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Precipitated Calcium Carbonate from Industrial Waste for Paper Making

(Kalsium Karbonat Termendak daripada Sisa Industri untuk Pembuatan Kertas)

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ABSTRACT

In this study carbide lime waste was used as raw material to produce precipitated calcium carbonate (PCC). Carbide lime is an industrial waste from acetylene gas industry which uses limestone in its production. The use of PCC as fillers in paper making can reduce the production cost and improve the paper properties such as opacity and brightness. PCC can be produced from carbide lime waste by ionic sucrose solution method. The sucrose solution of Brix 10° was first prepared by dissolving sugar (sucrose) in water followed by dissolution of carbide lime waste in the sucrose solution. The sucrose solution which had turned milky was then filtered to obtain a clear solution known as pregnant solution. The pregnant solution that contained calcium ions was subsequently used to produce PCC by introducing CO_2 *gas into the pregnant solution. The process is known as carbonation. The PCC was then used as fillers in paper making. The production of PCC by using calcium hydroxide as starting material was also carried out for comparison purposes. Based on the results, PCC prepared from carbide lime had purity of 98.14% while the one prepared from calcium hydroxide had 98.66%. Meanwhile, analysis of the paper properties demonstrated that both products gave equally good results. This proves that PCC prepared from industrial waste can be used for paper making.*

Keywords: Calcium hydroxide; carbide lime; industrial waste; PCC

ABSTRAK

Kalsium karbonat termendak (PCC) yang dihasilkan dalam kajian ini menggunakan sisa kapur karbida sebagai bahan mentah. Kapur karbida adalah sisa industri daripada industri gas asitelena yang menggunakan batu kapur dalam penghasilannya. Penggunaan PCC sebagai bahan pengisi dalam penghasilan kertas mampu mengurangkan kos penghasilan di samping menambah baik sifat kertas daripada segi kelegapan dan kecerahan. PCC boleh dihasilkan menggunakan sisa kapur karbida dengan menggunakan kaedah larutan ion sukrosa. Larutan sukrosa Brix 10° dihasilkan terlebih dahulu dengan melarutkan gula (sukrosa) ke dalam air, seterusnya sisa kapur karbida dilarutkan dalam larutan sukrosa. Larutan sukrosa yang telah menjadi keruh seterusnya ditapis untuk memperoleh larutan jernih yang dikenali sebagai larutan bunting. Larutan bunting yang mengandungi ion kalsium seterusnya digunakan untuk menghasilkan PCC dengan memasukkan gas CO_2 *ke dalam larutan bunting tersebut. Kaedah ini dipanggil pengkarbonatan. PCC ini kemudiannya digunakan sebagai pengisi dalam pembuatan kertas. Penghasilan PCC menggunakan kalsium hikdroksida sebagai bahan pemula juga dijalankan untuk tujuan perbandingan. Berdasarkan keputusan, PCC yang dihasilkan menggunakan kapur karbida mempunyai ketulenan 98.14% manakala yang menggunakan kalsium hidroksida mempunyai ketulenan 98.66%. Sementara itu, analisis sifat kertas mendapati kedua-duanya memberi keputusan yang hampir sama. Ini membuktikan bahawa PCC yang dihasilkan daripada sisa industri boleh digunakan dalam penghasilan kertas.*

Kata kunci: Kalsium hidroksida; kapur karbida; PCC; sisa industri

INTRODUCTION

The utilisation of precipitated calcium carbonate (PCC) as filler in paper making industry accounts for almost 40% of the world PCC consumption in 2011. Asia is the biggest consumer of PCC in paper which comprises about 14 Mt of the world consumption of filler grade calcium carbonate. The use of PCC in paper production has grown significantly nearly 6% per year in output from Asian countries (Roskill 2012). The production cost of paper making has lessened as the pulp consumption was reduced by the use of filler. Besides, the filler such as PCC can improve the optical properties of the paper.

Malaysia is endowed with limestone resources. One of its uses is to manufacture acetylene gas. The process involves the calcination of limestone at 1000°C to produce calcium oxide, CaO and carbon dioxide gas, CO_2. The CaO_2 will be burned with carbon at 2000°C to produce calcium carbide, CaC_2. The calcium carbide subsequently reacts with water to generate acetylene gas and at the same time produces calcium hydroxide, $Ca(OH)_2$ which is known as carbide lime.

The carbide lime is considered as the industrial waste from the production of acetylene gas and is classified as scheduled waste in Malaysia. The $Ca(OH)_2$ content in the carbide lime is quite high, more than 90%. Its black colour is inherited from the carbon that exists as impurity. However, carbide lime to a small extent is used to treat sewage water, stabiliser in road constructions and other applications for hydrated lime substitutes.

