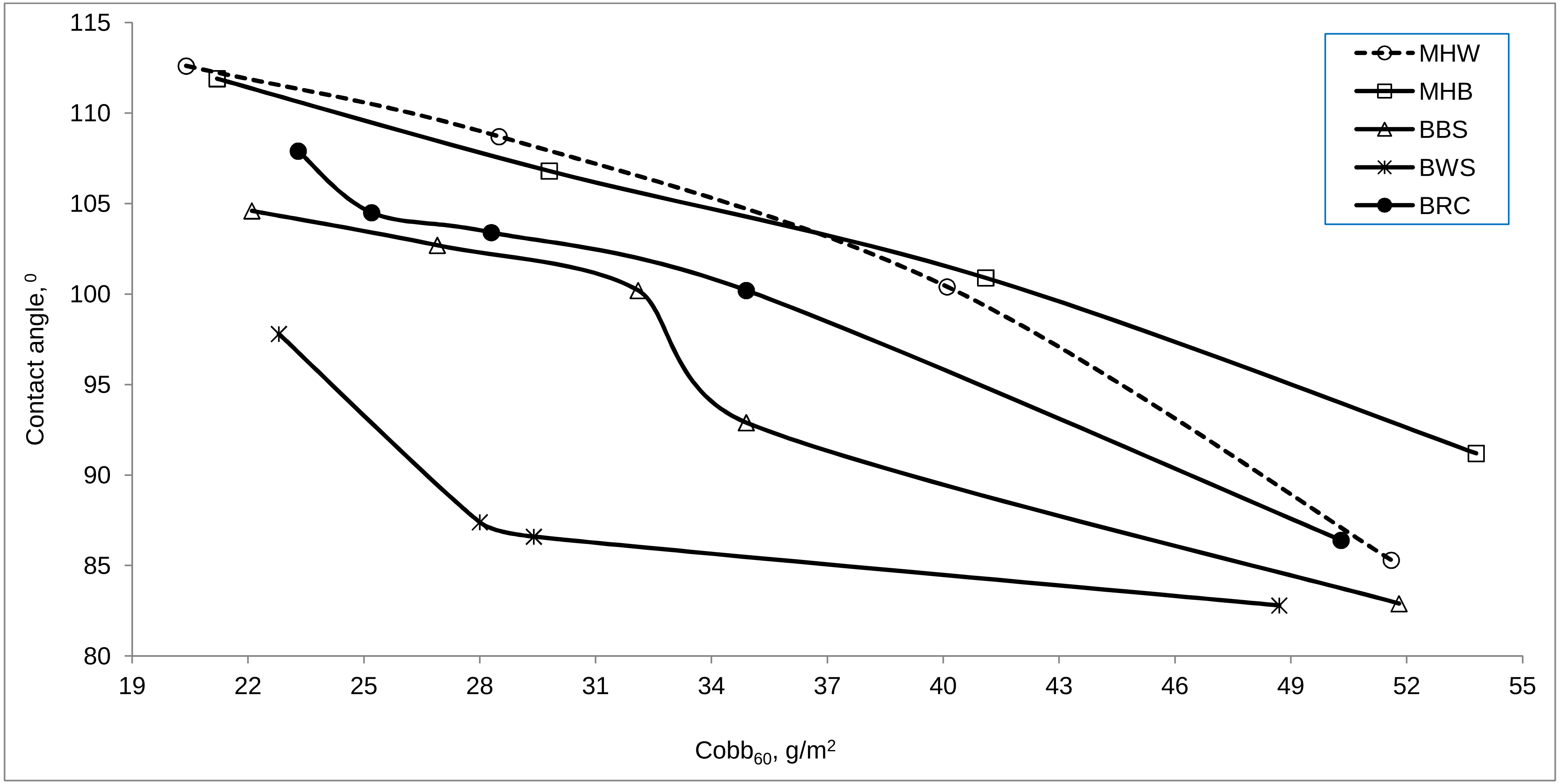


Figure 29: Cobb vs. contact angle relationship for different pulp furnishes in AKD sizing with talc filler

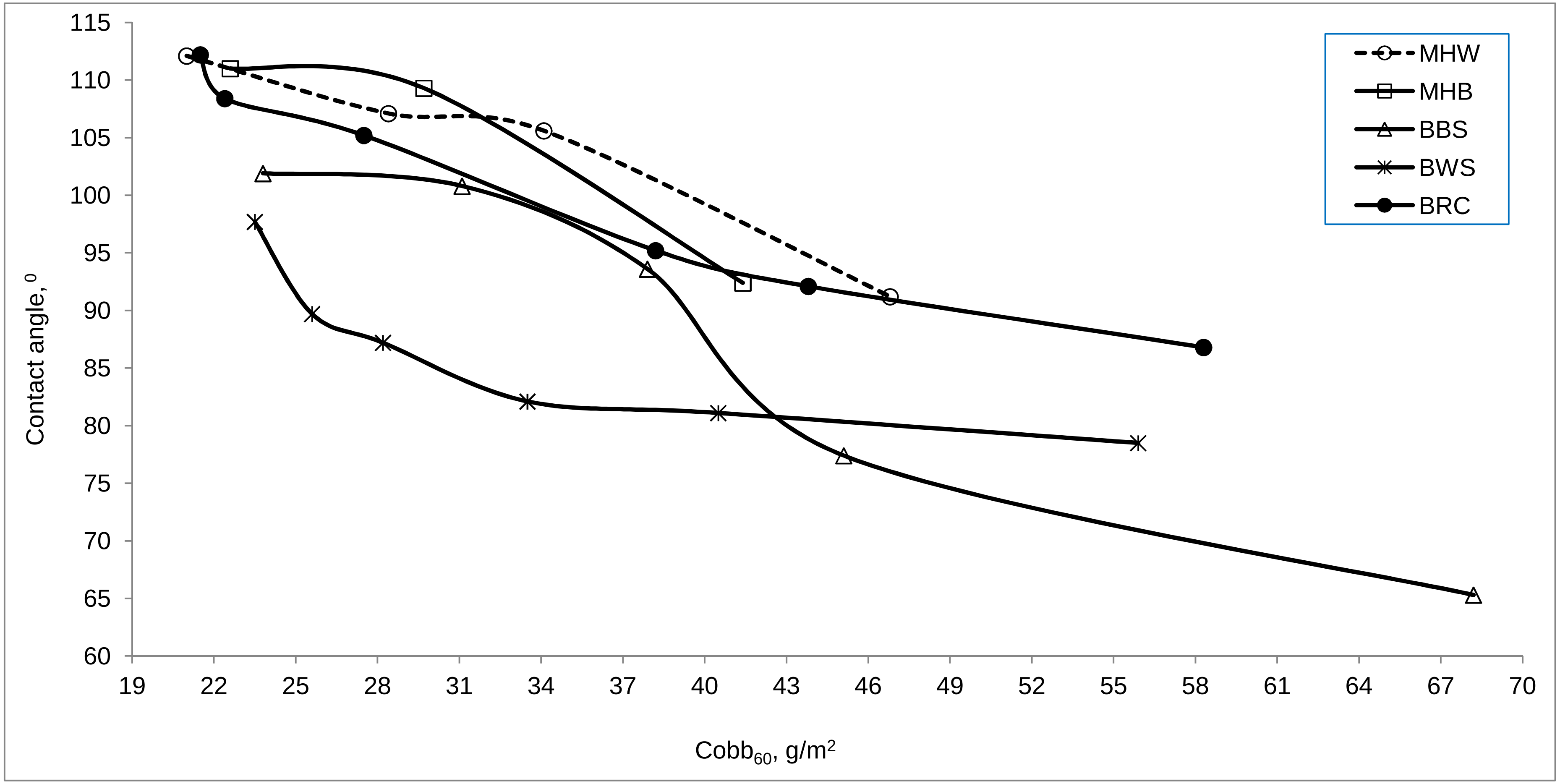


Figure 30: Cobb vs. contact angle relationship for different pulp furnishes in AKD sizing with GCC filler

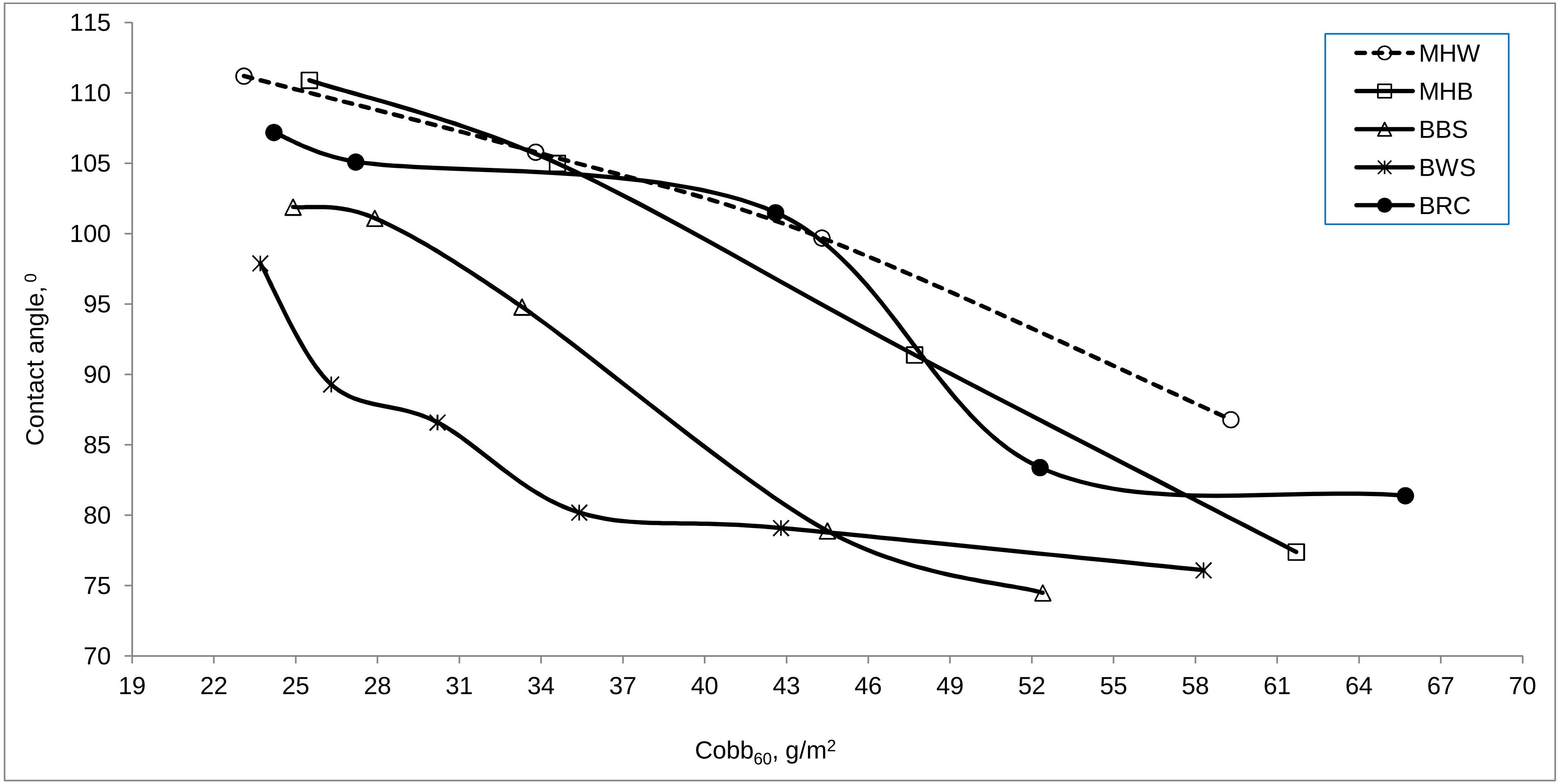


Figure 31: Cobb vs. contact angle relationship for different pulp furnishes in AKD sizing with PCC filler

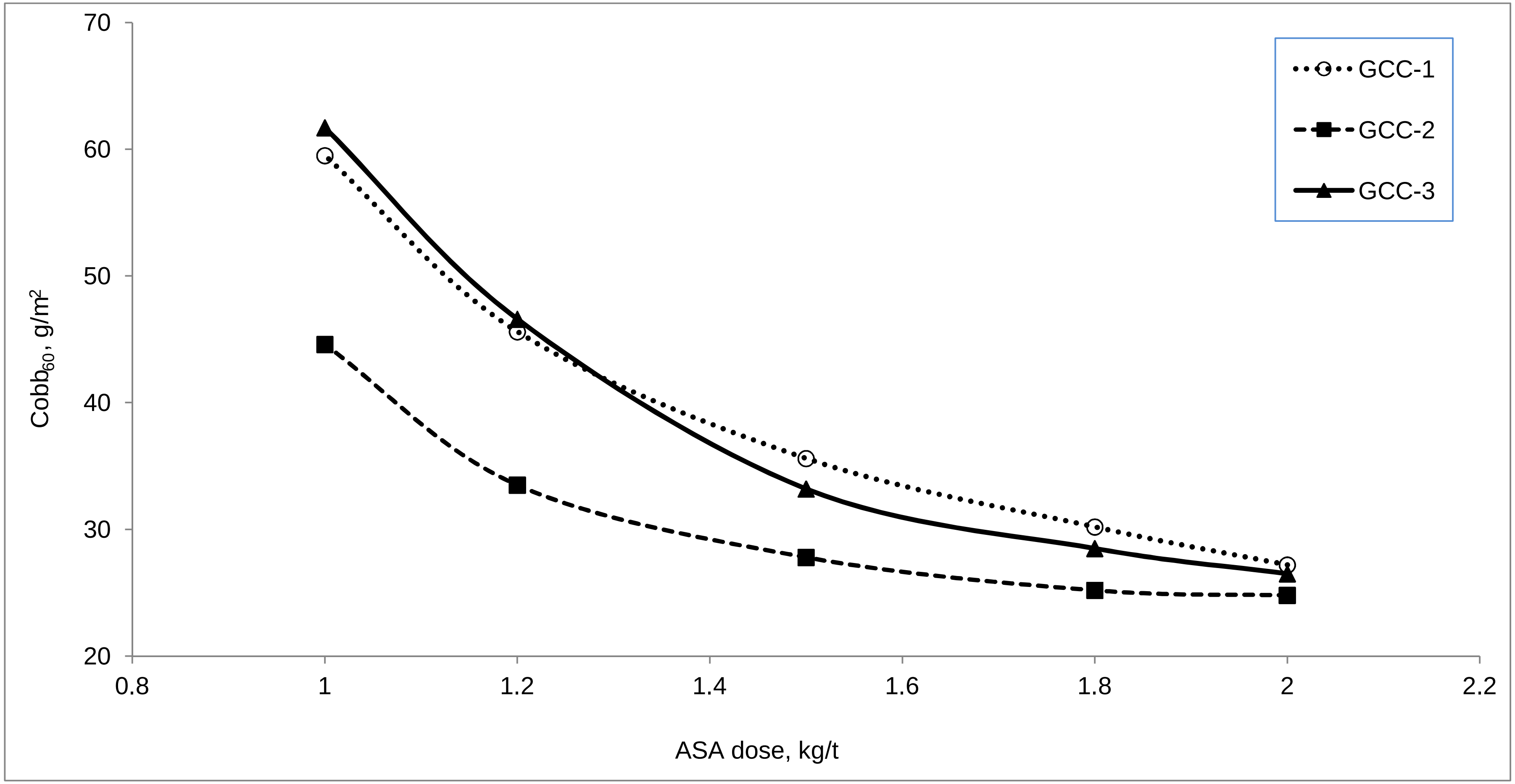


Figure 32: Sizing performance of different GCC fillers with MHB pulp in ASA sizing

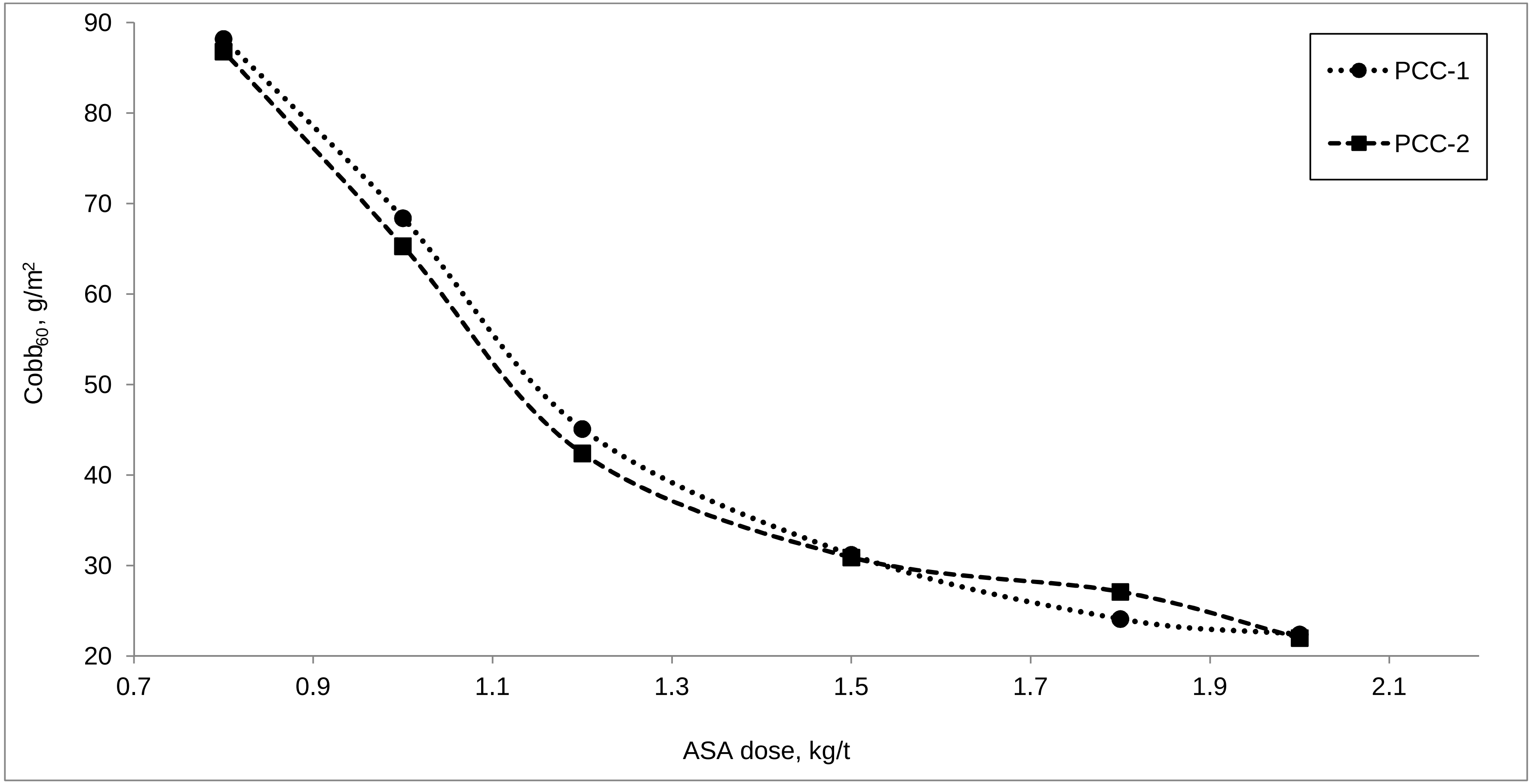


Figure 33: Sizing performance of different PCC fillers with MHB pulp in ASA sizing

