

## Mechanical and Optical Properties of CaCO<sub>3</sub> Lumen-Loaded Paper: Effect of Polyethylenimine and Alum

(Sifat Mekanik dan Optik Kertas CaCO<sub>3</sub> Berpengisi Lumen:  
Kesan Polietiliminina dan Alum)

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### ABSTRACT

*Precipitated calcium carbonate fillers were loaded into the lumen of bleached mixed tropical hardwood pulp using polyethylenimine (PEI) and alum. Our results indicated that the addition of (PEI) increased the degree of loading of precipitated calcium carbonate (PCC) into the lumen of fibers. The degree of loading also increased with the addition of alum together with PEI. The mechanical strengths of the produced lumen loaded paper increased with the addition of PEI and alum. Meanwhile the mechanical strength without alum had slightly increased the mechanical strengths of the paper. Electron micrographs revealed that the PCC fillers were successfully loaded into the lumen of the fibers.*

*Keywords: Lumen loading; mechanical properties; optical properties; recipitated calcium carbonate; polyethylenimine*

### ABSTRAK

*Pengisi kalsium karbonat termendak dimasukkan ke dalam lumen pulpa terluntur tropika campuran dengan menggunakan polietiliminina (PEI) dan alum. Keputusan menunjukkan pertambahan PEI telah meningkatkan darjah pemasukan kalsium karbonat termendak (PCC) ke dalam lumen fiber. Darjah pemasukan lumen ini juga meningkat apabila PEI dan alum digunakan serentak. Kekuatan mekanik kertas berpengisi lumen meningkat bagi kertas yang dihasilkan menggunakan PEI bersama alum. Namun tanpa penggunaan alum, kekuatan mekanik kertas mengalami sedikit peningkatan sahaja. Mikrograf menunjukkan pengisi PCC berjaya dimasukkan ke dalam lumen fiber.*

*Kata kunci: Kalsium karbonat termendak; pemasukan lumen; polietiliminina; sifat mekanik; sifat optik*

### INTRODUCTION

The use of mineral fillers in the consolidation of pulp fibers in papermaking has been practiced since the eighth century. Fillers such as CaCO<sub>3</sub>, clay, TiO<sub>2</sub> and talc are widely used in paper industries. The use of fillers can reduce the cost and improve brightness, opacity as well as the printability of the paper. This will enable the papermakers to raise the filler content as much as possible. However, if the filler content in the paper is too high, the strength is reduced due to the interference of the interfiber bonding (Middleton et al. 2003).

Precipitated calcium carbonate is one of the mineral fillers that have also been utilized in paints, polymers, adhesives and sealants industries. Klungness et al. (2000) used ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) to study the mechanical and optical properties of fiber-loaded paper. They found that PCC can be a key factor in developing lightweight and high-opacity printing papers. The loading degree of lumen loaded pulp with PCC can achieved up to 0.3 g filler/ g fiber (Middleton et al. 2003).

Lumen loading is a technique whereby the fillers are introduced into the fiber lumen while leaving the fiber

surfaces free of filler. Lumen loading techniques have been used to making CaCO<sub>3</sub> lumen loaded paper (Middleton et al. 1989; Middleton & Seallan 2003) and magnetic paper (Zakaria et al. 2004a; Zakaria et al. 2005). Lumen loaded pulp has two advantages over the conventional method i.e. the fillers are protected by the cell wall in the fiber lumen from dislodgement during papermaking process. The other advantage is that the outer surfaces of fiber free of filler which form a better inter-fiber bonding and has higher strength than conventional-loaded paper (Middleton & Seallan 1985).

Polymeric flocculants are widely used in papermaking as retention aids to increase the filler loading degree. Cationic polyacrylamide (CPAM) in the preparation of paper loaded with PCC (Middleton et al. 2003; Klungness et al. 2000). PAM, a cationic polyelectrolyte is able to form bridges and hetero-flocculation which are beneficial to produce paper with high loading degree (Zakaria et al. 2004b). The other polymeric flocculants that are used frequently with clay and CaCO<sub>3</sub> fillers are polyethylenimine (Alince & Van de Ven 1993) and polyethylene oxide (Goto et al. 1999).

In this study, PCC was impregnated into lumen of fibers using lumen loading approach. Different amounts of PEI with and without alum were added during lumen loading process to study its effect on the degree of loading as well as on the optical and mechanical properties.