In this study, the pulp used was beaten at 4000 revolutions to provide easiness for filler deposition during the impregnation process prior to paper making. Mossello et al. (2010) has reported that the major effects of beating were internal and external fibrillation of the fibres, fine formation of hairs and discharge of chemical components. Fibrillated fibres result to increase in density and bond strength of the paper sheet.

Cationic polyacrylamide (PAM) is a retention aid that can solve the detachment problem arises during the addition of filler particles to the pulp fibres. It can increase the retention of the filler on the fibres and this would prevent drained-out of the smaller particles during sheet consolidation. A few researchers (Cho et al. 2006; Vanerek et al. 2006) had studied the uses of PAM to enhance the deposition of PCC to pulp fibres.

Generally, only high grade limestone is required to produce PCC. Due to scarcity of high grade limestone, the number of PCC and paper manufacturers in Malaysia is limited compared to other Asian countries. Therefore, in this study the calcium-based industrial waste was used in producing PCC as it shows that the purity of the PCC produced from this waste was similar to the PCC produced from natural high grade limestone. This new technique is predicted to become popular in the future as it offers a more economical approach in PCC manufacturing.

Materials and Methods

The bleached mixed tropical pulp fibres used in the study were mechanically treated with PFI mill at 4000 revolutions according to TAPPI T 428. The pulp was obtained from Sabah Forest Industries (SFI) Sdn. Bhd. The Pulp (24 g) was dispersed in 1800 mL of water and disintegrated for 5 min for well dispersed.

PAM used in the study was purchased from Aldrich Chemicals with molecular weight 10000. For the treatment process, PAM was dispersed in 100 mL of water and poured into the pulp suspension after the impregnation.

Sucrose solution was used to prepare the calcium sucrate solution. A beaker was filled with 1 L water followed by 100 g sucrose. Then the beaker was transferred onto a hotplate. The temperature of the hotplate was set and stirred for several minutes to dissolve the sucrose. After all the sucrose had dissolved, brix reading was determined by using refractometer. The reaction between sucrose and water is shown in (1).

$$C_{12}H_{22}O_{11(s)} + H_2O_{(l)} \rightarrow C_{12}H_{22}O_{11(aq)} \qquad (1)$$

The prepared sucrose solution with 10° Brix was used to formulate calcium sucrate solution. 1 L of the sucrose solution was filled into a beaker. The beaker was transferred to a hotplate with magnetic stirrer bar and warmed up with certain rotation per minute before 36 g of hydrated lime or carbide lime was added into the beaker. The reaction occurred between sucrose solution and carbide lime was shown in (2). After the colloidal solution became homogenise, the solution was filtered by using filter paper. The filtrate was a clear pregnant solution (calcium sucrate) and was used to produce PCC by introducing CO_2 gas into it. The precipitation of PCC was considered complete when the pH of the solution attained were around 7.5 to 8.5. The solution was then filtered to get the PCC. The PCC obtained from the process was used as filler in the paper making process.

$$C_{12}H_{22}O_{11(aq)} + Ca(OH)_{2(s)} \rightarrow \text{Calcium Sucrate}_{(aq)}. \quad (2)$$

24 g OD of beaten pulp and 2 L of water were put into a disintegrator and disintegrated for 5 min. Then, 30 g of PCC was added in the disintegrator and further disintegrated until the 2000 revolutions completed. The process is called impregnation. The pulp suspension filled with PCC was then used to produce paper by using hand sheet machine. The hand sheet was dried at room temperature before the physical testing. The morphology analysis had been carried out in order to observe the deposition of filler particles on the sheet. The method of producing hand sheet with the treatment of retention aid, PAM was slightly different. The pulp suspension was treated with 3% w/w PAM with dried pulp after impregnation process. The suspension was stirred using mechanical stirrer at 700 rpm for an hour. After the treatment process, the ensuing process was the same as the sample without treatment. The samples prepared in the study were as follows:

A. Paper produced using PCC from 100% pulp; B. Paper produced using PCC from carbide lime without PAM; C. Paper produced using PCC from carbide lime with PAM; D. Paper produced using PCC from hydrated lime without PAM; and E. Paper produced using PCC from hydrated lime with PAM.

