

Properties of Paper Manufactured from Kenaf as Function of Alkaline pH Medium and Retention of Precipitated Calcium Carbonate

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ABSTRACT

The objective of this study was to have a better understanding of the effect of alkaline pH medium in the retention of filler in papermaking using kenaf bleached pulp. Three stages of experiments were carried out involving papermaking at alkaline pH medium 8 to 13, usage of precipitated calcium carbonate (PCC), Albacar (ABC) of needle-shaped and Albafil (ABF) of circular-shaped, and the application of low and high molecular weight of polyacrylamides (PAM LM and PAM HM). Paper samples were manufactured based on TAPPI Test Method T295 om-88. Characterisation of specimens in terms of filler content, tensile, tear and burst strength were carried out. The results showed that pH medium influenced the inter-fibre bonding of the fibres during papermaking whereby pH 8-9 is found as the best medium in producing stronger paper. The findings are significant in order to suit the pH according to certain shape and size of such fillers.

Keywords: Alkaline papermaking, kenaf, paper strength, precipitated calcium carbonate, retention

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INTRODUCTION

Alkaline papermaking was initiated in Scotland using ground chalk to gain whiter products. This was also widely used in Europe since 1950s. In 1970s, due to the introduction of inexpensive filler namely ground calcium carbonate and improvements in alkaline sizing agents have increased the application of alkaline

papermaking (Gill & Scott, 1987). In 2002, about 70% of paper mills converted to alkaline papermaking due to availability of good alkaline sizing agents and precipitated calcium carbonate (PCC). The percentage rose where the conversion to alkaline papermaking reached 80% in North America and 85% in Western Europe (Chapnerkar, 2004). The most important advantage using alkaline medium in producing paper is alkaline papers could last for hundreds of years whereas acid paper disintegrates within 30 to 40 years. This is due to the use of calcium carbonate that neutralizes acid and prevents acid hydrolysis, which causes the disintegration of cellulose (Casey, 1981).

Since the 8th century, papermakers began substituting virgin pulp during papermaking with mineral fillers. There are many types of fillers such as clay, titanium dioxide, calcium carbonate, and PCC. Precipitated calcium carbonate is produced synthetically and used extensively in alkaline papermaking due to its contribution to paper brightness, opacity, maintaining bulk, sheet porosity and reducing fibre usage. It is also the most common mineral used in fine papers due to its high purity and light scattering (Kocman & Bruno, 1996). These benefit the papermakers in reducing manufacturing cost and improving printability (Kamiti & van de Ven, 1994). Filler decreases the energy demand in papermaking process because of the slighter amount of fibrous mass per unit weight of paper (Chauhan, et al., 2012). Precipitated calcium carbonate can be found at different crystalline forms such as rhombohedral (barrel-shaped), prismatic,

spherical, symmetrical, scalenohedral rosette-shaped and aragonite needle-like (Passaretti, et al., 1993). Such modified fillers can be a good approach to improve function and reduce drawbacks (Shen, et al., 2009).

Another important additive in alkaline papermaking is the retention aid. The demand for retention aid increased due to the incorporation of fillers in alkaline papermaking. Polyacrylamide (PAM) is a well-known retention aid and is widely used in the papermaking industry. It can be applied as anion, cation and neutral charge polymer. Based on Reynolds & Wasser (1981) PAM is usually used as cationic polymer. Additionally, the molar mass of PAM is an important factor in obtaining effective retention aid of filler. Polyacrylamide also functions as a dry strength agent in papermaking. The advantage of using PAM is its effectiveness at a wide range of pH, good performance without alum and its suitability in many types of pulp either virgin pulp or secondary pulp. It can increase the strength of paper such as its tensile, burst, internal bonding and fold. It also provides better retention for fine and fillers, easier drying process and increase paper size.

Based on a previous study, the pH equilibrium of PCC is reported to be around 9.4 where no additional chemicals are needed to adjust the pH because the PCC buffers the system (Chapnekar, 2004). Therefore, a study was carried out to investigate the influence of alkaline pH medium in the retention and precipitation performance

of PCC on kenaf whole stem fibres and in order to reduce undesired precipitation of calcium carbonate. The selected range of alkaline pH medium is 8-13. According to Berger, et al. (2008) kaolins, a kind of fillers with different morphologies, help to influence and prognosticate the properties of supercalendered paper. Therefore, PCC of different morphologies were selected and tested for their ability to retain fibres as the controlled alkaline medium. Besides, the polymers of high and low molecular weight polyacrylamide were used in order to enhance mechanical strength characteristics of the paper.