## EXPERIMENTAL

### MATERIALS AND METHODS

Bleached mixed tropical hardwood pulp from Sabah Forest Industries, Malaysia, was used in this study. The pulp was disintegrated at 3000 rpm for 5 minutes to ensure that all the fibers were well dispersed. Pulp (15 g) was dispersed in 1250 mL distilled water containing 0.1 g/L aluminium sulfate (alum).

The precipitated calcium carbonate (PCC) used, was in powder form with particle size less than 0.2  $\mu\text{m}$ . The filler suspension was prepared by dispersing 30 g of PCC in 250 mL distilled water containing 0.1 g/L alum.

Polyethylenimine (PEI) with  $M_w$  750,000 was purchased from Aldrich Chemicals. It was dispersed in 250 mL distilled water containing 0.1 g/L alum with different amount of PEI (0-3%).

Aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) was used as additive in this experiment. Alum (0.2 g) was diluted in 2 L of distilled water and used to prepare pulp, filler and retention aid suspensions.

Lumen loading involves three stages; impregnation, treatment and washing. At impregnation stage, filler suspension was added into pulp suspensions and stirred at the standard rotor speed of 3000 rpm for 30 minutes. Subsequently PEI was added during the treatment stage for different duration and stirred at 600 rpm. After treatment, the fillers on the fiber surface were removed by washing with filtered water in a self designed fiber classifier, containing a filter screen (45  $\mu\text{m}$ ) for 30 – 60 minutes. The lumen loaded pulp was then used to produce paper and

tested according to the standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI) (Zakaria et al. 2004b). Produced paper without alum was prepared using similar method using distilled water.

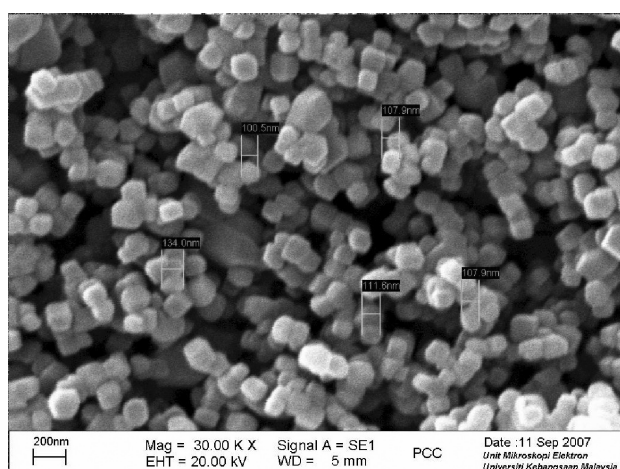
The ash content of the produced paper was determined by ignition at 900°C for 4 h. The results gathered were used to obtain the degree of lumen loading of the paper produced (Zakaria et al. 2004b)

### RESULTS AND DISCUSSION

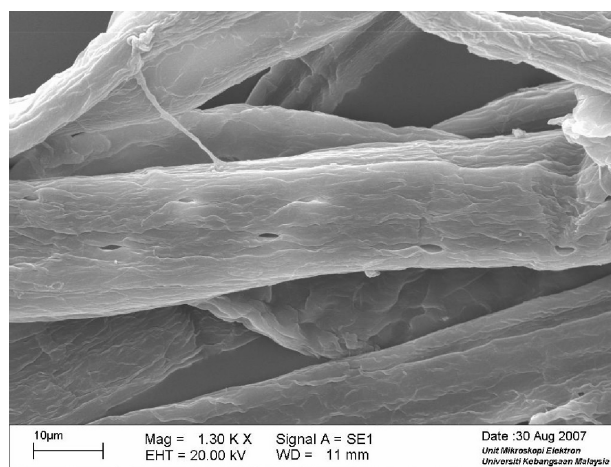
Figure 1 shows the micrograph of (a) PCC and (b) mixed tropical hardwood pulps used in this research. The PCC used was in cubical shape with particle size less than 0.2  $\mu\text{m}$ . The pit holes of the bleached mixed tropical hardwood pulp were approximately 2  $\mu\text{m}$ .

Figure 2 shows the effect of PEI on the degree of loading of the paper (with and without alum). It can be seen that the degree of loading increased with the addition of PEI for paper produced with and without alum. PEI acts as flocculent for  $\text{CaCO}_3$  and fibers, which will enhance retention of filler in the lumen of fiber. Without PEI, the paper produced with alum possesses slightly higher degree of loading than that of without alum.