Results and Discussion

Table 1 shows the results of X-ray fluorescence (XRF) analysis for the PCC produced from carbide lime and hydrated lime. The results showed that calcium oxide content of the PCC prepared from carbide lime is 54.96% which is equal to 98.14% of calcium carbonate. Meanwhile the XRF result for the PCC purity produced from high grade limestone is 98.66%. The results showed a slight difference in limestone grade. Therefore, it can be concluded that high purity PCC can also be produced from the carbide lime waste. Industrially, only high grade limestone is used to produce PCC. The industries use conventional method in which impurities in limestone will be mixed together with the precipitated calcium carbonate during the recarbonation process. Hence, the high grade limestone that has more than

TABLE 1. Chemical composition (%) of PCC

Sources of PCC	Na_2O	MnO	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	TiO_2	P_2O_5	Lost on ignition
Carbide lime	0.04	0.01	0.22	0.06	0.34	0.01	54.96	0.01	0.02	0.03	44.30
Hydrated lime	0.07	-	0.25	0.43	0.94	0.03	55.25	0.05	-	-	42.98

98% purity needs to be used as the starting material so as to reduce the impurity content in the final product (Boynton 1979). From Table 1, the oxides that are considered as impurities are Na_2O, MnO, MgO, Al_2O_3, SiO_2, K_2O, Fe_2O_3, TiO_3 and P_2O_5. In this study, PCC produced from the carbide lime waste was of high grade, suitable to be used for paper making.

Table 2 shows the results of physical and optical testing (opacity and brightness) for the paper produced. Sample A was hand sheet made of 100% pulp without fillers. Sample B was the hand sheet using PCC fillers produced from carbide lime waste. Sample C was the hand sheet prepared from PCC fillers of carbide lime and treated with PAM. While sample D was the hand sheet prepared from PCC fillers produced from hydrated lime and Sample E was also prepared from the same material as in sample D but treated with PAM. The data tabulated in Table 2 showed that there was no significant difference between the two types of PCC used in the paper. It clearly showed that the paper properties for the sample using PCC from carbide lime is quite similar with the paper properties using PCC from hydrated lime (high grade limestone). The paper properties were also compared with sample A, the paper produced from 100% pulp. Sample A served as a reference for true properties of paper as it was produced without fillers. As observed from Table 1, the paper properties such as tear, tensile and burst indices started to decline when PCC was introduced during the paper making. This trend is caused by the presence of PCC that prevents fibre-to-fibre contact during sheet consolidation (Green et al. 1982).

However, the optical properties of the paper were improved with PCC. This indicates that the presence of PCC contributes to the enhancement of the optical properties of the paper. This was also proven by other researchers (Ciullo 1996; Ulla & Kerstin 1986). The evaluation of the optical properties can be clearly observed in Figure 1 which shows the dominant graphs of the optical properties for the paper produced. The graph showed that the paper produced using PCC from carbide lime and hydrated lime with and without PAM has higher percentage of opacity and brightness as compared to the paper prepared from 100% pulp. This proved that the PCC was able to improve the optical properties of the paper. This also indicated that the PCC produced was purer and with fewer impurities attributed to good optical properties (Kamiti & van de Ven 1994). Meanwhile, the percentage of loading degree of the samples using PCC produced from hydrated lime with the aid of PAM has the highest result, 21.32% as shown in Figure 2. The results also indicated that the use of PAM can increase the percentage of loading degree even though it was not so obvious for both PCC type produced. Rohaya et al. (2010) in their study had used PEI as the retention aid which was also a cationic polyelectrolyte. They found that the use of the retention aid had increased the percentage of loading degree. The percentage of loading degree denotes the total PCC deposited or retained in the paper. The optical properties were enhanced as the deposition of PCC increased. Despite the enhancement of the optical properties, the loading degree must be controlled in order to regulate the physical properties of the paper according to specifications required.

Figure 2 shows the micrograph obtained from the field emission scanning electron microscope (FESEM) analysis. The micrograph is the PCC produced from carbide lime (Figure 2(a)) and hydrated lime (Figure 2(b)). Both samples are cubical shape, but the particles were stacking together that make them appear coarser (5 to 10 microns). PCC from hydrated lime is considered as perforated cubic. Meanwhile, Figure 3 shows the micrographs of the paper produced using PCC from carbide lime waste; Figure 3(a) shows the fibre surface and Figure 3(b) is the cross sectional view where PCC particles can be seen in between the fibre web. While Figure 4 shows the micrographs of the paper produced using PCC from hydrated lime; Figure 4(a) shows the fibre surface and Figure 4(b) is the cross sectional view of the sheet. These two figures show that

TABLE 2. The results of paper properties

Samples	Tear index mNm^2/g	Tensile index Nm/g	Burst index $kPam^2/g$	Opacity %	Brightness %	Loading degree %
A	10.89	67.19	4.86	71.97	84.65	-
B	7.64	32.55	2.02	74.06	85.58	16.83
C	7.81	38.96	2.60	82.36	84.63	18.13
D	6.94	33.31	2.06	75.98	86.06	19.32
E	7.51	31.16	2.03	78.28	86.11	21.32