MATERIALS AND METHODS

Raw Material

The whole stem of kenaf chips, 2 cm in diameter, was pulped and bleached. The unbleached kenaf pulp was obtained from

kraft pulping with 17% alkali active and 25% sulphidity. Bleaching was carried out according to D₁EpD₂ sequences (D₁: bleaching using chlorine dioxide at first stage, Ep: extraction with NaOH, D₂: bleaching using chlorine dioxide at second stage). The whole stem was used throughout the experiment. Filler employed in the experiment was PCC of two types supplied by Specialty Minerals Incorporation, USA, labelled as Albacar (ABC) and Albfil (ABF). Both fillers were received in the dry state and are white in colour. Table 1 shows the properties of the fillers. Two cationic polyelectrolytes – a higher (HM) and lower (LM) molecular mass PAM were used as retention aids. The PAMs were obtained from Malaysian Adhesives Chemical Sdn. Bhd., Shah Alam, Selangor, Malaysia. Table 2 displays the properties of PAMs used for the experiments.

Table 1

The properties of two types of precipitated calcium carbonate used throughout the study

| Typical properties of raw material | PCC ABC | PCC-ABF |
|--|---------|-------------|
| Particle shape | rosette | symmetrical |
| Median particle size, μm (Sedigraph 5100) | 1.3 | 0.7 |
| Dry brightness (Hunter Y, Rd value) | 98 | 98 |

Table 2

The properties of PAMs used throughout the study

| Typical properties | Viscosity (poise) | Polimerisation rate (min) | Molecular weight (g/mol) |
|--------------------|-------------------|---------------------------|--------------------------|
| PAM LM | 21.5 | 60 | 300,000 |
| PAM HM | 45.0 | 180 | 3,000,000 |

Manufacturing Paper Samples

The papermaking was carried out in three stages (a) the preparation of control paper at a range of pH medium from 8 to 13, labelled as P-8, P-10 and P-12, (b) the preparation of filled-paper at a range of pH medium from 8 to 13 with the addition of PCC and (c) the preparation of selected filled-papers with the addition of PAM. These samples were labelled as ABC-126, ABC-123, ABF-106, ABF-103, ABC-8, ABC-10, ABC-12, ABF-8, ABF-10 and ABF-12. In the second stages of experiment, the mixture of kenaf bleached fibres and PCC fillers were carried out at a

ratio, 1:2. The polymer at 1% (g/g pulp) was added to the mixture and stirred in a British disintegrator, subjected to 3,000 rpm for ~25 mins. The amount of polymer was selected at 1% due to its best performance of filler loading and paper strength as reported in a previous study (Ainun, 2010). The mixture was adjusted to a required pH such as pH 8-9 or pH 10-11 or pH 12-13 throughout the papermaking process. The papermaking was carried out according to TAPPI T 295 om-88 producing basis weight of 60 g/m² paper. Table 3 shows the content of each sample.

Table 3
Content of paper produced in the experiment

| Sample | pH medium | Type of PCC | Type of PAM |
|---------|-----------|-------------|-------------|
| P-8 | 8-9 | - | - |
| P-10 | 10-11 | - | - |
| P-12 | 12-13 | - | - |
| ABF-8 | 8-9 | ABF | - |
| ABF-10 | 10-11 | ABF | - |
| ABF-12 | 12-13 | ABF | - |
| ABC-8 | 8-9 | ABC | - |
| ABC-10 | 10-11 | ABC | - |
| ABC-12 | 12-13 | ABC | - |
| ABC-126 | 12-13 | ABC | PAM HM |
| ABC-123 | 12-13 | ABC | PAM LM |
| ABF-106 | 10-11 | ABF | PAM HM |
| ABF-103 | 10-11 | ABF | PAM LM |

Morphological Observation of the PCC and Handsheets

A model of Leica Scanning Electron Microscope was used to observe the morphology of PCC ABC and ABF. The aggregates of PCC located on the surface and cross-cut of filled-papers were also

observed. Prior to scanning, the PCC and papers were coated with gold for a sharper view of micrograph.