Figure 3 shows the tensile index of the produced  $\text{CaCO}_3$  loaded paper using PEI. The tensile strength of the paper with alum increased with the addition of PEI. However, without using alum, the tensile strength decreased at 1% and 2% PEI. The introduction of alum has enhanced the functionality of PEI. This is inconsistent with previous study on the preparation of paper using magnetic filler, which reported that the addition of alum has disrupted the system and reduced the tensile strength of paper. Although the paper produced using PEI and alum contains higher loading degree as shown in Figure 1, its tensile strength increased with the addition of PEI. Therefore, we can conclude that PEI has improved both the degree of loading and the tensile strength of paper.



(a)



(b)

FIGURE 1. SEM micrograph of (a) precipitated calcium carbonate (PCC) and (b) pit holes of mixed tropical hardwood pulp

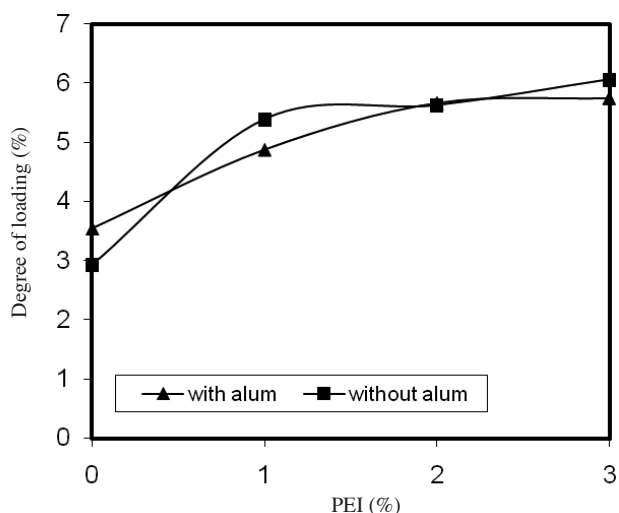


FIGURE 2. Effect of PEI on degree of loading of paper

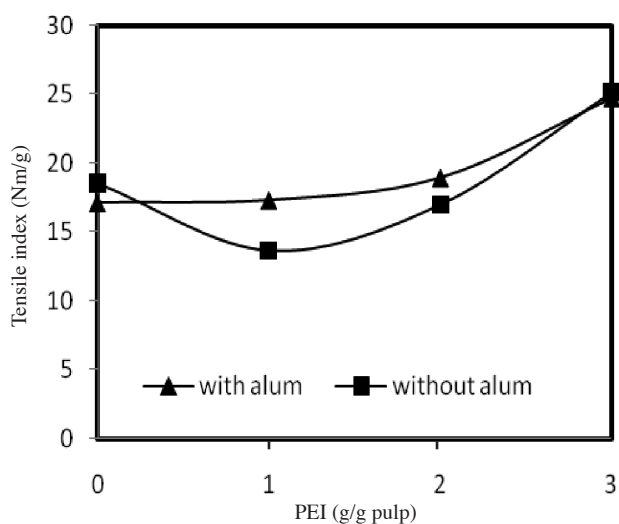


FIGURE 3. Tensile index of paper from bleached mixed tropical pulp using PEI (0-3%) with and without alum

Lumen loaded paper possesses higher tensile strength due to stronger fiber-fiber bonding, most likely due to less interference on fiber bonding from filler deposited within the lumen of fibers (Klungness et al. 2000; Ulla et al. 1986).

The effect of addition of PEI and alum on the tear strength of paper is shown in Figure 4. The addition of 1% of PEI has reduced the tear strength from 4.58 to 3.92 mNm<sup>2</sup>/g. The tear strength then increased to 4.83 and 6.97 mNm<sup>2</sup>/g for the addition of 2 and 3% of PEI, respectively. The tear strength of paper produced with PEI gave higher tear strength as compared to paper without alum. This is consistent with the tensile strength results (Figure 3), revealing the advantages of the addition of alum.

The effect of PEI is shown in Figure 5. The burst index of the paper with alum increased as the PEI increased. However, without using alum, the burst strength of paper decreased with the addition of 1 and 2% of PEI. This