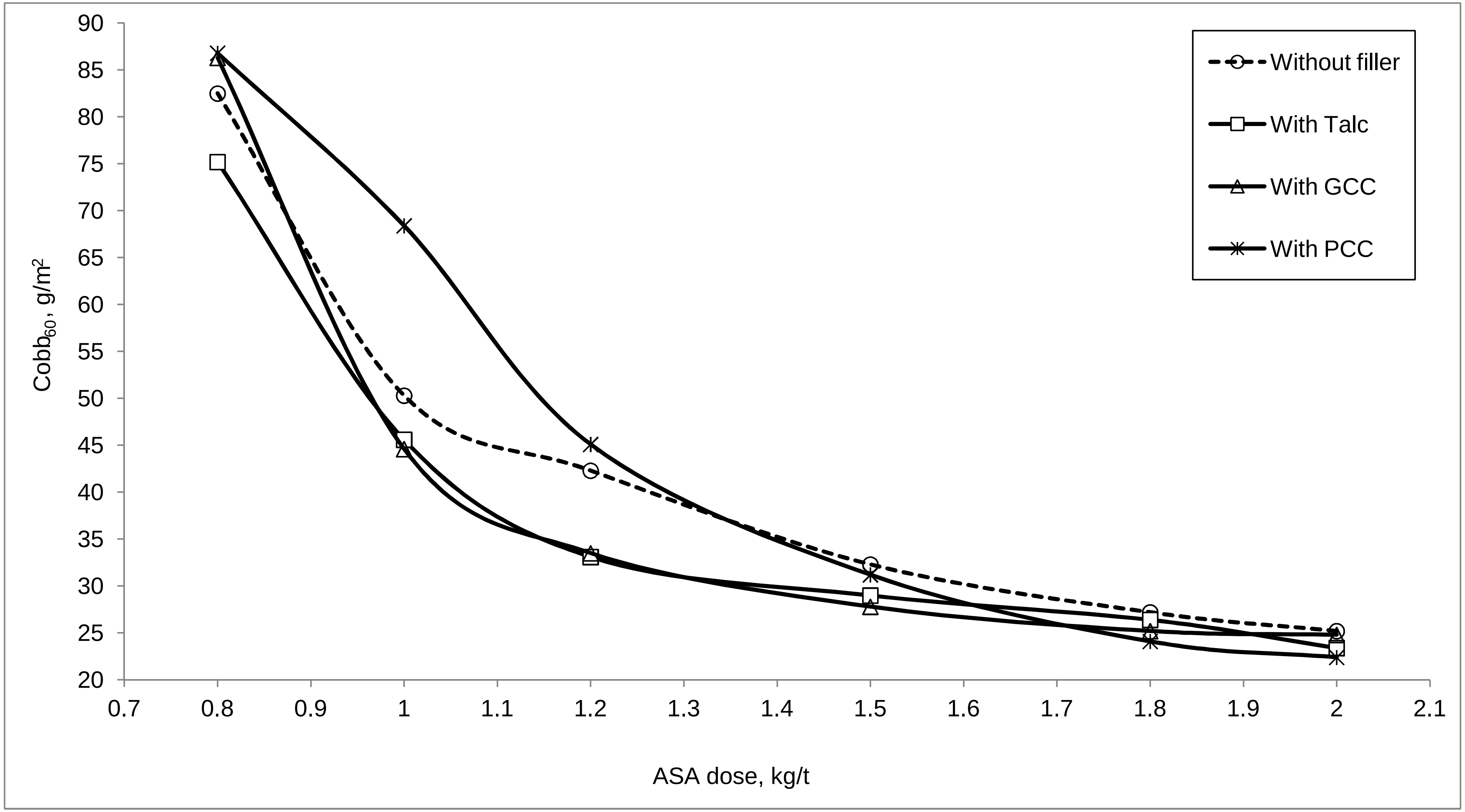


Figure 34: Effect of filler on $Cobb_{60}$ value with MHB pulp in ASA sizing

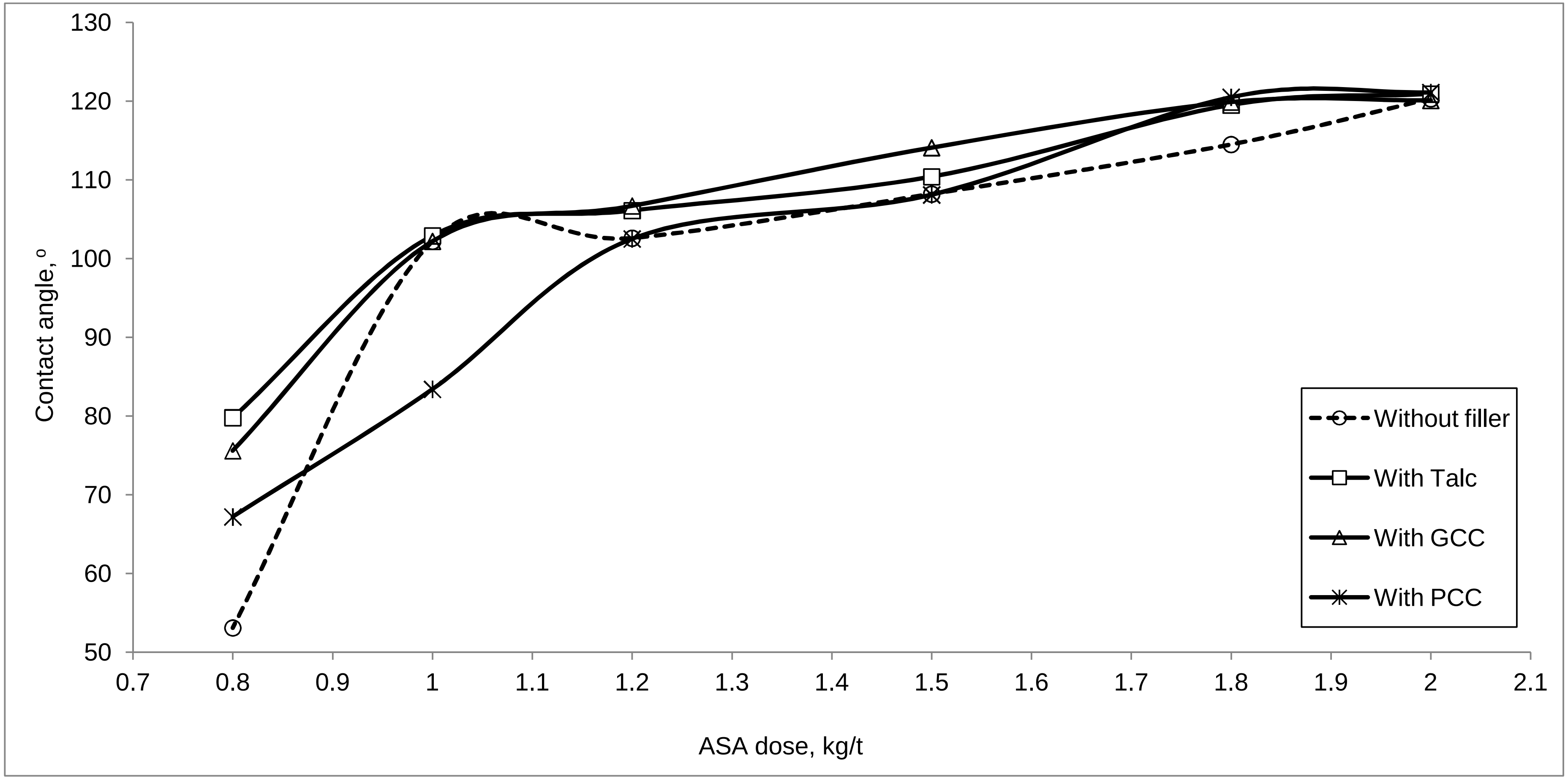


Figure 35: Effect of filler on contact angle with MHB pulp in ASA sizing

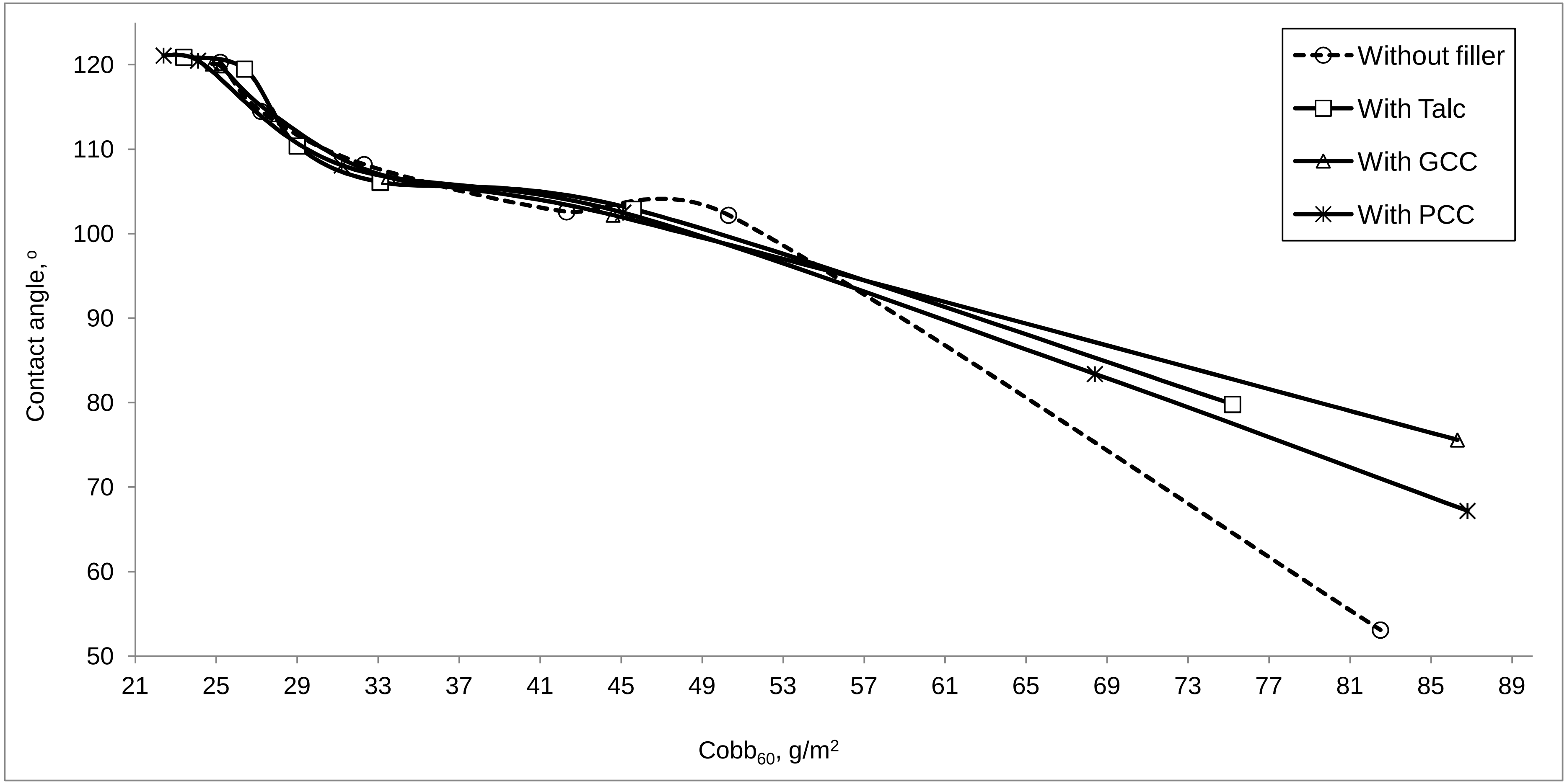


Table 36: Cobb$_{60}$ vs. contact angle relationship of MHB pulp in ASA sizing with different fillers