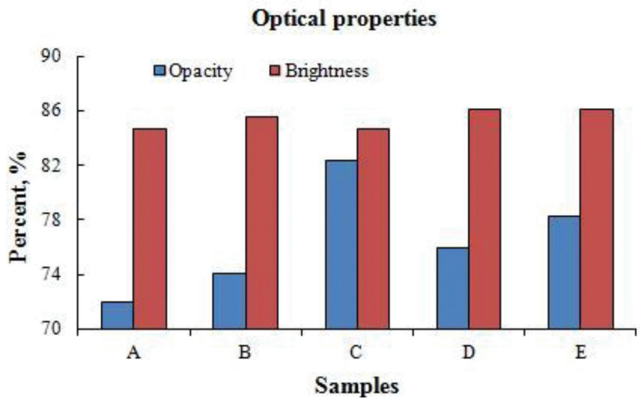

FIGURE 1. Results of optical properties of the paper produced

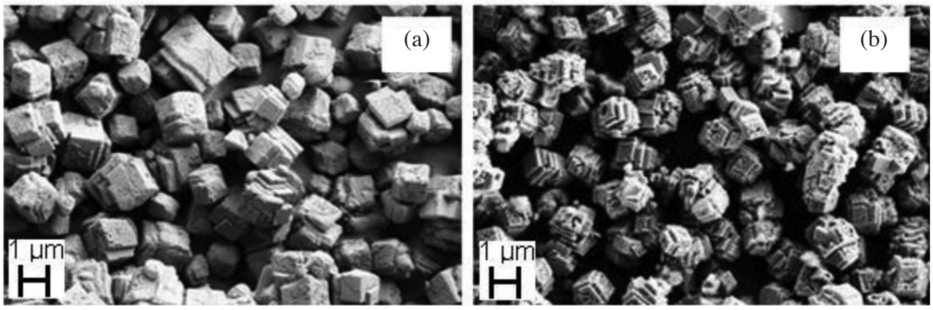

FIGURE 2. FESEM micrograph of PCC produced from
(a) carbide lime and (b) hydrated lime

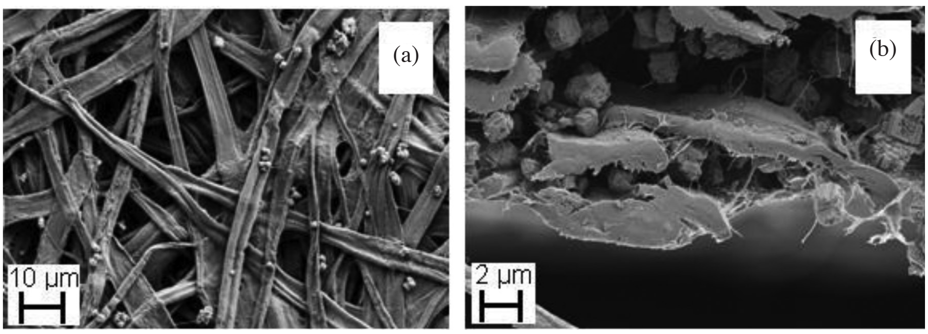

FIGURE 3. FESEM micrograph of paper produced using PCC from carbide lime waste,
(a) fibre surface and (b) cross sectional view

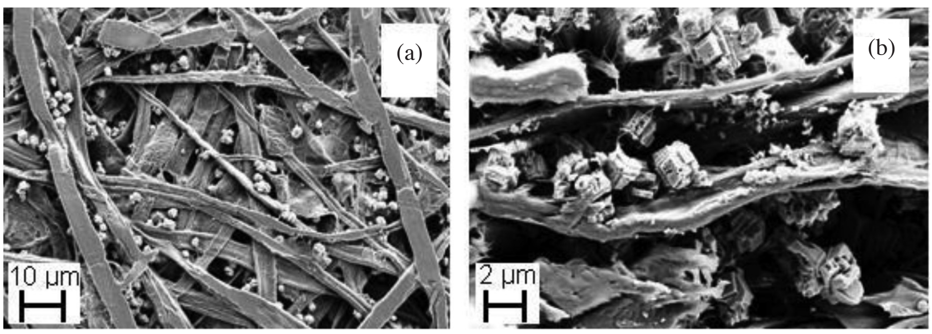

FIGURE 4. FESEM micrograph of paper produced using PCC from hydrated lime,
(a) fibre surface and (b) cross sectional view

PCC was deposited on the paper surface and in between the fibre web.

CONCLUSION

It can be concluded that the PCC produced from the industrial waste such as carbide lime can be used as filler in paper production. The analysis showed that the paper properties for both using PCC from carbide lime and hydrated lime were similar. The optical properties of the paper using PCC from both carbide and hydrated lime were improved.

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