Testing of the Samples

Filler content was determined by ashing the paper according to TAPPI Standard T413

but the ignition temperature is modified to 600°C. Ashing at 600°C is reported as the optimum temperature for isolating PCC in paper and at the same time protecting its' structure (Ferreira, et al., 2005). Tensile, tear and burst strength of the paper were measured according to TAPPI Test Methods T494, T414 and T403 om-02 for 'Tensile Properties of Paper and Paperboard', 'Internal Resistance of Paper' and 'Bursting Strength of Paper' respectively.

RESULTS AND DISCUSSION

Morphological Observation of Filler Particle Shape, Control Paper and Filled-paper

Micrographs of the PCCs are shown in Figure 1a and b. Both fillers are different in shape and size. The ABC is observed as rosette, needle-shaped while the ABF is symmetrical, circular-shaped. The diameter of PCC ABC is in the range of 100-600 nm

with 450-900 nm length while the PCC-ABF has 300-500 nm of diameter. Micrographs of kenaf whole stem control-papers prepared at alkaline medium of pH 8-9 are shown in Figure 2. Figure 3 illustrates the micrographs of the kenaf whole stem filled-papers using PCC ABC and ABF. The selected samples were ABC-12 and ABF-10 which performed high level of filler content of 20.69% and 29.04% respectively (Figure 5). Morphologically, the paper surface displayed that the distribution of fillers is better in sample ABF-10 rather than in ABC-12. Almost all fibre surfaces were covered with the flocs of fillers. The thickness of filler deposition on the fibre surfaces and in between the fibre linkages can be seen in the micrographs. These results indicated that shape and size of fillers influence the efficiency of filler retention. Circular-shaped fillers are proven to be better in terms of retention compared with needle-shaped ones.

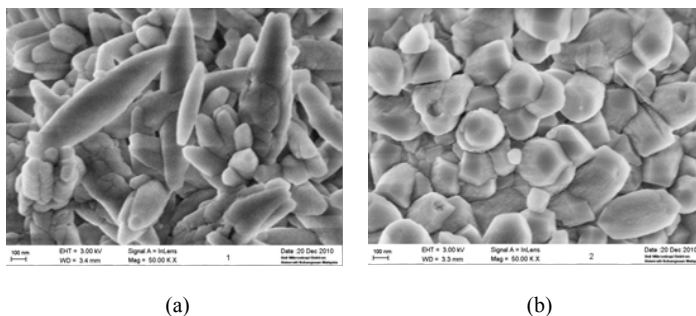


Figure 1. SEM micrographs of (a) PCC ABC and (b) PCC-ABF

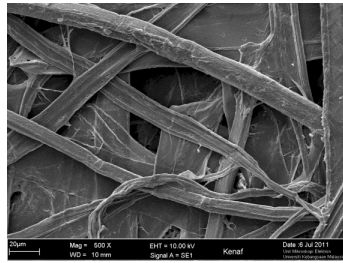


Figure 2. SEM micrograph of kenaf whole stem control papers prepared at alkaline medium of pH 8-9

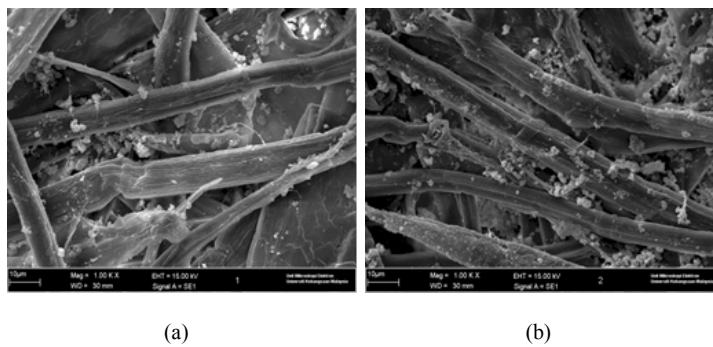


Figure 3. SEM micrographs of paper samples containing (a) PCC ABC and (b) PCC-ABF

The Properties of Control-paper Specimens Prepared at a Range of Alkaline Medium

Paper produced at pH 8-9 as shown in Figure 4 has better strength of tensile and burst indices compared with that produced at pH 10-11 and pH 12-13. It is believed that, inter fibre bonding is excellent at pH range of 8-9. The medium is believed to have achieved the stabilization level which means the electrostatic diffuse layer overlap forces is far from the isoelectric point (Borkovec & Papastavrou, 2008).