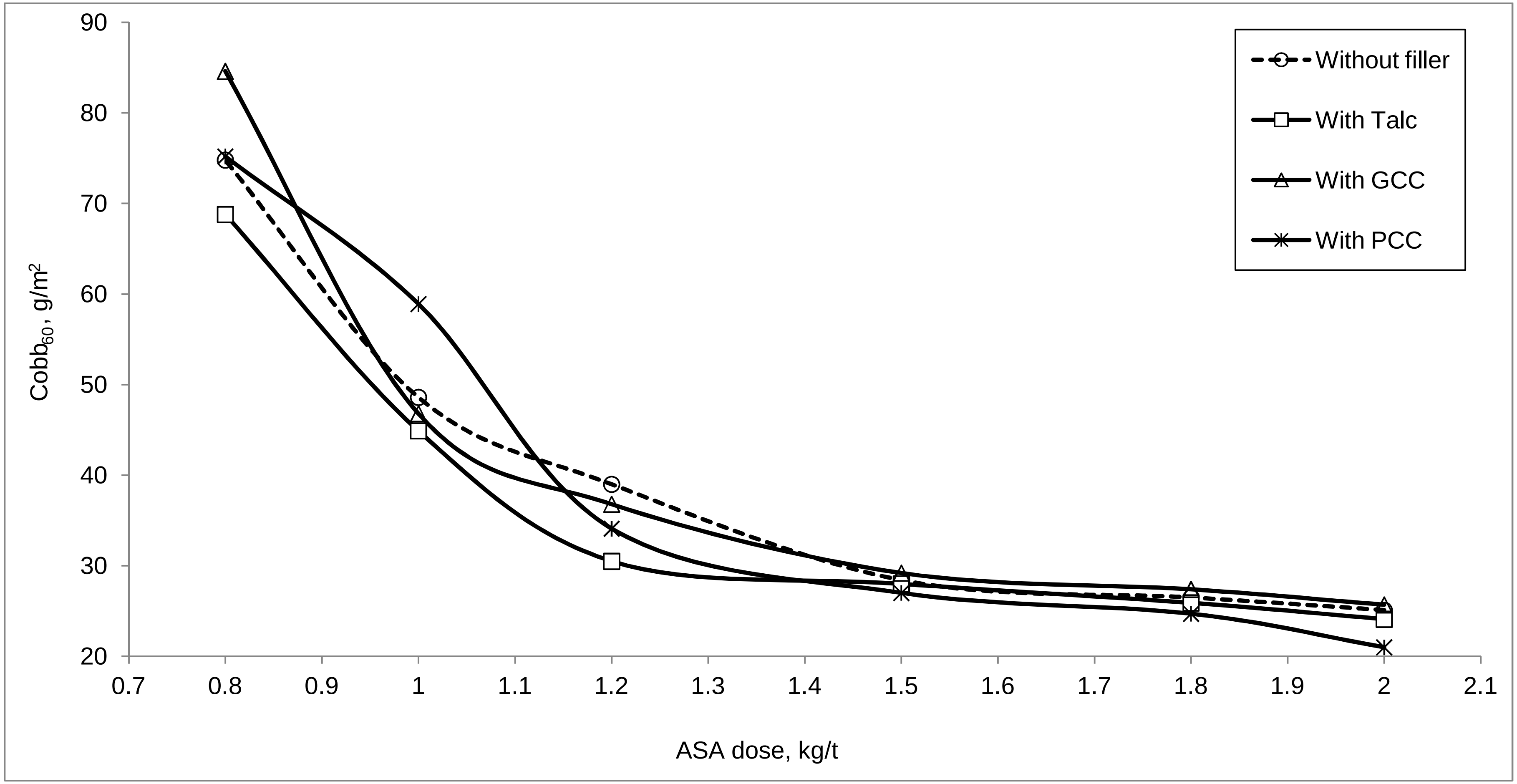


Figure 37: Effect of filler on Cobb$_{60}$ value with MHW pulp in ASA sizing

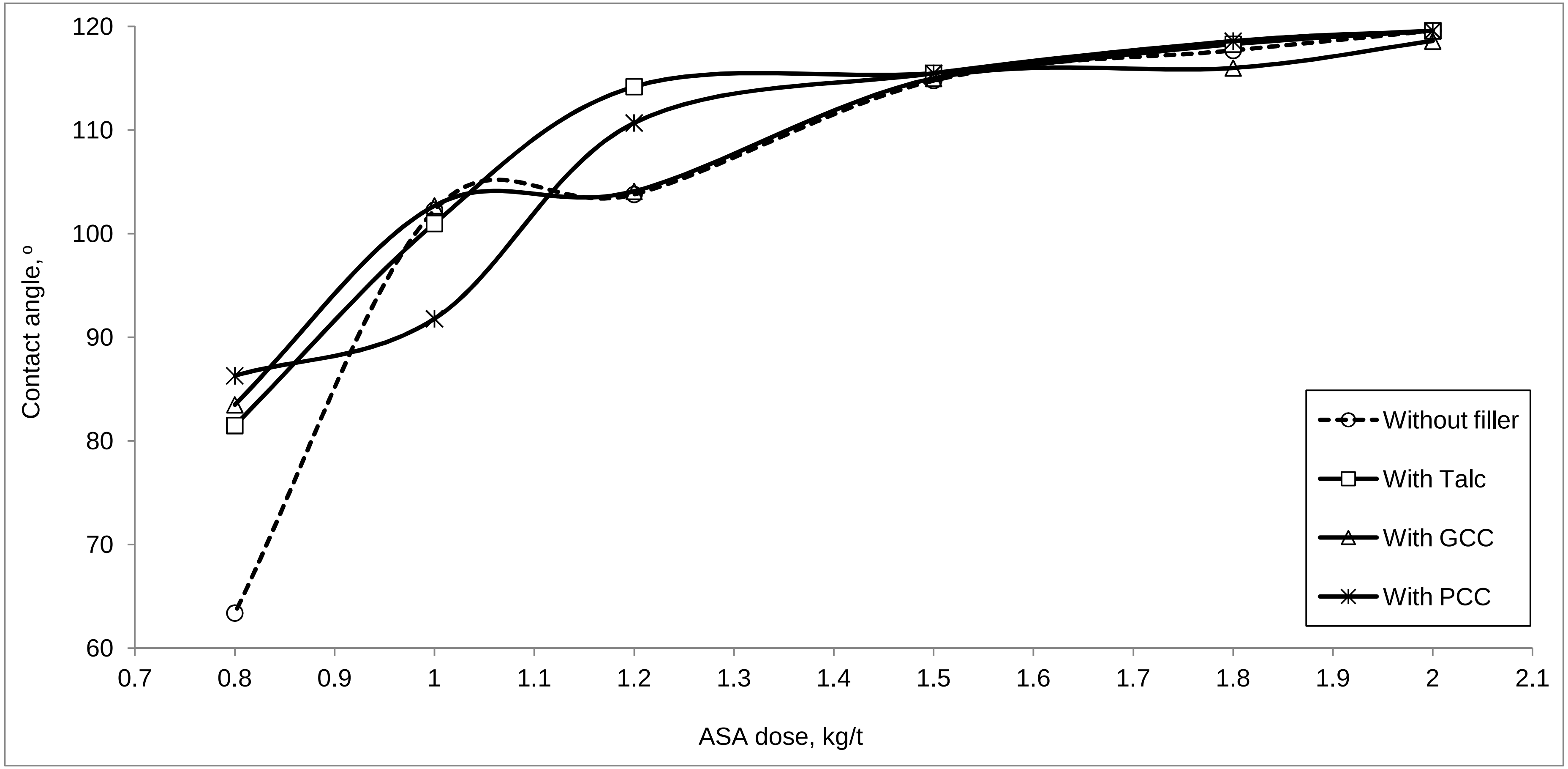


Figure 38: Effect of filler on contact angle with MHW pulp in ASA sizing

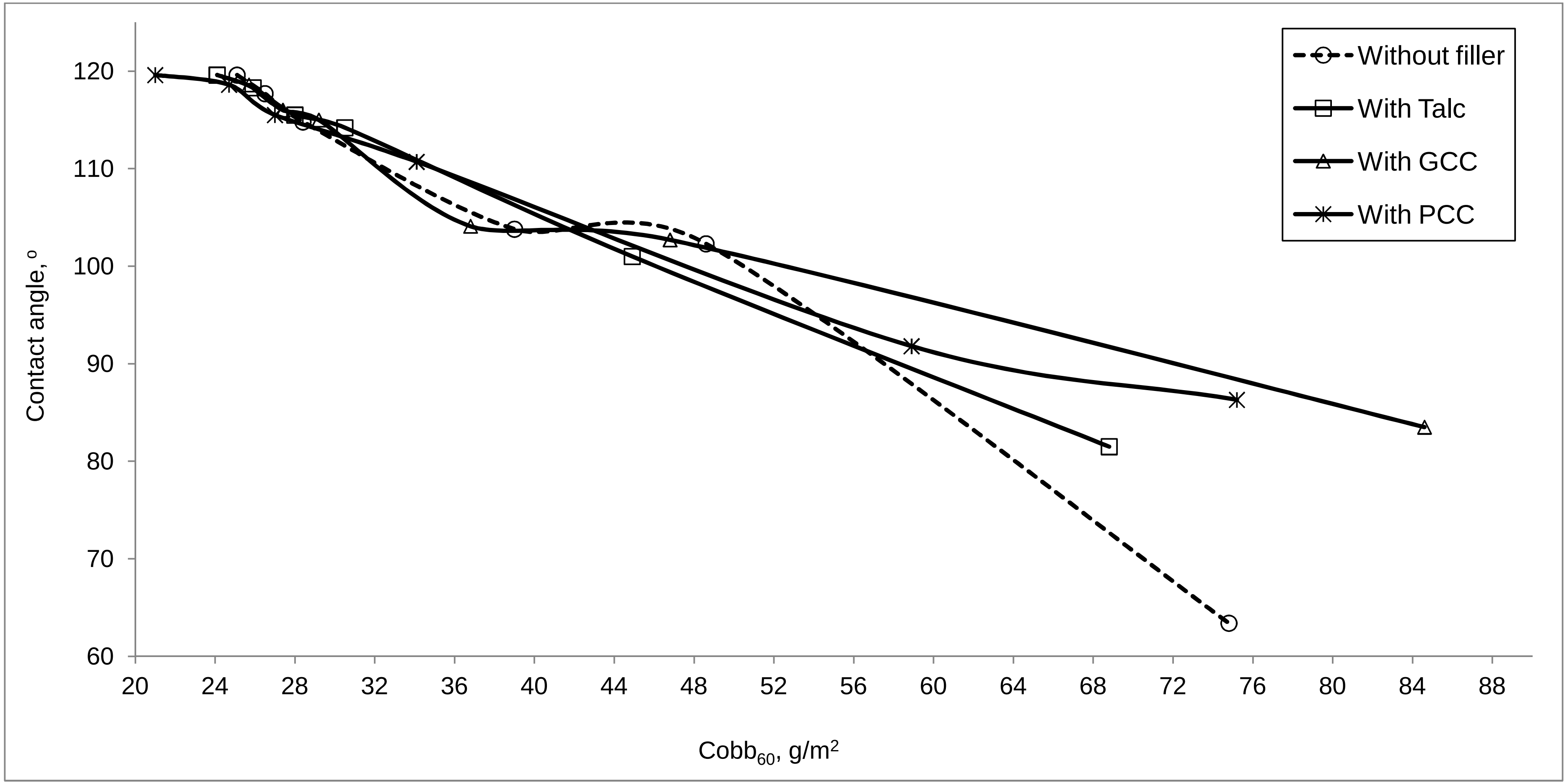


Table 39: Cobb$_{60}$ vs. contact angle relationship of MHW pulp in ASA sizing with different fillers

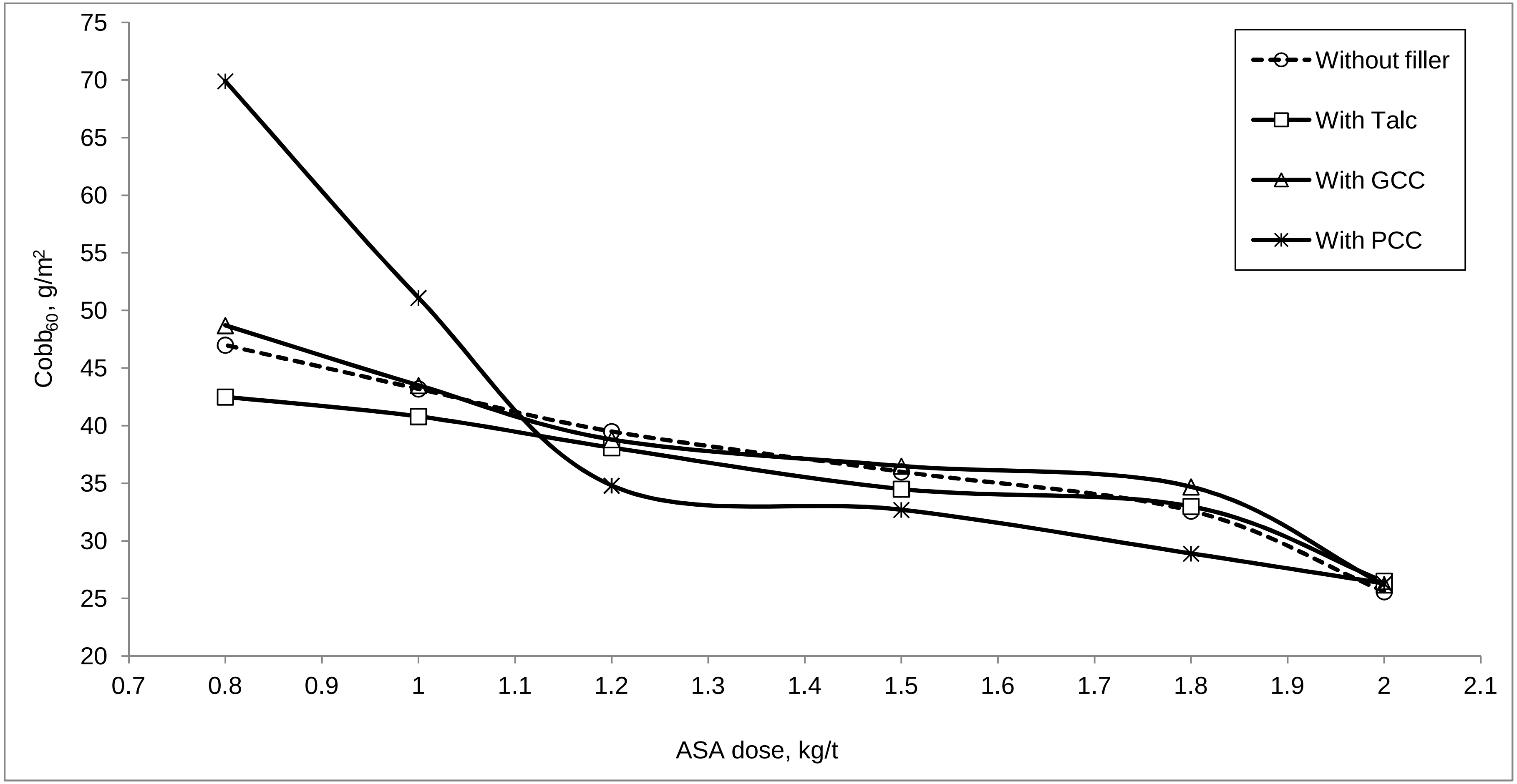


Figure 40: Effect of filler on $Cobb_{60}$ value with BBS pulp in ASA sizing

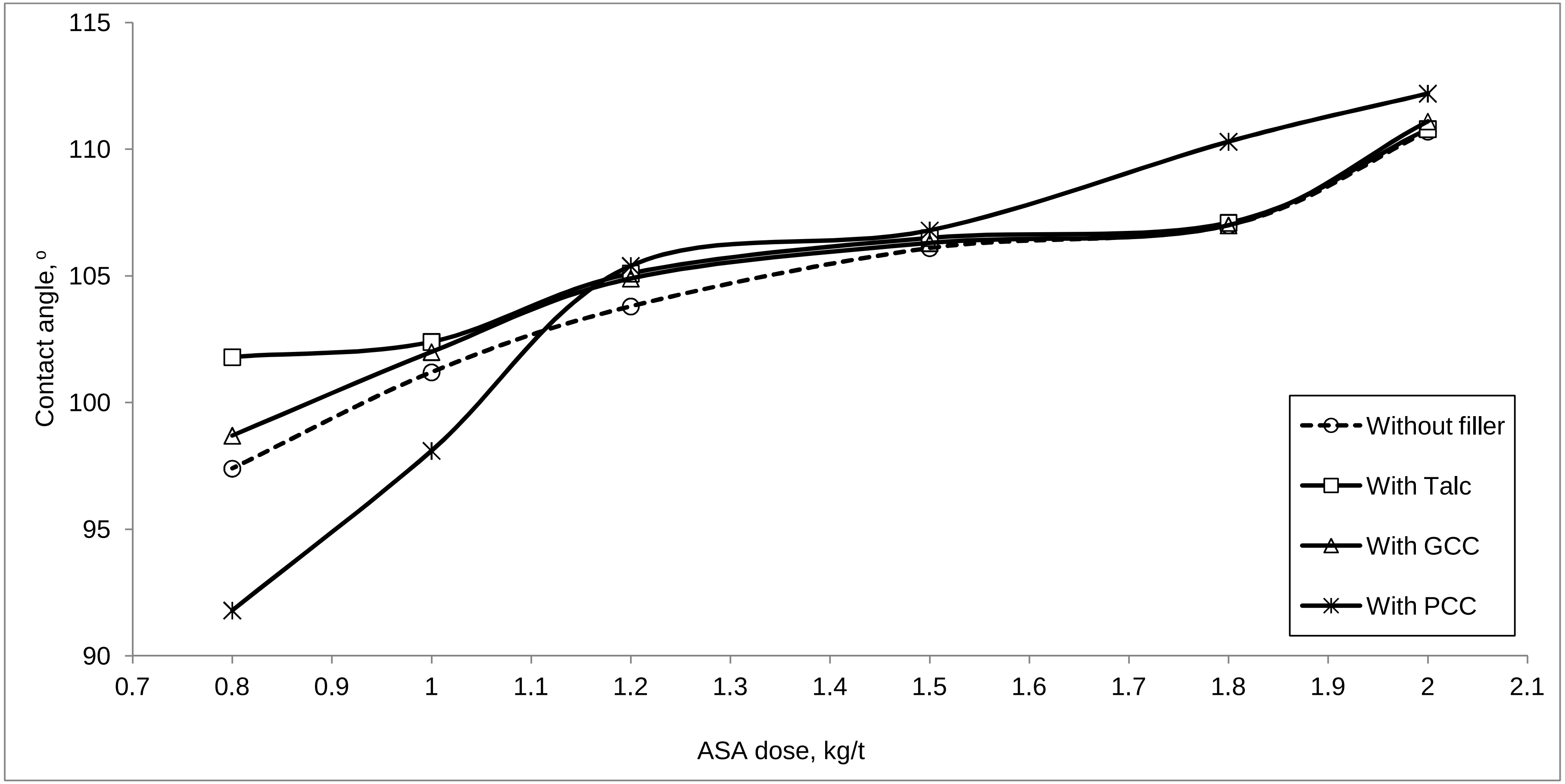


Figure 41: Effect of filler on contact angle with BBS pulp in ASA sizing

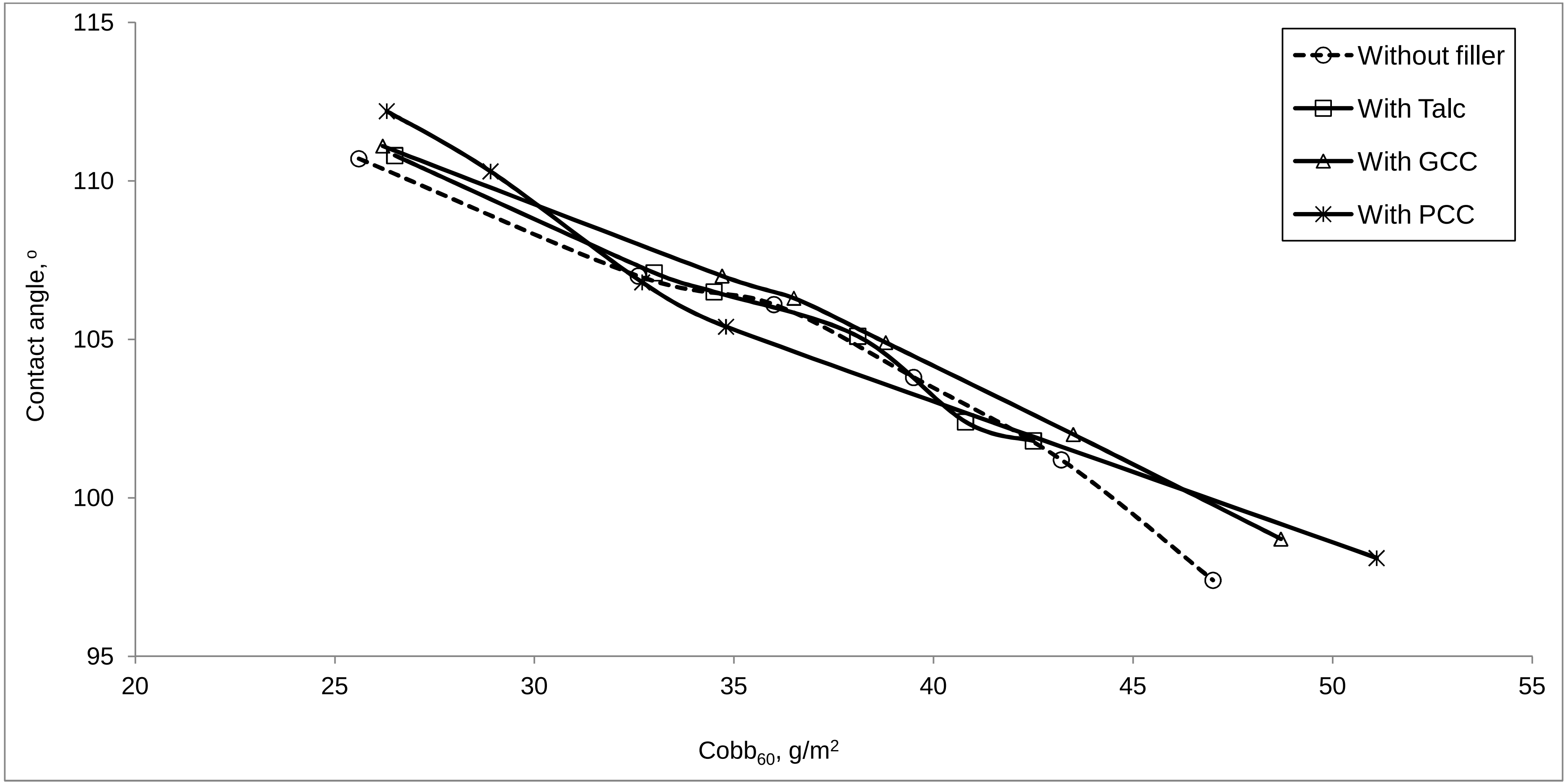


Table 42: $Cobb_{60}$ vs. contact angle relationship of BBS pulp in ASA sizing with different fillers

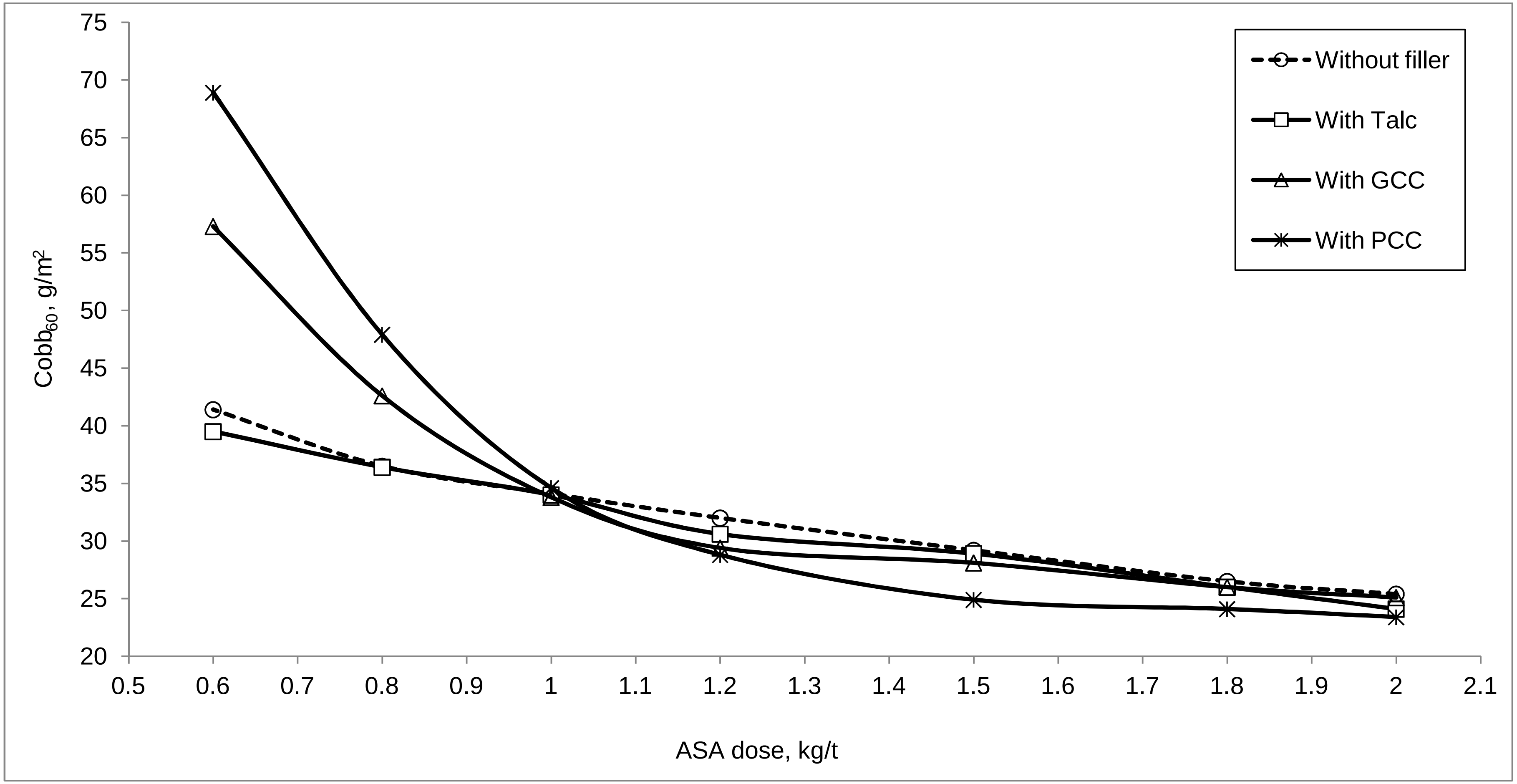


Figure 43: Effect of filler on $Cobb_{60}$ value with BWS pulp in ASA sizing

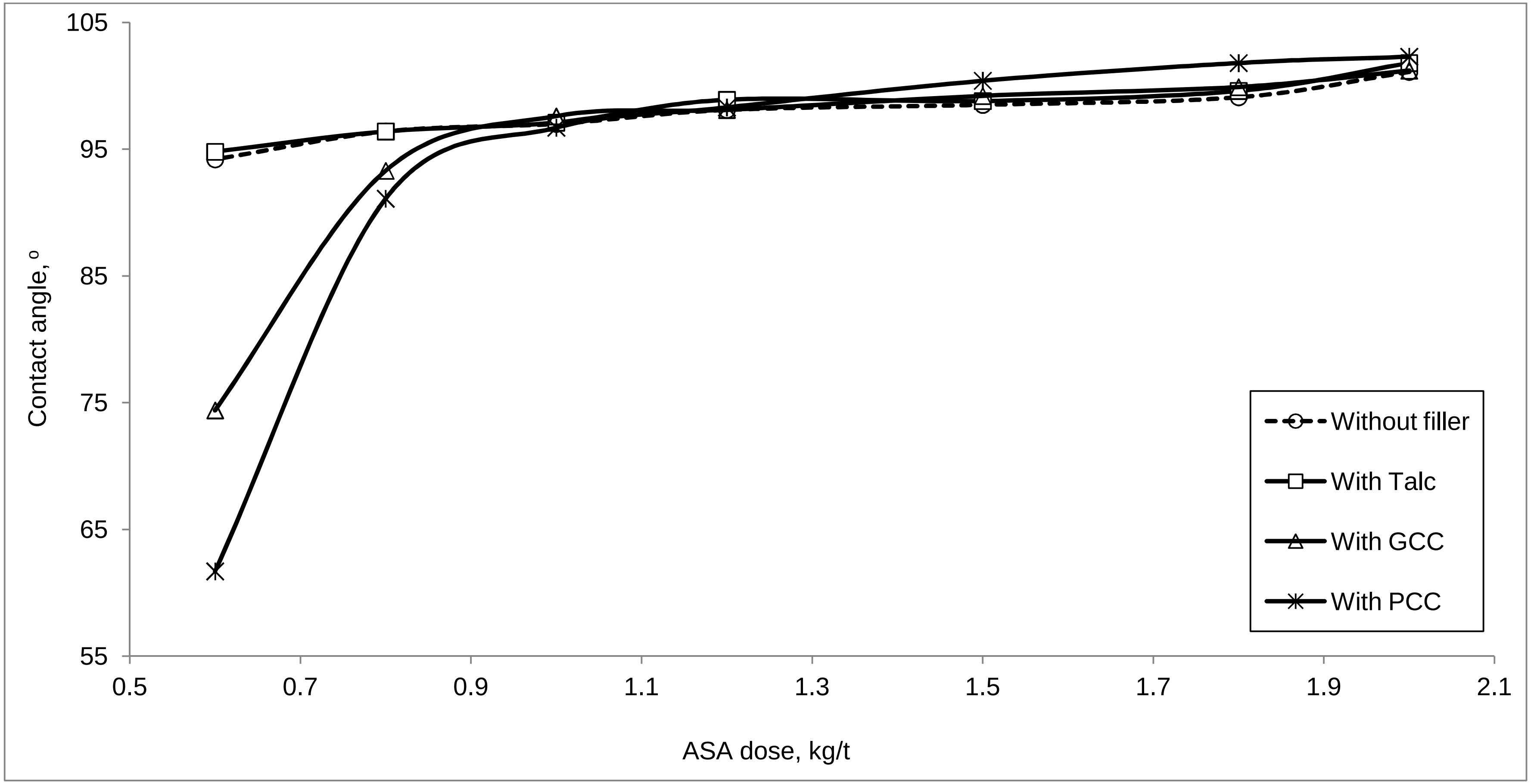


Figure 44: Effect of filler on contact angle with BWS pulp in ASA sizing

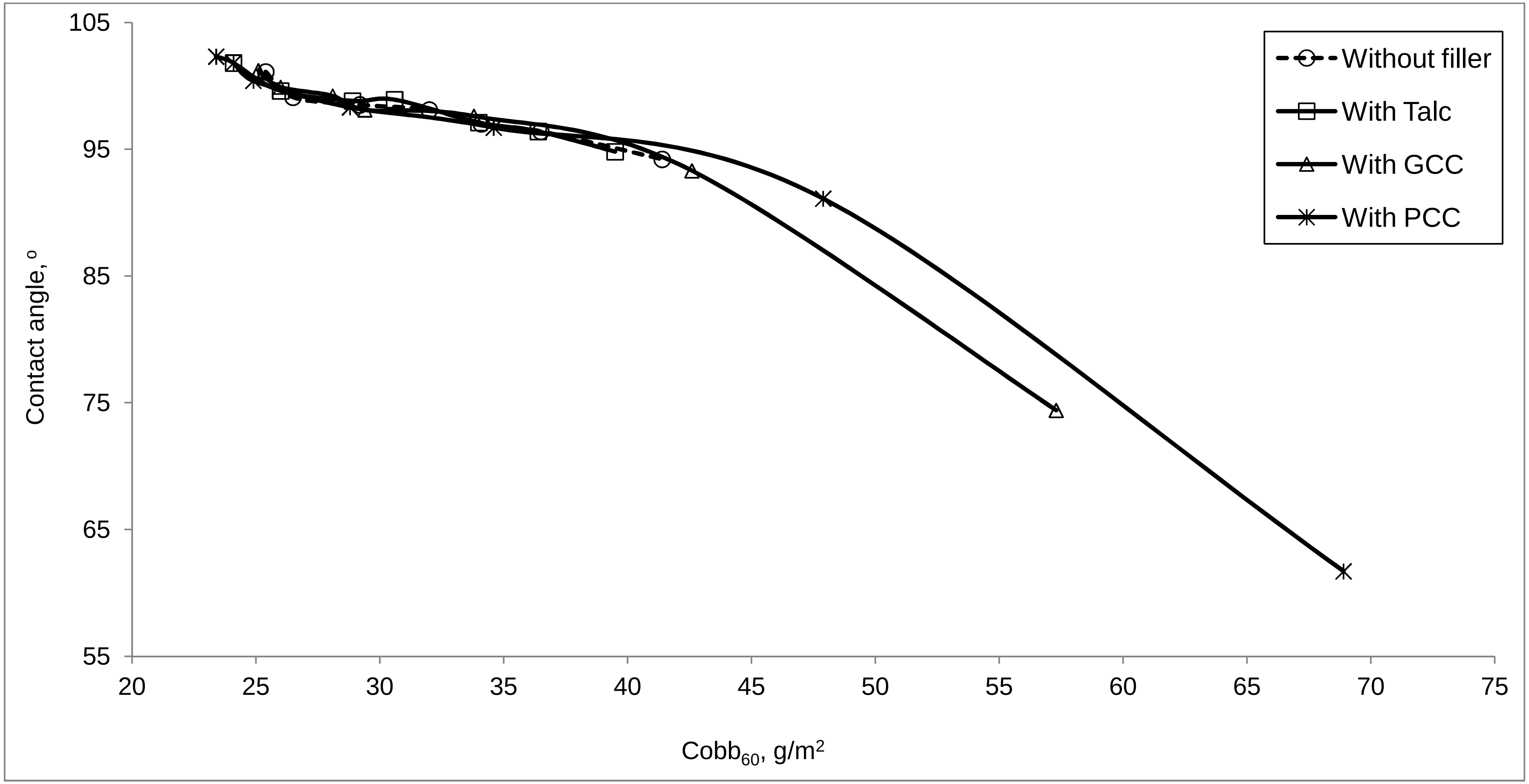


Table 45: $Cobb_{60}$ vs. contact angle relationship of BWS pulp in ASA sizing with different fillers