The neutralisation produces optimum negative-positive attraction between fibres in the slurry during papermaking. However, tear strength for P-10 is higher than P-8 which correlates with fibre length and strength of fibres, and energy of fibre-to-fibre interactions (Przybysz, et al., 2016). The number of fibres in the paper sheet and surface area of fibre per unit mass of paper may be more in P-10 rather than in P-8. Chauhan et al. (2012) showed that less fibre in a paper sheet may decrease the tear strength of paper.

Kenaf Paper Filled with Precipitated Calcium Carbonate

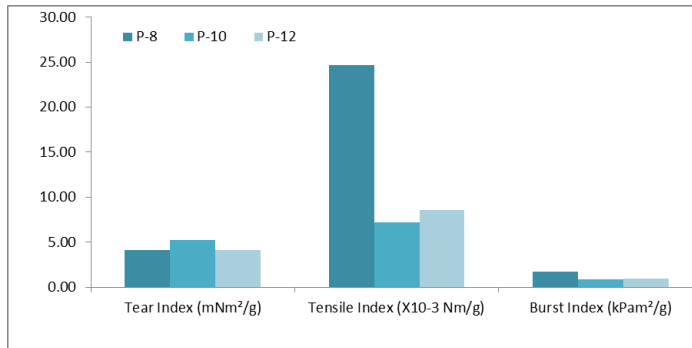


Figure 4. Mechanical properties of produced paper at pH 8-9, pH 10-11 and pH 12-13

The Properties of Filled-paper Prepared at a Range of Alkaline Medium with the Addition of PCC and PAM

The first objective of this experiment is to determine the influence of alkaline medium in the attachment of PCC. Six samples were prepared which involved ABC and ABF in making papers at 3 ranges of alkaline medium (see Table 4). Previously, the alkaline medium of pH 8-9 produced the best mechanical strength of control-paper. However, the addition of PCC ABC and ABF, has substantially changed the trend.

The filler content for both series of paper containing ABC and ABF have shown the best retention at different alkaline medium, pH 12-13 and pH 10-11 respectively. These results can be seen from samples ABC-12 and ABF-10 having filler content of 20.69% and 29.04% correspondingly. In filler loading technique, 20-30% of filler content is categorised as having high filler content in paper. Due to the presence of high content of fillers, the tear, tensile and burst strength for these samples has dropped to the lowest among the series of ABCs and ABFs.

Table 4

Mechanical properties and filler content of produced paper using ABC and ABF at pH 8-9, pH 10-11 and pH 12-13

| Samples | Tear Index (mNm ² /g) | Tensile Index (X10-3 Nm/g) | Burst Index (kPam ² /g) | Filler content (%) |
|---------|----------------------------------|----------------------------|------------------------------------|--------------------|
| ABC-8 | 4.15 | 12.10 | 1.054 | 15.58 |
| ABC-10 | 3.62 | 12.60 | 0.615 | 14.81 |
| ABC-12 | 3.27 | 7.50 | 0.972 | 20.69 |
| ABF-8 | 4.44 | 13.90 | 1.105 | 12.55 |
| ABF-10 | 4.49 | 10.20 | 0.543 | 29.04 |
| ABF-12 | 4.75 | 10.60 | 0.599 | 19.00 |

The performance of ABF as filler retention was better compared with ABC. This may be due to its filler size and shape. The circular-shaped of filler is believed to floc and attach easier onto the fibre surfaces and in between fibre linkages. This is in contrast to needle-shaped of ABC which has higher surface area and less stable during the filler flocculation and filler-fibre attachment.