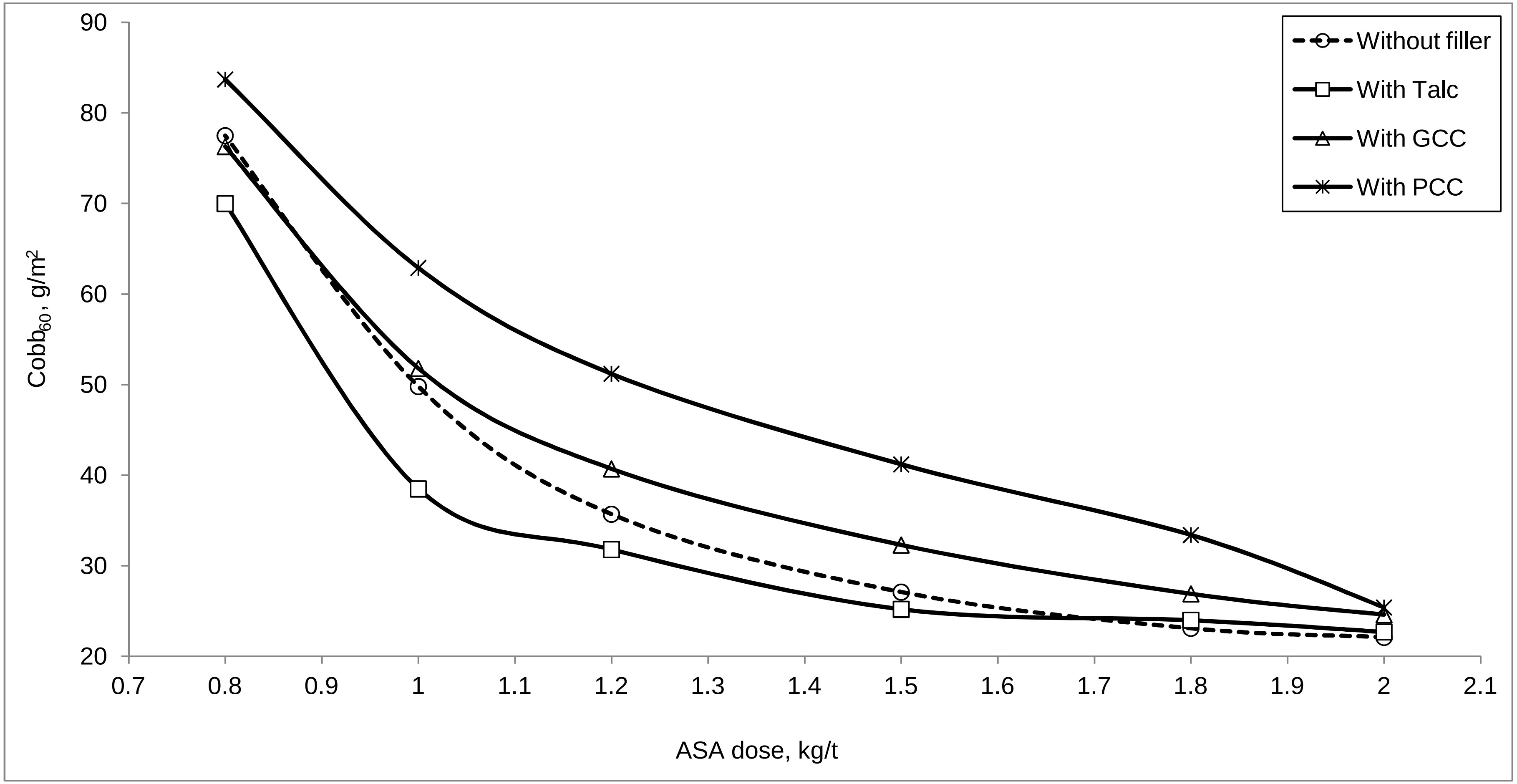


Figure 46: Effect of filler on $Cobb_{60}$ value with BRC pulp in ASA sizing

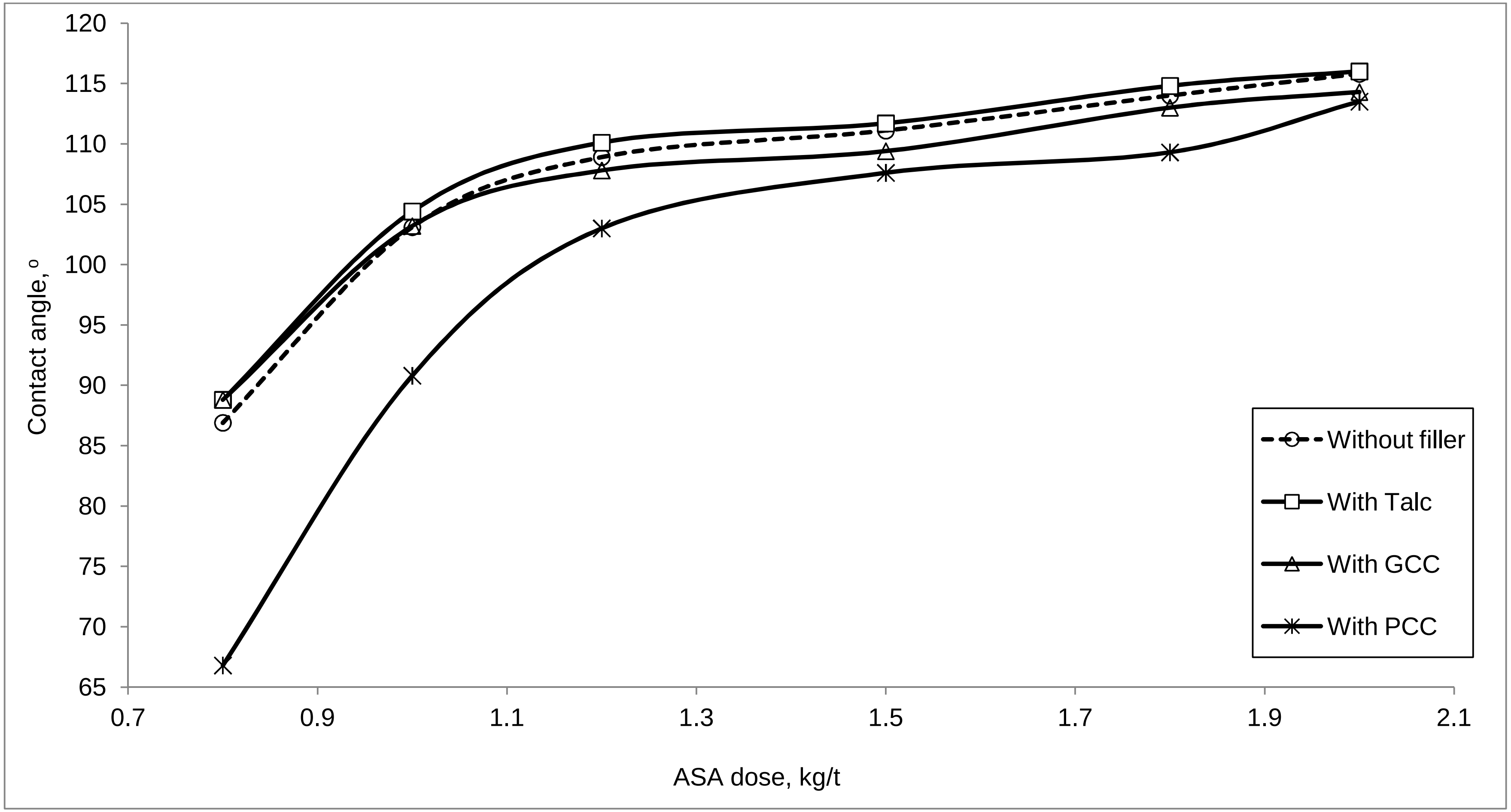


Figure 47: Effect of filler on contact angle with BRC pulp in ASA sizing

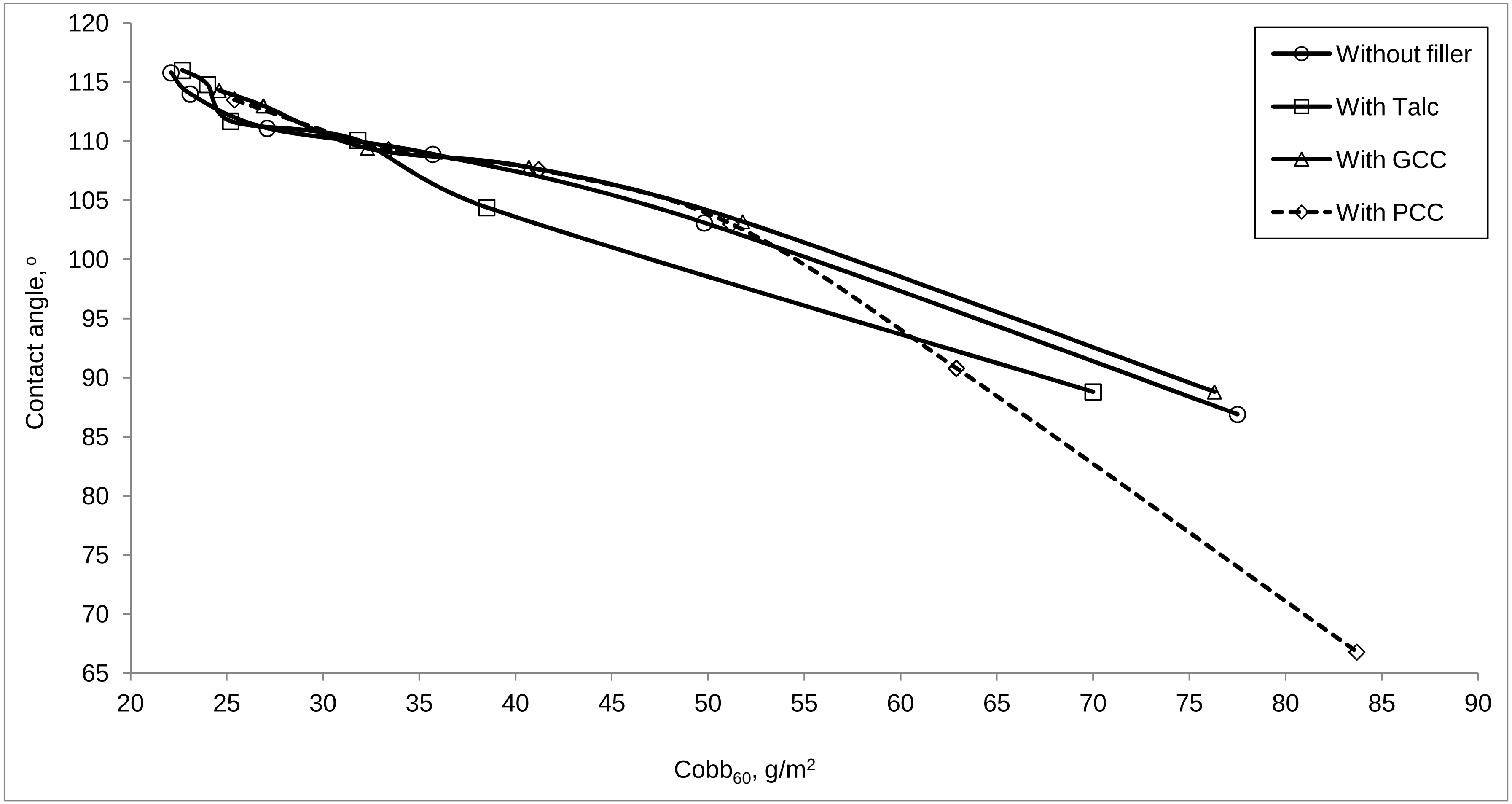


Table 48: $Cobb_{60}$ vs. contact angle relationship of BRC pulp in ASA sizing with different fillers

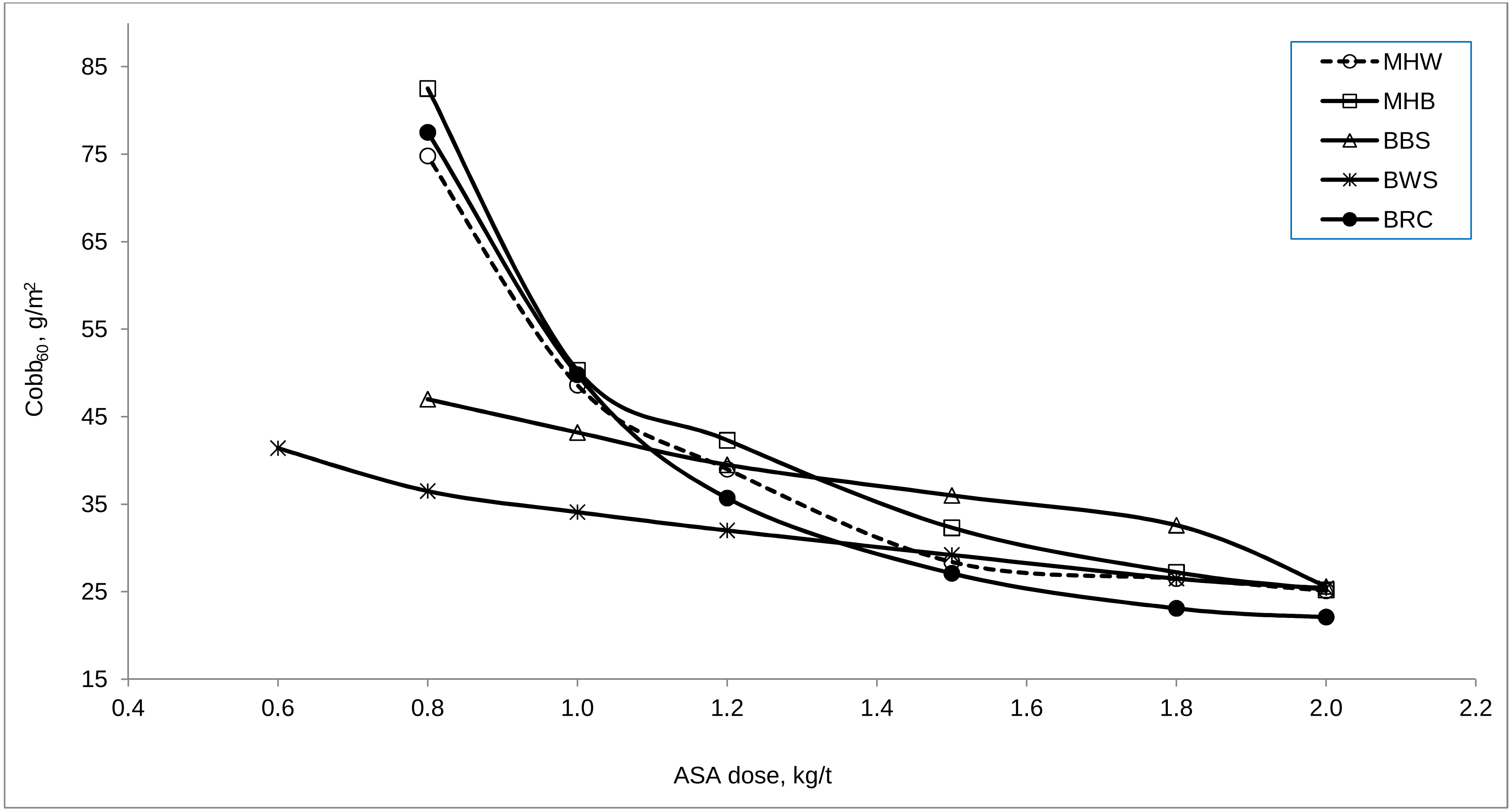


Figure 49: Comparison of $Cobb_{60}$ value of different pulp furnishes in ASD sizing (without filler)

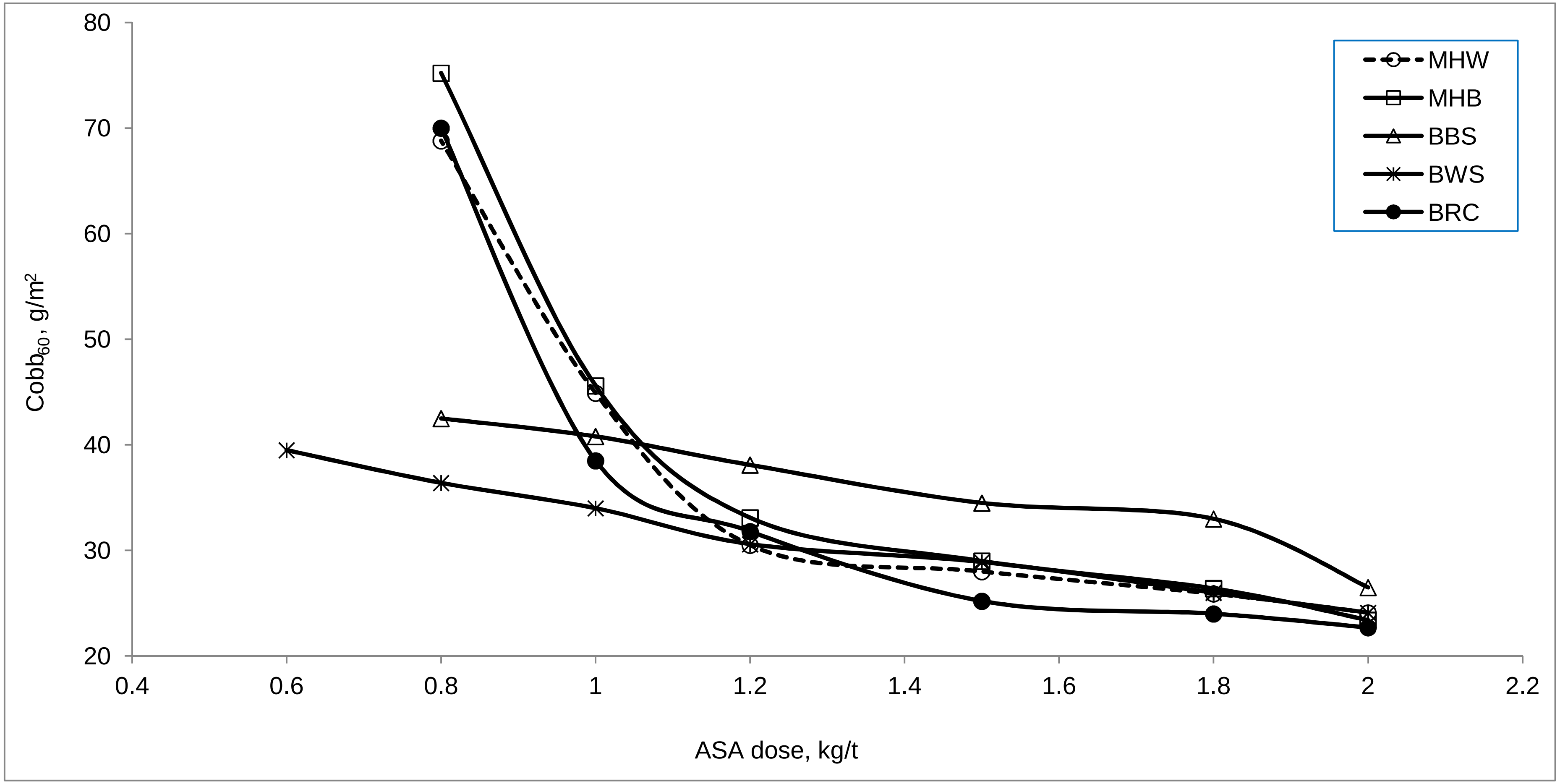


Figure 50: Comparison of $Cobb_{60}$ value of different pulp furnishes in ASA sizing with talc filler

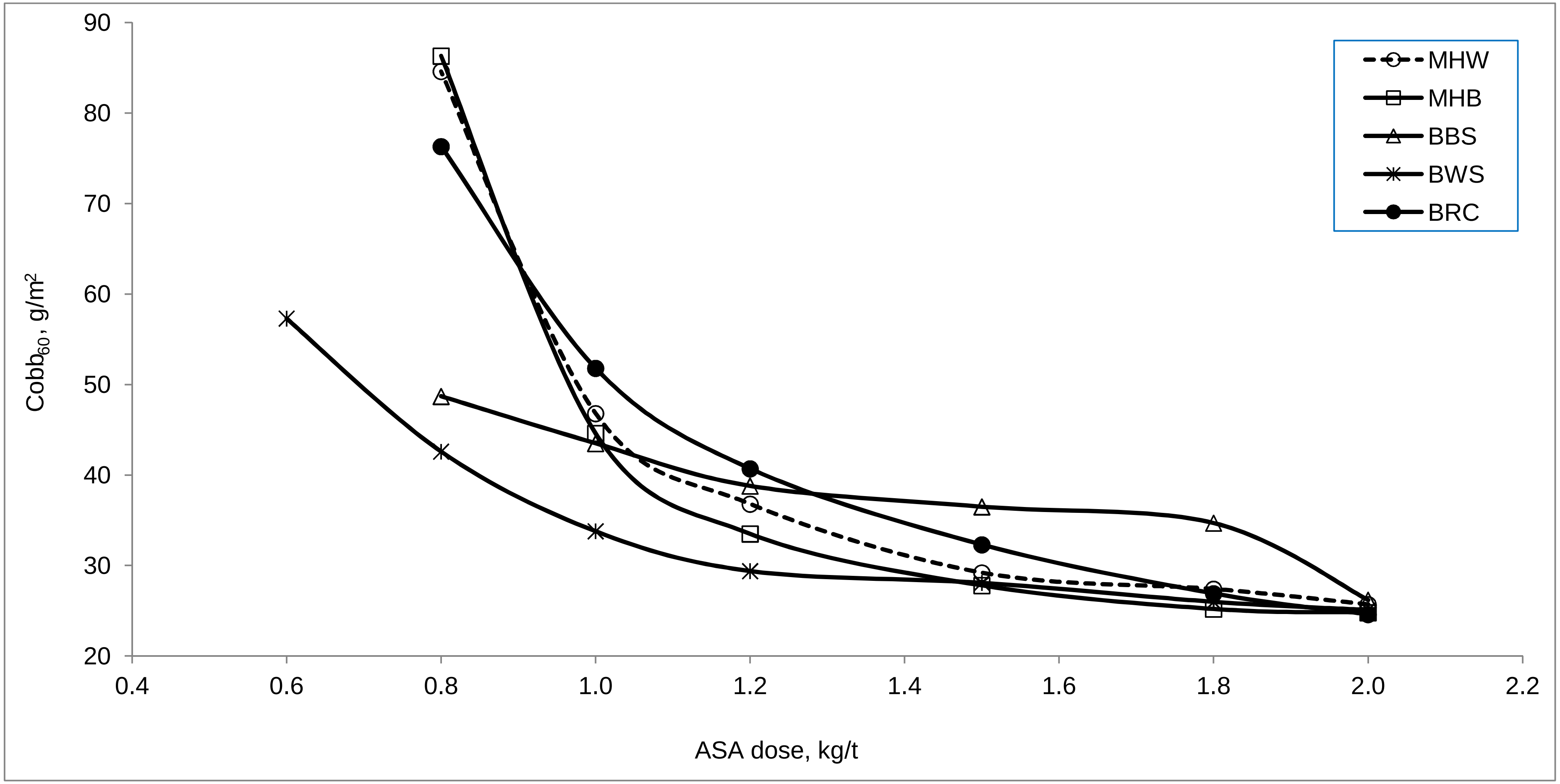


Figure 51: Comparison of $Cobb_{60}$ value of different pulp furnishes in ASA sizing with GCC filler

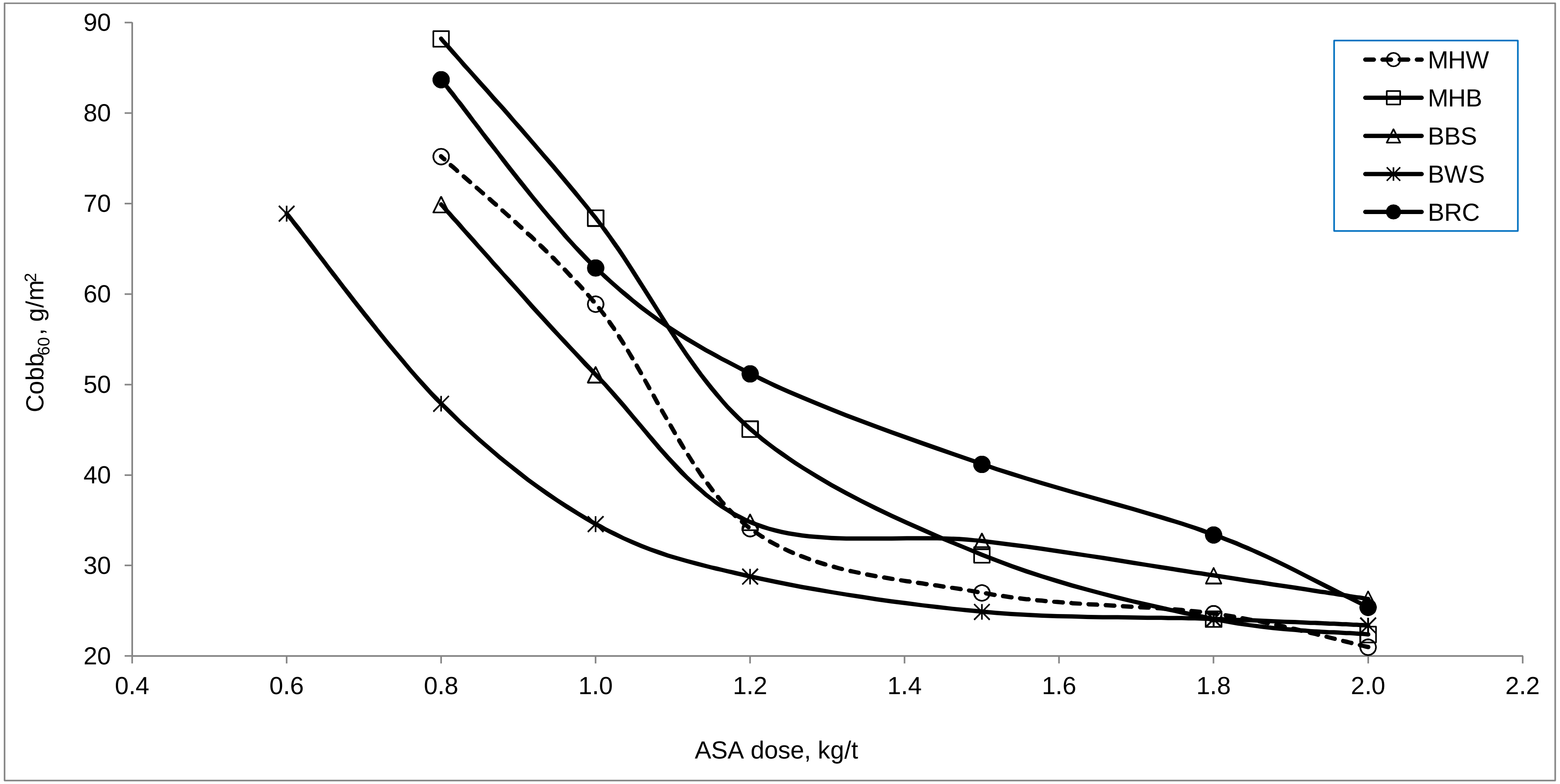


Figure 52: Comparison of $Cobb_{60}$ value of different pulp furnishes in ASA sizing with PCC filler

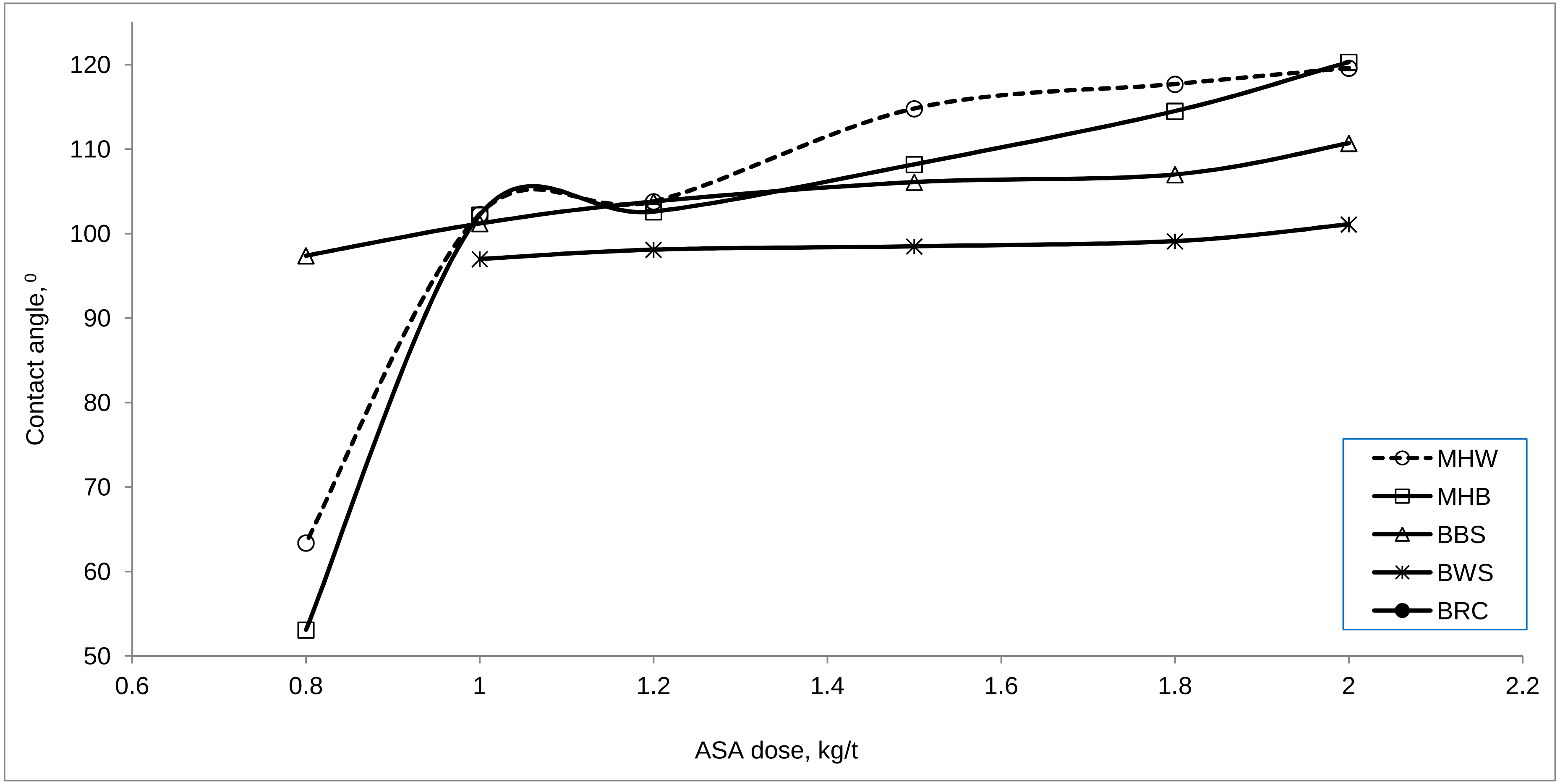


Figure 53: Comparison of contact angle of different pulp furnishes in ASA sizing (without filler)

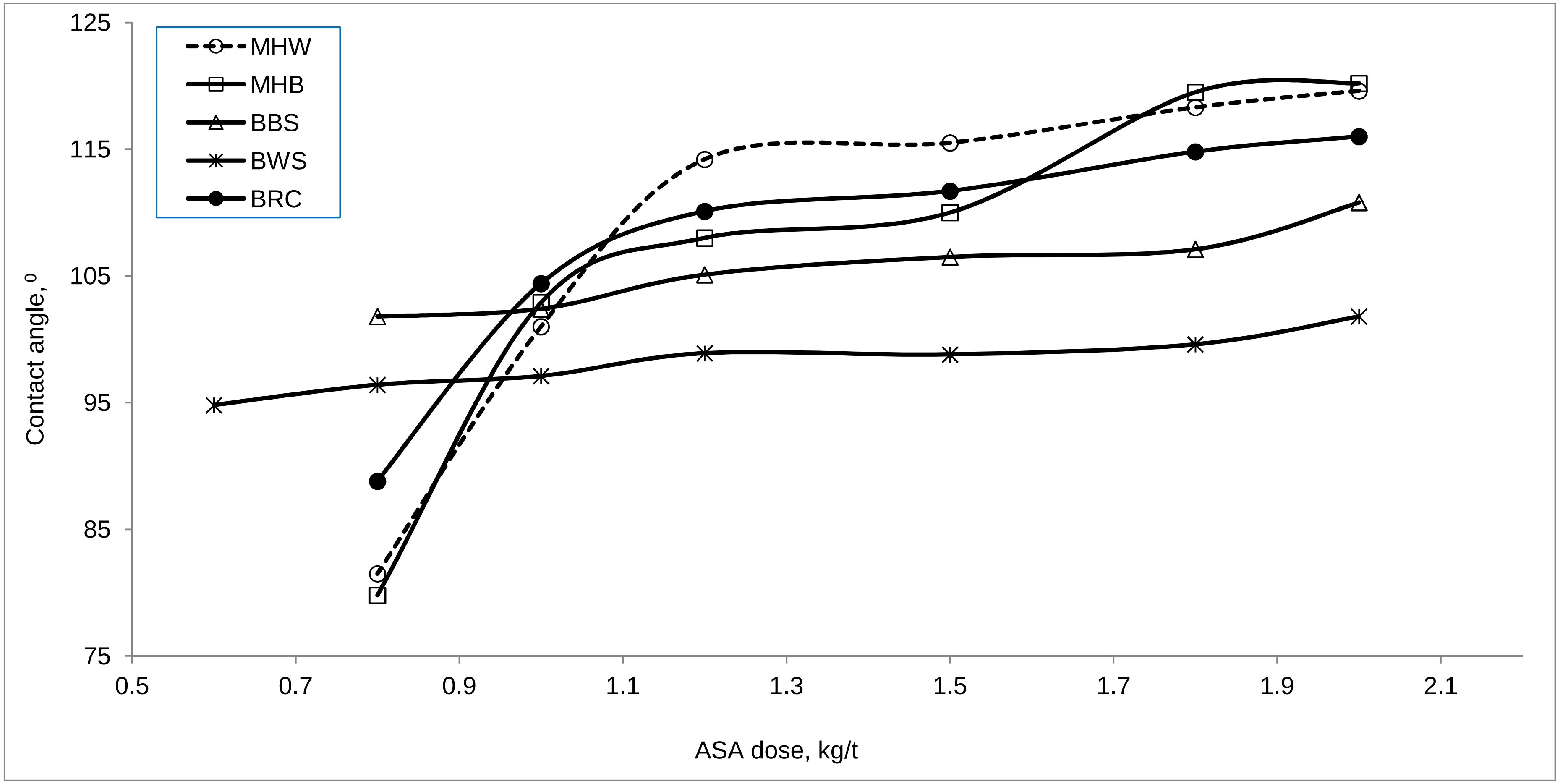


Figure 54: Comparison of contact angle of different pulp furnishes in ASA sizing with talc filler

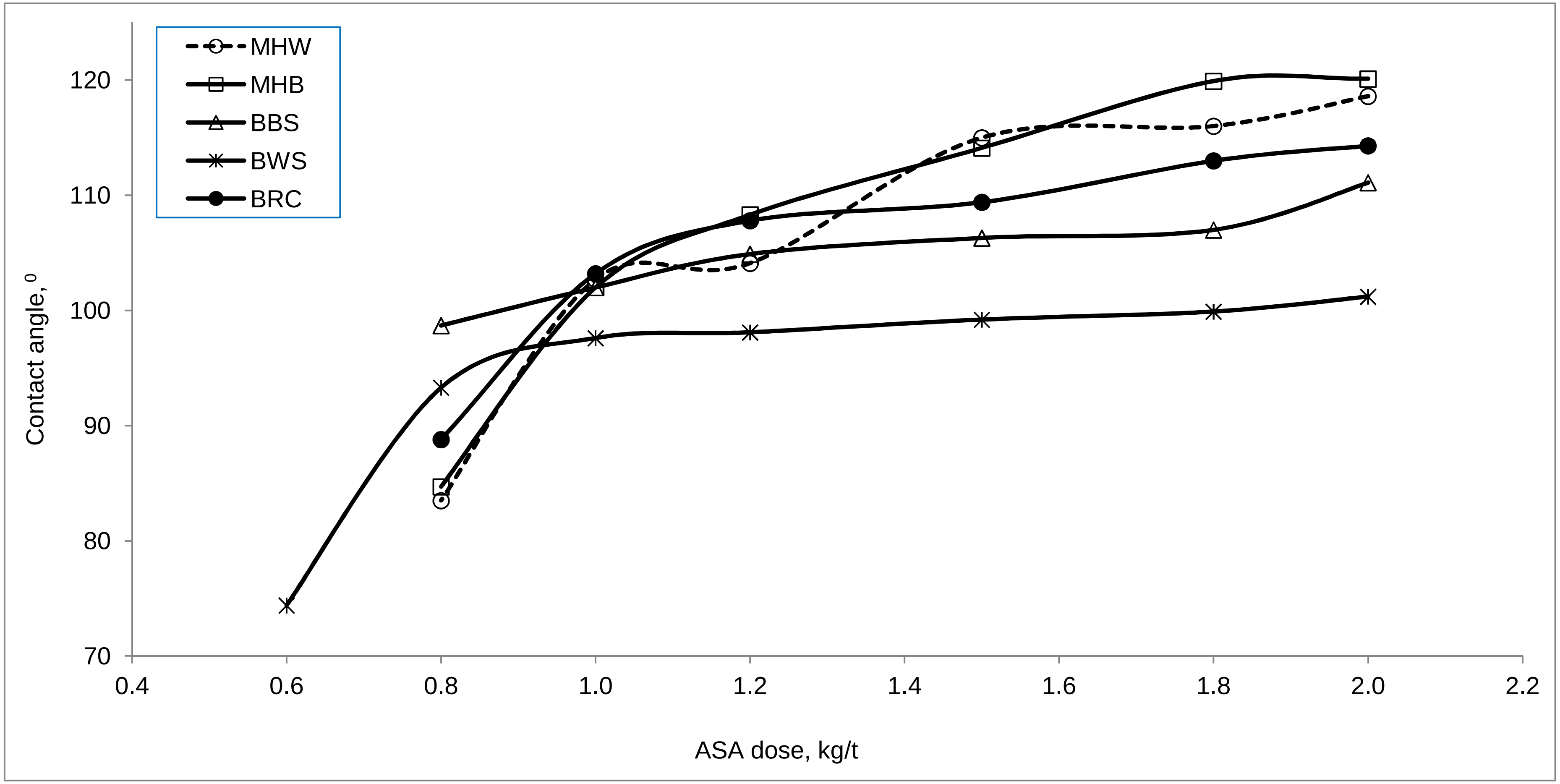


Figure 55: Comparison of contact angle of different pulp furnishes in ASA sizing with GCC filler

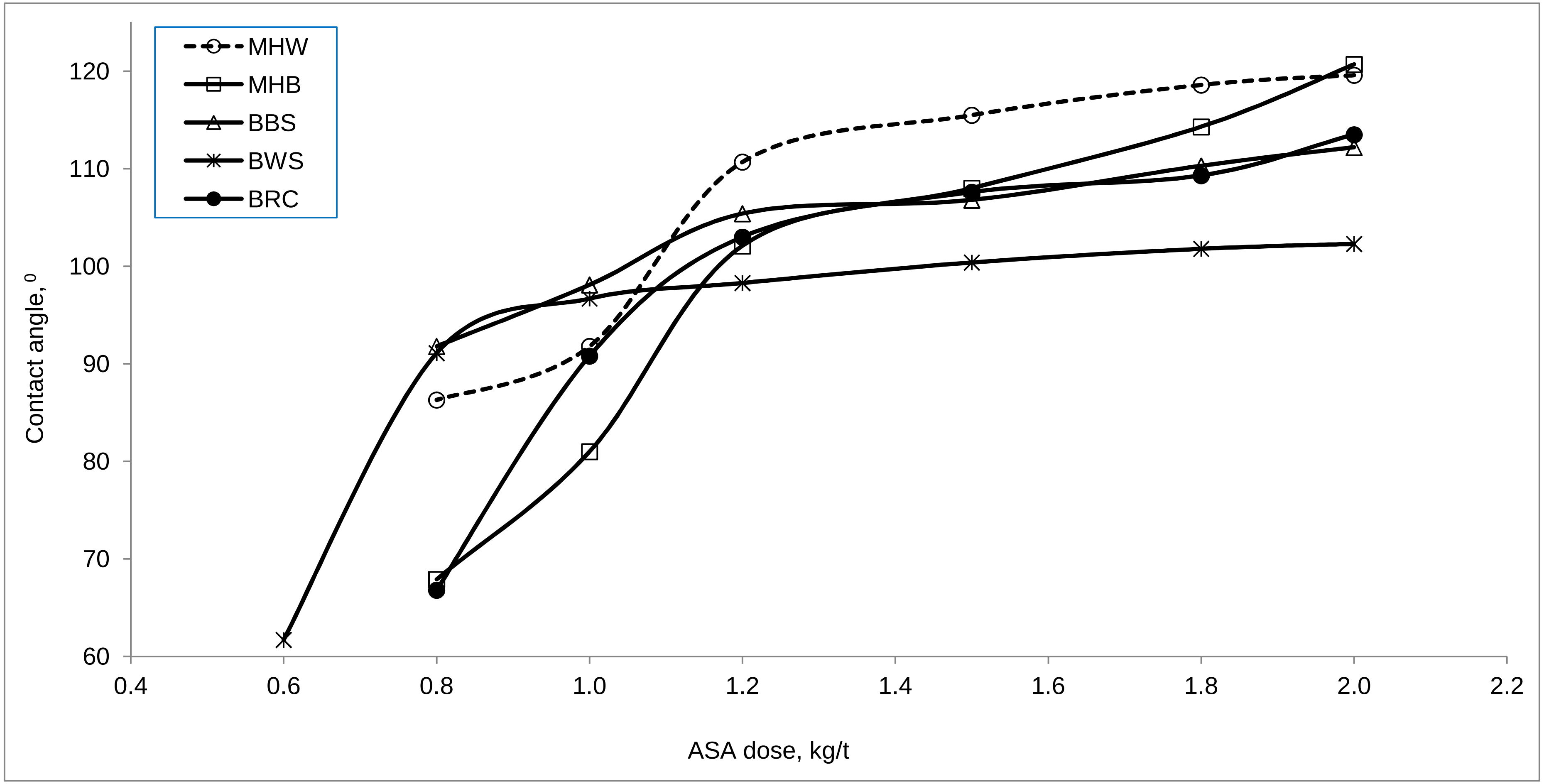


Figure 56: Comparison of contact angle of different pulp furnishes in ASA sizing with PCC filler