The second objective of this experiment was to determine the effect of adding PAM to improve the mechanical properties of filled-papers. There are four samples prepared using ABC and ABF at pH 12-13 and pH 10-11 accordingly, added with PAM LM and HM. The PAM is a bridging polymer which may act in enhancing filler content

or paper strength. Regardless of the polymer involved, the results were not promising as shown in Figure 5. The expected results were not obtained which could be due to the congeniality among fillers-fibres-retention aids that affected the amount of filler in attaching the fibre surfaces. Ainun (2010) reported that the presence of retention aid disturbed and influenced the location and distribution of the magnetic fillers in their papermaking. As explained by Alince, et al. (2001), opposite charge of fibres (negative charges) and fillers (positive charges) produced electrostatic attractions which induced the PCC to attach on the fibres. The presence of such polymers may influence the electrostatic attraction as well.

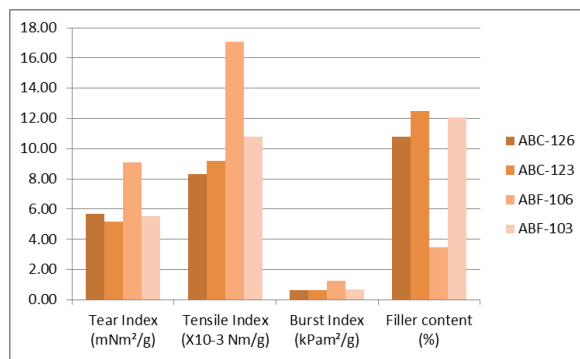


Figure 5. Mechanical properties and filler content of produced paper, using ABC and ABF at pH 12-13 and pH 10-11 respectively, with and without PAM

Based on Figure 5, samples which utilised lower molecular weight of PAM, ABC-123 and ABF-103 were found to load better than these of ABC-126 and ABF-106. No study was carried out at pH 8-9 because retention of both fillers was found better at solution of pH 10-11 and pH 12-13 as

discussed earlier. This showed that PAM HM did not aid better filler loading. It is believed that the mutual attraction between PCC-ABC or ABF with the fibres is better with the presence of low molecular weight of PAM. This is confirmed by Alince (1988) who found that cationic polyethyleneimine

affected the mutual attraction between fibres and fillers (clays) particles, thus decreasing the amount of filler attachments in his papermaking. In addition, higher molecular weight of PAM tends to attract and form bigger and heavier flocs of fillers which then is subjected to filler dislocation and prone to be washed away (Ainun, 2010). Studies have shown the presence of such polymer in the suspension leads to higher flocculation (Gaudreault, et al., 2009). Therefore, the PCC are disabled to disperse properly onto the fibre surfaces. Ek, et al. (2009) also highlighted over saturation at fibre surfaces results in desorption process.

According to Alinec (1988), the rate of polymer adsorption on filler is faster than on fibres. Appropriate usage of retention aid chemical may greatly influence the retention and drainage of the filler (Cadotte et al., 2007).

In this study, the addition of PAM LM is believed to be optimally adsorbed on the PCC which produces flocs of fillers and attaches onto the fibres. However, there is a decrease in value compared with samples without polymer addition which can be seen from ABC-12 and ABF-10 as illustrated in Figure 6. As explained earlier, a phenomenon that may occur during the pulp preparation is the forming of filler aggregation and flocculation after adding PAM. These flocs may become bigger and at certain level will be rejected from the papermaking system. The choice of retention aid for specific filler is crucial in papermaking (Chauhan, et al., 2012). Based on Gaudreault et al. (2009), higher molecular weight polymers

can also function to pre-flocculate the filler into coarser aggregates to secure enhanced first-pass retention. However, the characteristics of the filler suspension, such as pH, temperature, consistency and ionic composition, can dramatically affect the efficiency of these additives (Pelton, Allen, & Nugent, 1980) and make them more difficult to use. It is generally accepted that fillers often form aggregates before sheet formation which could include fines (Li, et al., 2002). Furthermore, both deposition and filtration retention mechanisms predicted that filler retention is particle size dependent.

High filler content was achieved by sample ABC-123 and ABF-103 of 12.49% and 12.09% filler content respectively (see Figure 5). Due to the content of fillers, the strength properties decreased compared with those of ABC-126 and ABF-106. If comparison is made between sample ABC-12 and ABC-123, the percentage of filler decrement is 60.37%. The percentage of filler decrement between ABF-10 and ABF-103 was 41.63%.

CONCLUSION

Alkaline medium of pH is important to provide good inter-fibre bonding which leads to high mechanical strength of paper. The pH acts as a medium provider for the filler to respond whereby different filler acts differently in dissimilar pH medium.

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