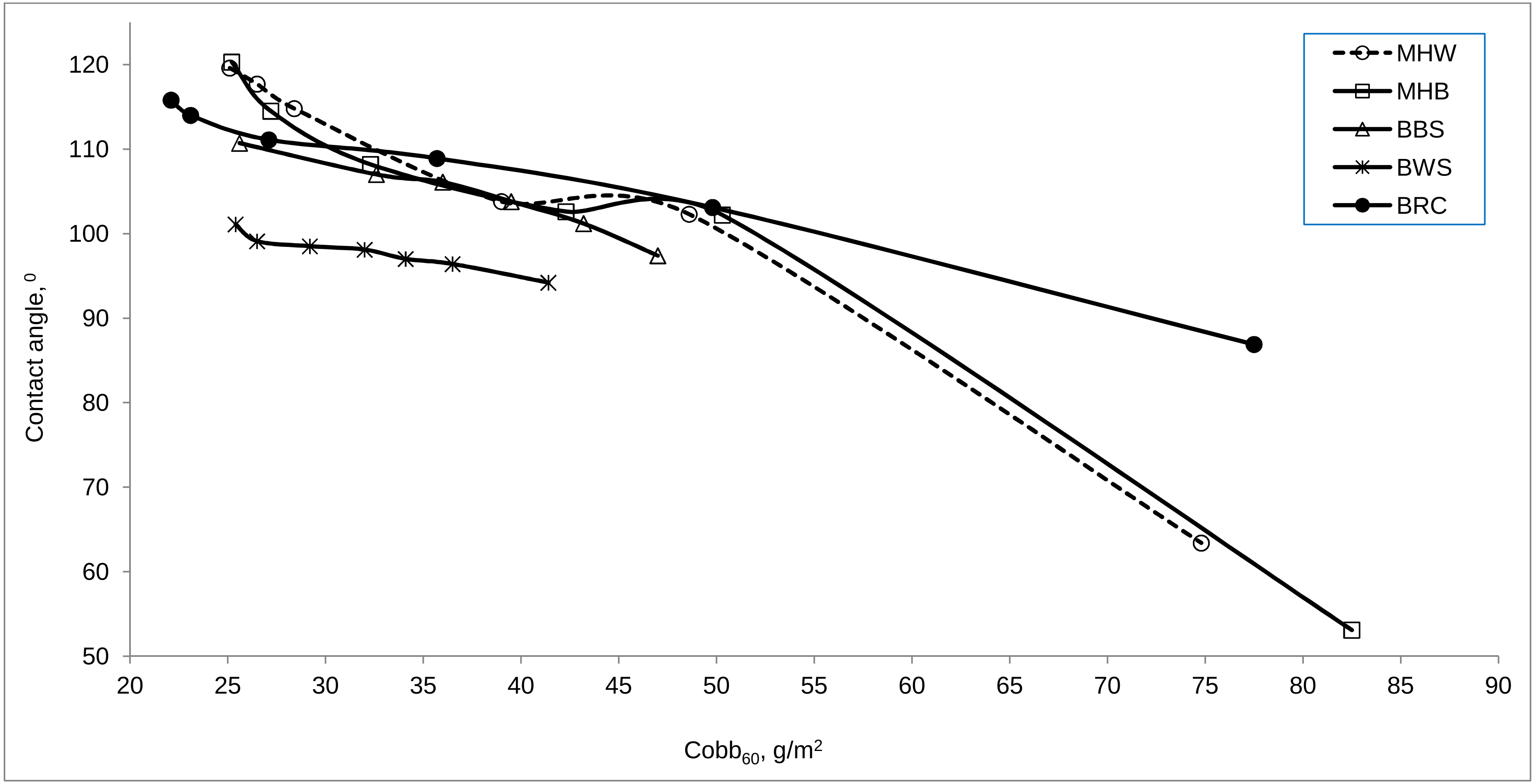


Figure 57: $Cobb_{60}$ vs. contact angle relationship for different pulp furnishes in ASA sizing (without Filler)

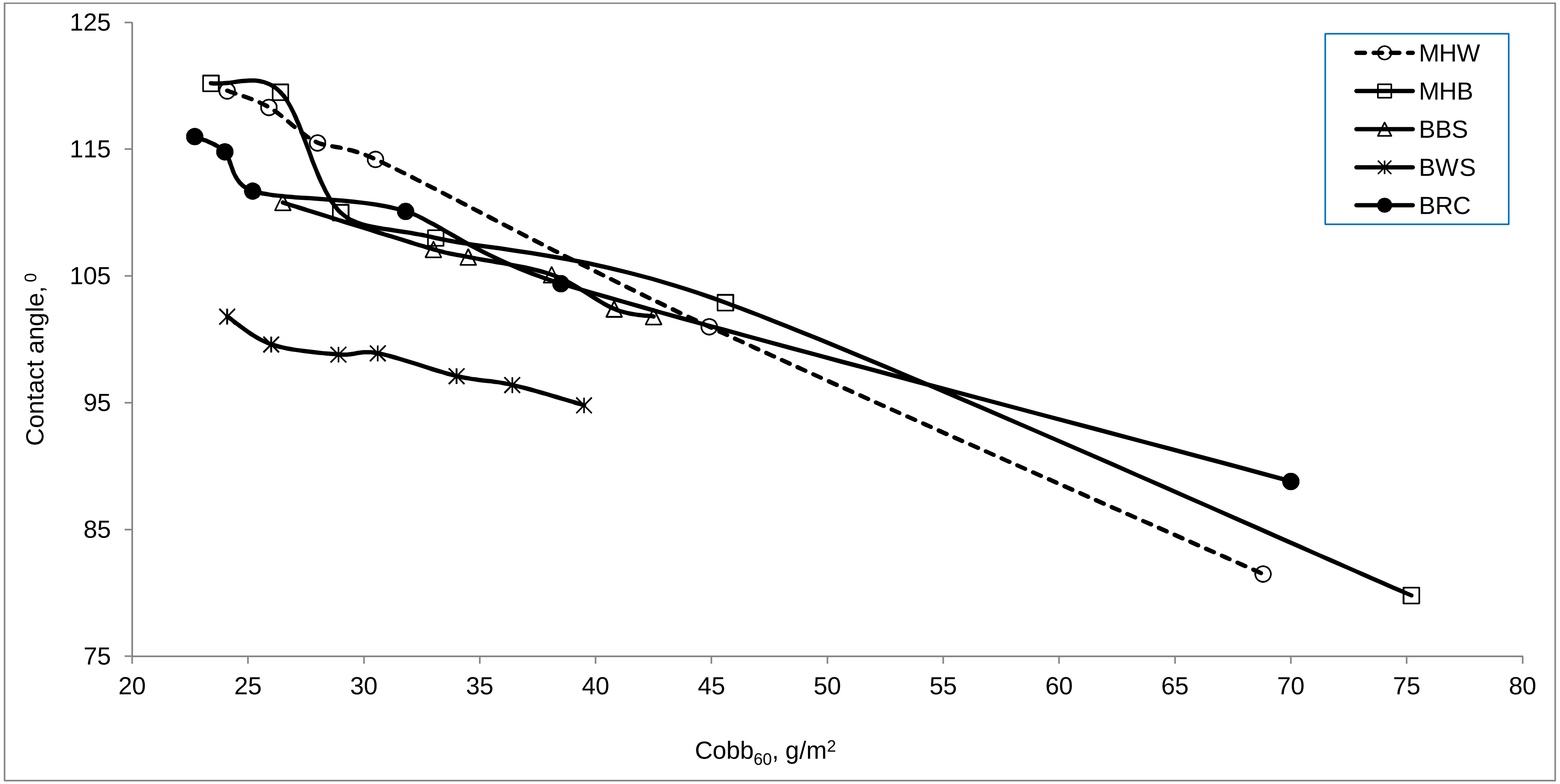


Figure 58: Cobb vs. contact angle relationship for different pulp furnishes in ASA sizing with talc filler

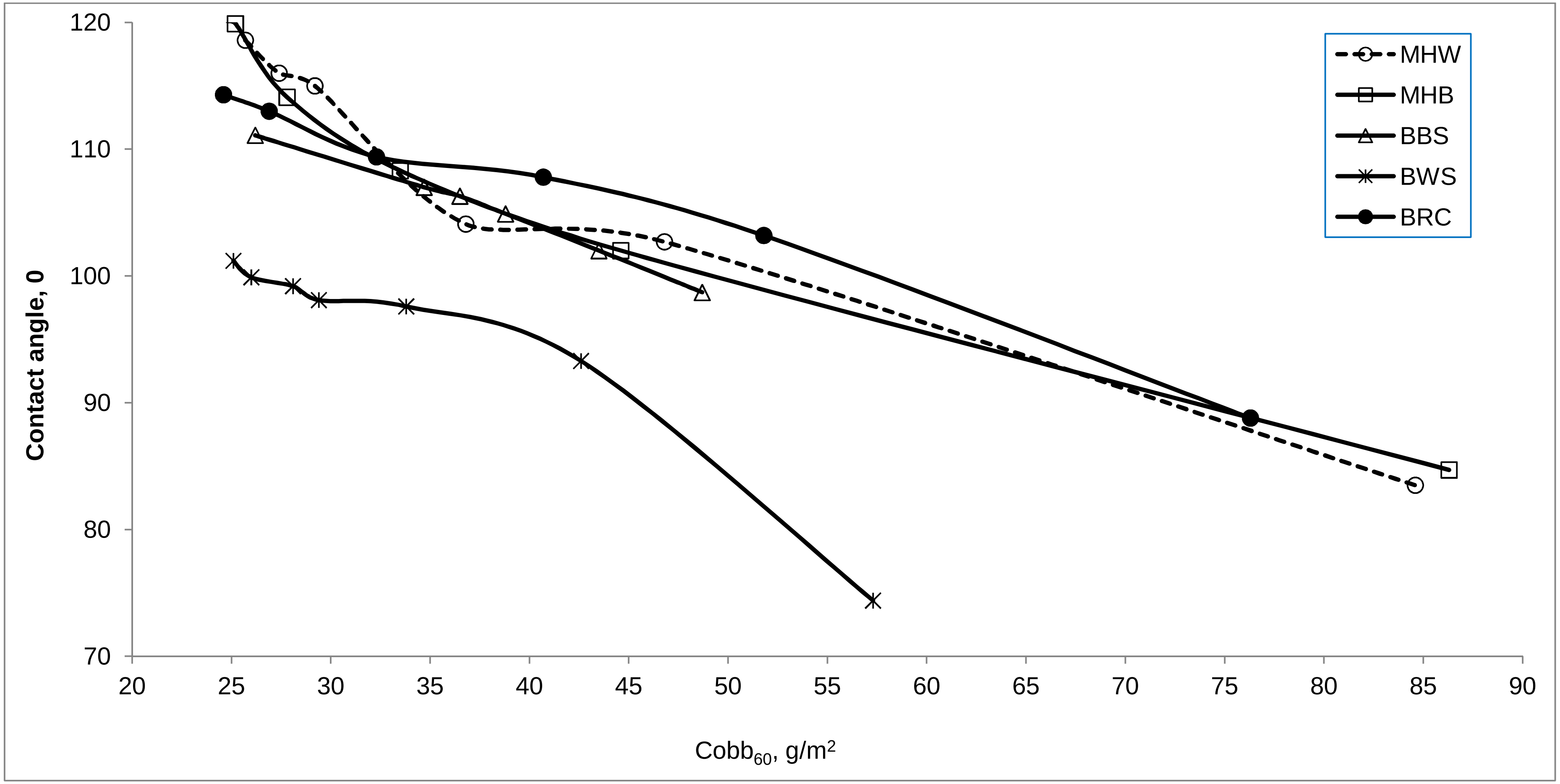


Figure 59: Cobb vs. contact angle relationship for different pulp furnishes in ASA sizing with GCC filler

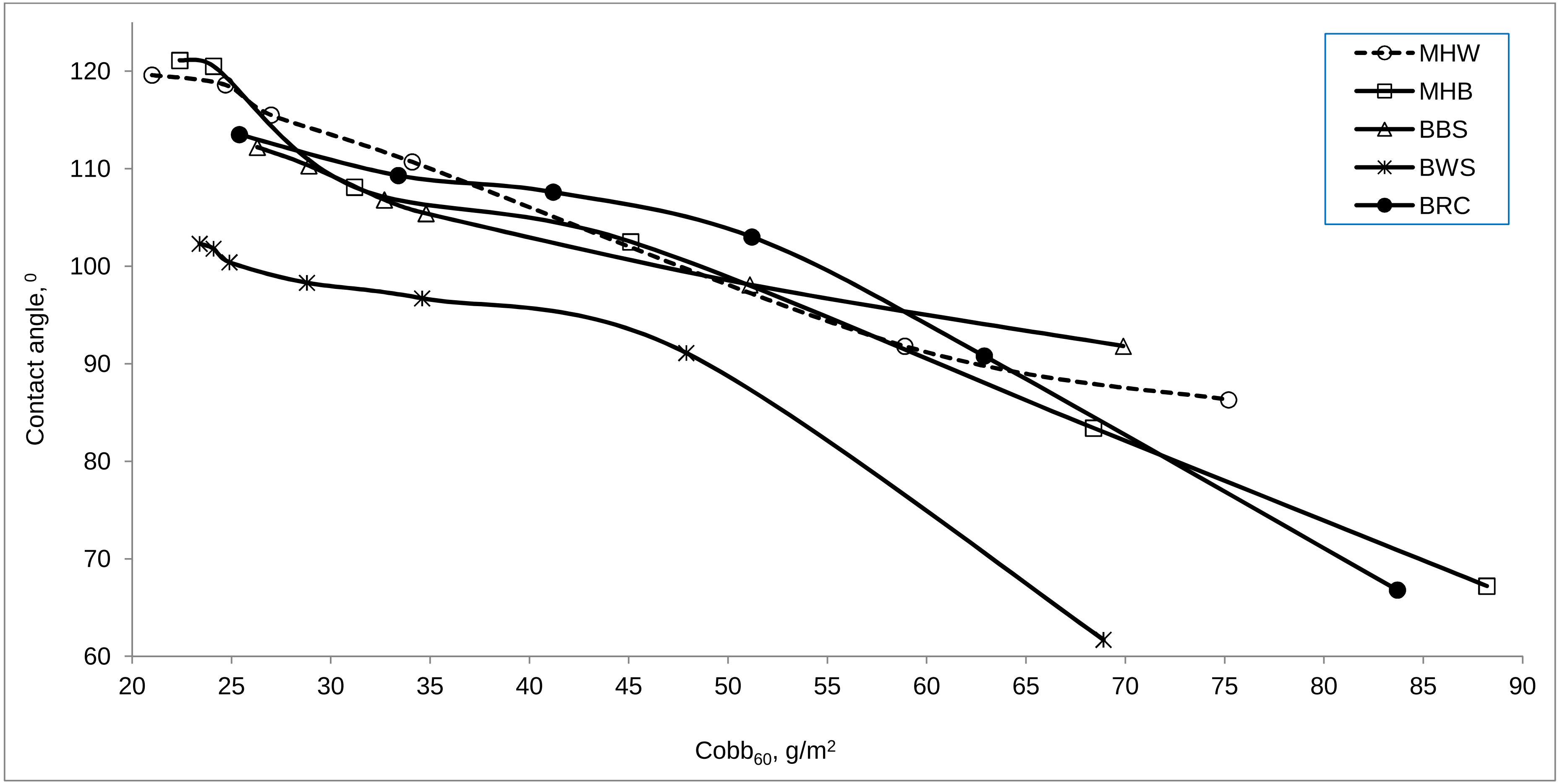


Figure 60: Cobb vs. contact angle relationship for different pulp furnishes in ASA sizing with PCC filler

**ANNAXURE-1**

## A study on why GCC-2 is compatible with ASA sizing & GCC-1 with AKD

It was found that shifting of chemical equilibria towards right is actually responsible for inferior sizing performance of GCC-1 with ASA sizing. The two responsible factors for which are as follows, More cationicity introduced by the wet end chemicals in case of ASA sizing as reflected by the values of zeta potential as shown in fig. 1. Cationic nature of GCC-1 with low anionic demand

Table 1: Sizing performance of ASA emulsion With GCC-1 as filler (After Maintaining ZP)

| ASA, kg/t | $Cobb_{60}$, $g/m^2$ | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV |
|---|---|---|---|---|---|
| 2.0 | 24.3 | -228.1 | -7.8 | 0.421 | -7.2 |
| 1.8 | 26.5 | -233.3 | -9.1 | 0.409 | -8.8 |
| 1.2 | 38.6 | 282.3 | -9.5 | 0.395 | -9.4 |

Sequence: MHB pulp + Cartaflex IGS, 0.8kg/t + PAC,4 kg/t + CS, 2 kg/t + ASA + GCC, 250 kg/t – make-up to 0.33% cy + CPAM, 100 g/

Table 2: Optimization of Dispersant (PA-40) dose for GCC filler

| | GCC-1 | | | GCC-2 |
|---|---|---|---|---|
| | Without dispersant | Using Dispersant (PA-40) | | |
| | | AS such | 10% diluted | |
| GCC concentration, % | 10 | | | |
| Wieght of PA -40 consumed, mg | Nil | 22 | 2.4 | Nil |
| Streaming potential, mv | +256 | -539 | -382 | -632 |
| Charge, μeq/l | +30 | >4000 | -398.6 | -390 |

Table 3: Sizing performance of ASA emulsion With GCC-1 as filler (using PA-40 as dispersant)

| ASA, kg/t | $Cobb_{60}$, g/m$^2$ | Potential, mV | Charge, μeq/l | Conductivity, mS | Zeta potential, mV |
|---|---|---|---|---|---|
| 2.0 | 25.2/27.2 | -244.3 | -6.2 | 0.399 | -7.2 |
| 1.8 | 26.5/30.2 | -263.6 | -6.7 | 0.393 | -8.6 |
| 1.2 | 37.2/45.6 | -289.0 | -7.3 | 0.391 | -10.7 |

Sequence: MHB pulp + Cartaflex IGS, 0.8kg/t + PAC,4 kg/t + CS, 2 kg/t + ASA + GCC, 250 kg/t – make-up to 0.33% cy + CPAM, 100 g/t

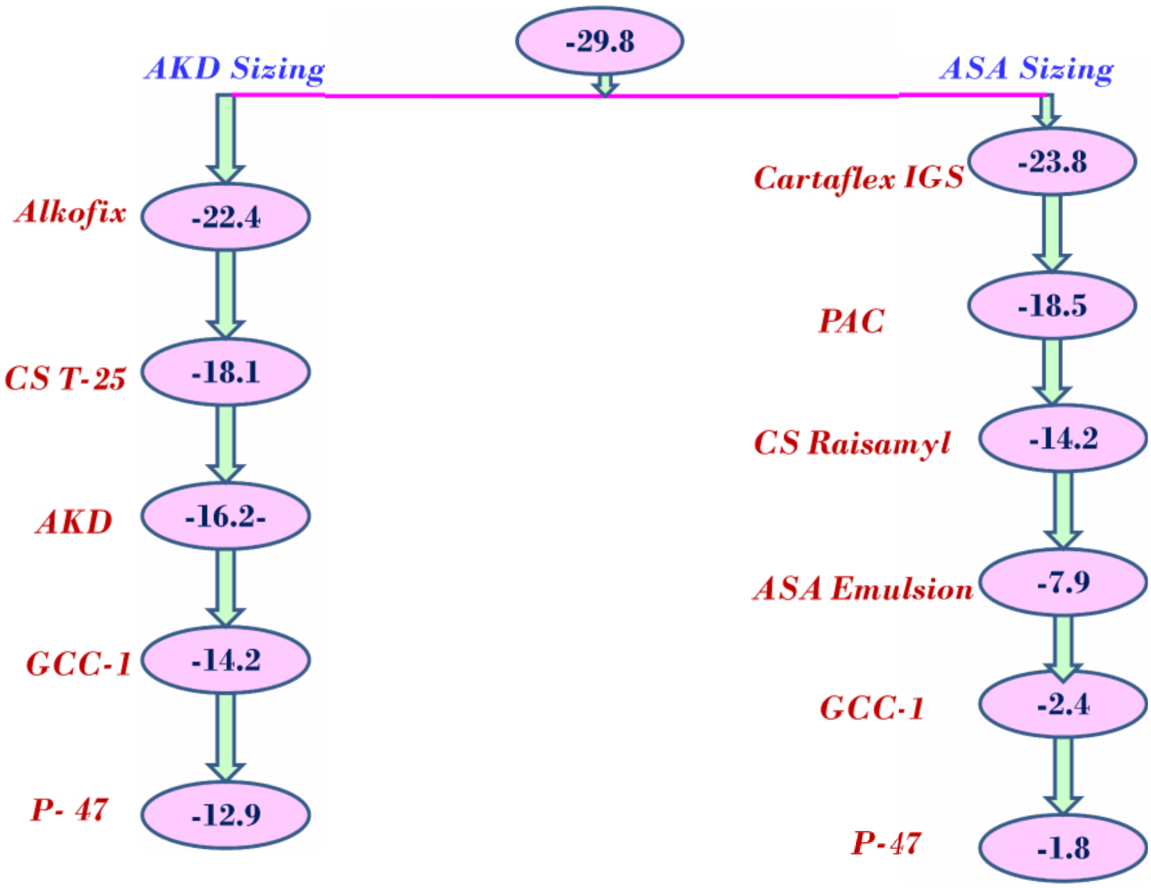


Fig:1 Study on charge demand of pulp stock at various stages during its preparation using different sizing agents

**ANNAXURE-2**

## Study on why contact angles using Agro residues for paper making are on lower side

### Surface roughness and contact angle

- Contact angle is directly related to the surface roughness

  The roughness ( r ) of a surface is defined as: r = True area/projected area

- For a rough surface, the contact angle is defined by Wenzel equation:

  where r = "surface roughness"

$$\cos\theta_{Apparent} = r \cos\theta_{True}$$

According to this equation, the roughness of a surface further decreases the contact angle if the contact angle is < 90° , whereas the roughness further increases the contact angle if the contact angle is > 90° (1).

- A droplet can sit on a solid surface in two distinct configurations or states (Fig.1). It is said to be in Wenzel state when it is conformal with the topography.
- Wenzel's equation explained earlier is used to compute the apparent contact angle.
- The other state in which a droplet can rest on the surface is called the Fakir state, where it is not conformal with the topography and only touches the tops of the protrusions on the surface.
- This leads to the formation of a composite surface with trapped air pockets.

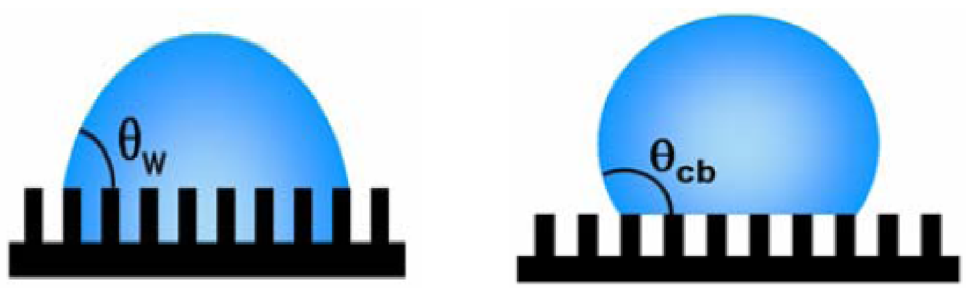


Figure:- 1 Wenzel state (Stable)　　　　Fakir State (Metastable)

- The apparent contact angle of a sessile droplet varies not only with physical texture or the roughness but also with the chemical texture determined by the composition of the solid surface

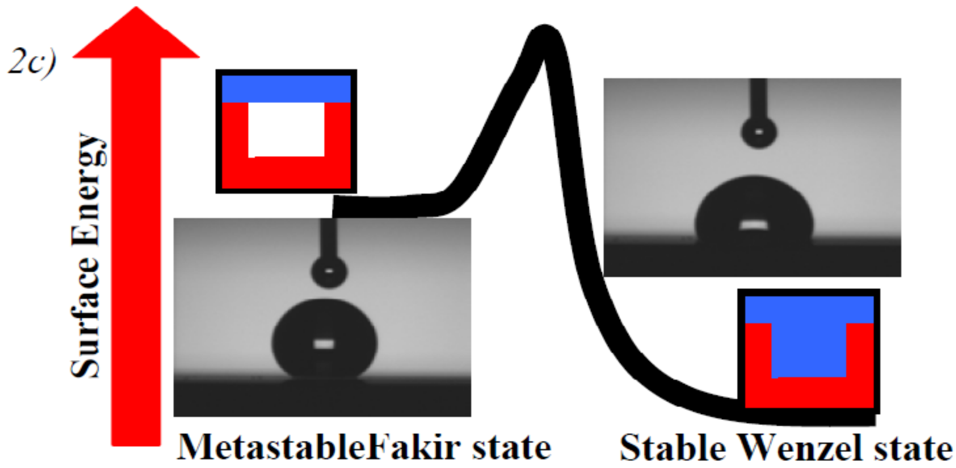


Figure:-2 Schematic drawing to show the energy barrier that stabilizes the metastable Fakir state (2)

Table:-1 Contact angles of commercial paper samples

| Sample | Furnish composition | Sizing chemical | $Cobb_{60}$, $g/m^2$ | Smooth | | Rough | |
|---|---|---|---|---|---|---|---|
| | | | | Contact angle, ° | Surface energy, mN/m | Contact angle, ° | Surface energy, mN/m |
| HBSP, Shreyans-70 | BWS-95%, SW-5% | AKD (No surface sizing) | 31 | 96.2 | 25.36 | 108.6 | 17.93 |
| HBSP, Shreyans-60 | | | 25 | 95.6 | 25.73 | 104.5 | 20.33 |
| HBSP, Shreyans-80 | | | 23 | 97.1 | 24.81 | 102.4 | 21.61 |
| HBSP, Shreyans-64 | | | 21 | 97.4 | 24.65 | 108.3 | 18.06 |
| Emami Cream wove DLX-80 | Imp. Office waste 35%, Ind. Off record 43% Ind text books 22% | AKD | 18 | 107.6 | 18.48 | 115.6 | 13.93 |
| Emami Maplitho-60 | Imp. Office waste 35%, Ind. Off record 43% Ind text books 22% | AKD | 20 | 108.5 | 17.98 | 113.8 | 14.94 |
| TNPL Copier-80 | BBG-95%, SW-5% | AKD, Surface sizing with starch | 22 | 107.8 | 18.39 | 115.5 | 13.97 |
| Century Excel-70 | MHW 95%,SW 5% | | 15 | 112.5 | 15.64 | 115.9 | 13.79 |
| Century Premium 60 | MHW 10%, BRC 90% | AKD & ASA (No surface sizing) | 24.1 | 105.2 | 19.92 | 114.2 | 14.70 |
| Century Premium 70 | | | 21.7 | 102.6 | 21.47 | 113.3 | 15.21 |
| Century SS Maplitho 70 | MHW 5%, SW 7%, BBG 88% | AKD, Surface sizing with starch | 24.2 | 106.8 | 18.94 | 113.4 | 15.18 |

**Effect of super calendering on paper properties**

Table 2. Effect of super calendering on physical properties of paper

| Furnish | | Roughness, ml/min | | Air permeance, Gurley S |
|---|---|---|---|---|
| | | Felt | Wire | |
| Wheat straw | Without filler | 46 | 333 | 336 |
| | With GCC | 28 | 291 | 190 |
| | With PCC | 34 | 301 | 82 |
| Bagasse | Without filler | 92 | 348 | 29 |
| | With GCC | 87 | 334 | 26 |
| | With PCC | 84 | 356 | 19 |

Table 3. Effect of super calendering on sizing properties of paper

| Furnish (Without filler) | Cobb, g/m$^2$ | | Contact angle, degree | | Surface energy, mN/m | |
|---|---|---|---|---|---|---|
| | Felt | Wire | Felt | Wire | Felt | Wire |
| Wheat straw | 23.5 | 24.2 | 97.5 | 104.3 | 24.60 | 20.36 |
| | 28.8 | 29.4 | 86.8 | 101.8 | 31.37 | 21.84 |
| Bagasse | 24.2 | 25.3 | 101.7 | 103.3 | 21.86 | 21.06 |
| | 30.1 | 31.6 | 100.9 | 102.5 | 23.01 | 21.49 |

Effect of super calendering on Roughness

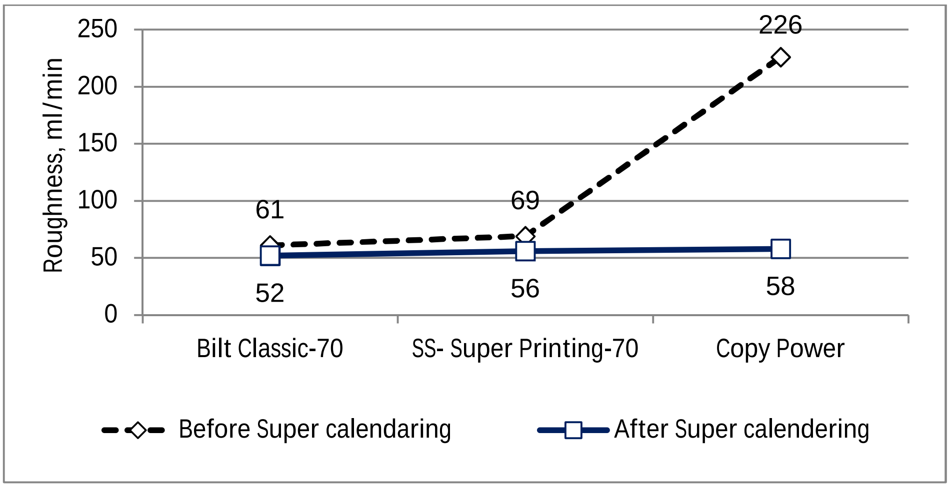


Figure 3. Effect of super calendering on felt side of paper

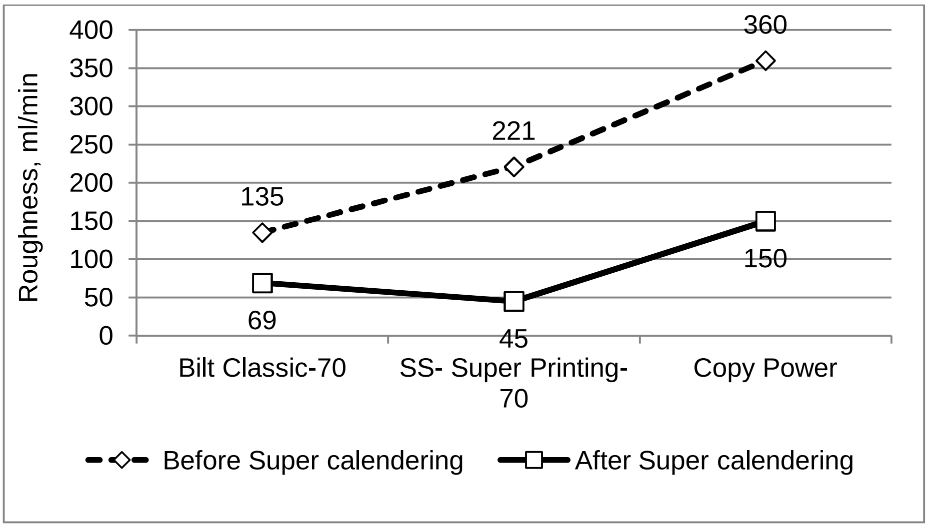


Figure 4. Effect of super calendering on felt side of paper

**Effect of super calendering on contact angles**

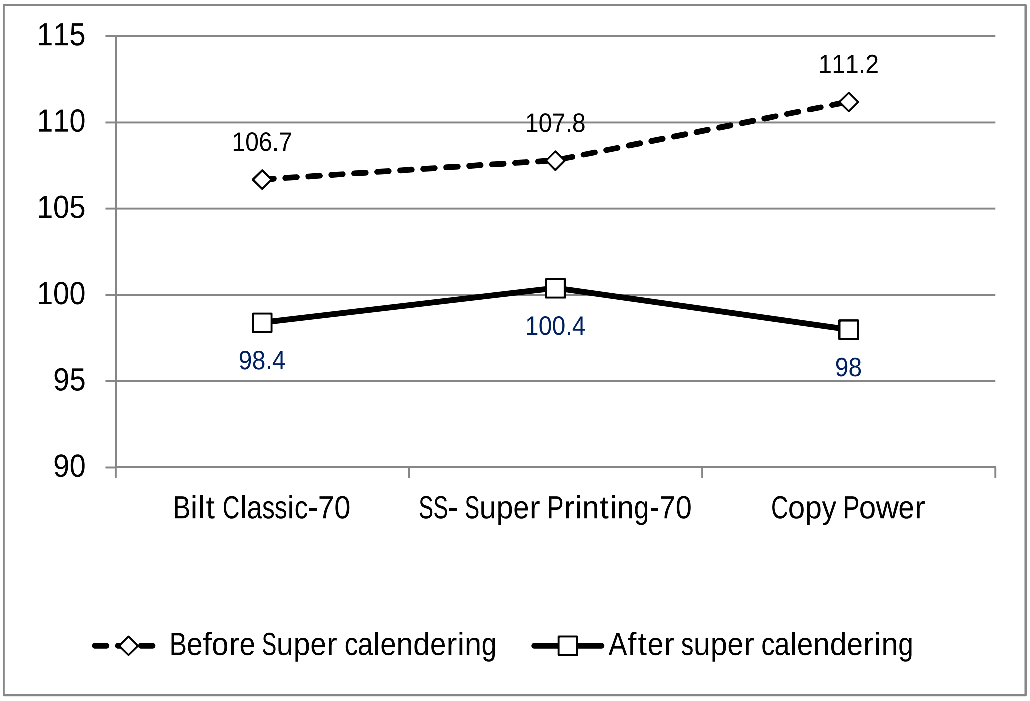


Figure 5. Effect of super calendering on contact angle of felt side of paper

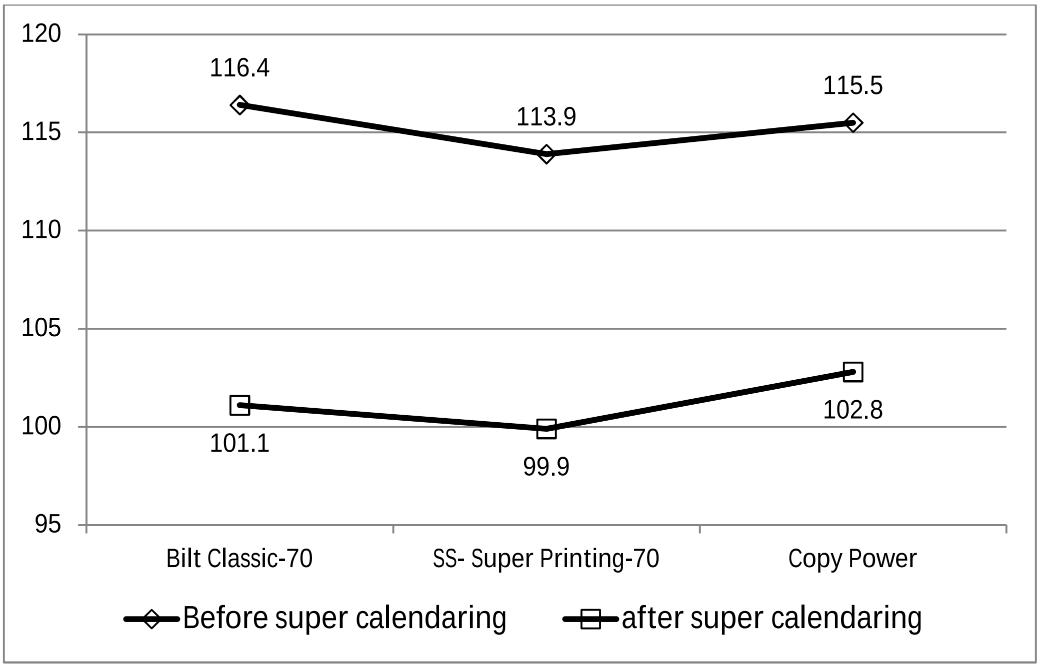


Figure 6. Effect of super calendering on contact angle of felt side of paper

## REFERENCES

1) http://www.gsishop.com/webmagzine/20020925/contact.htm#top
2) ENGINEERING SURFACE ROUGHNESS TO MANIPULATE DROPLETS IN MICROFLUIDIC SYSTEMS, Ashutosh Shastry, Marianne J. Case and Karl F. Böhringer , Department of Electrical Engineering, University of Washington, Seattle, USA

***** End of Report *******