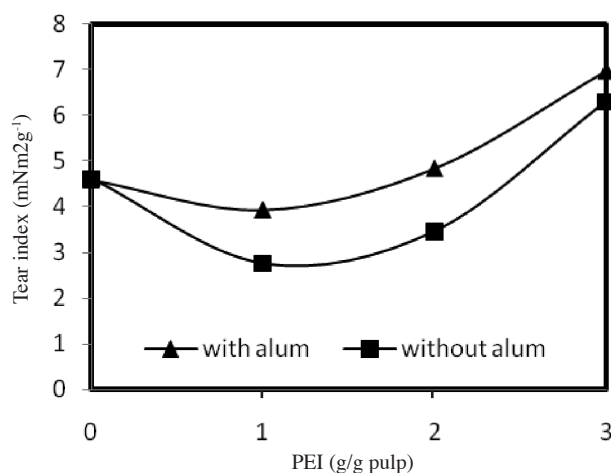


FIGURE 4. Tear index values for paper from bleached mixed tropical pulp using PEI (0-3%) with or without alum

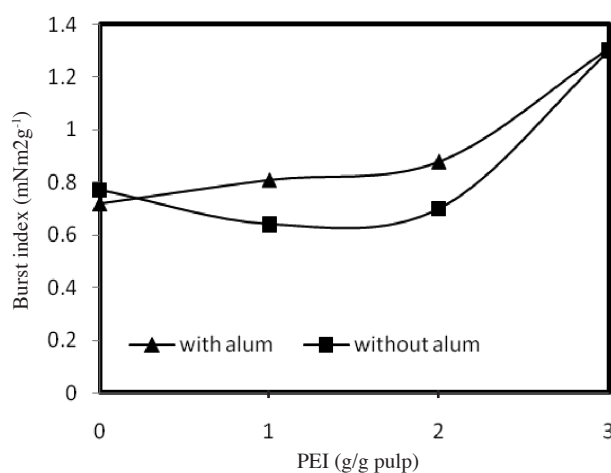


FIGURE 5. Burst index of paper produced using PEI (0-3%) (with or without alum)

indicates that 1 and 2% of PEI alone are not sufficient to improve the burst strength of paper. The folding endurance of the paper produced is presented in Figure 6. The number of folding of the paper showed the highest values with the addition of 3% PEI for both papers with and without alum.

In Figure 7, the brightness of the papers for both alum and without alum decreased slightly with the addition of PEI (with and without alum). This can be attributed to the photo-yellowing effect of PEI due to the degradation of carbonyl compounds (De la Orden et al. 2006). Similar result was observed in the opacity of the paper (Figure 8). Both papers with and without alum decreased in opacity with the increased of PEI. This is associated with the finite size of the CaCO<sub>3</sub> filler. Klungness et al. (2000) reported that the brightness and opacity of loaded paper were slightly lower than those paper made from direct-loaded pulp.

Figure 8 shows the optical properties of paper from bleached mixed tropical hardwood pulp using 3% PEI with

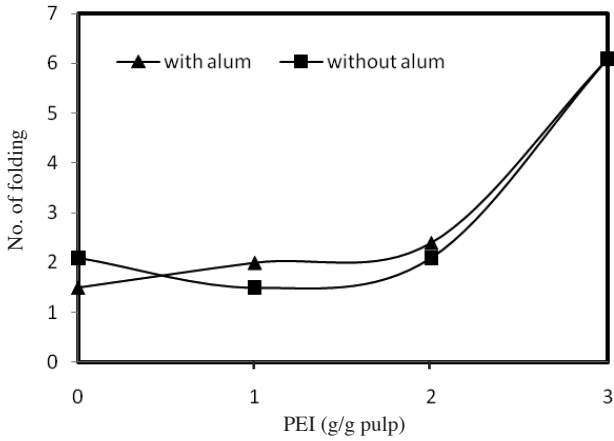


FIGURE 6. Number of folding for paper from bleached mixed tropical pulp using PEI (0-3%) with or without alum

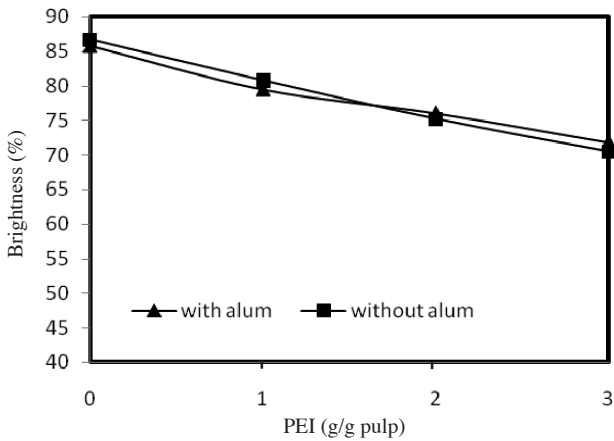


FIGURE 7. Brightness for produced paper from bleached mixed tropical pulp using PEI (0-3%) with or without alum

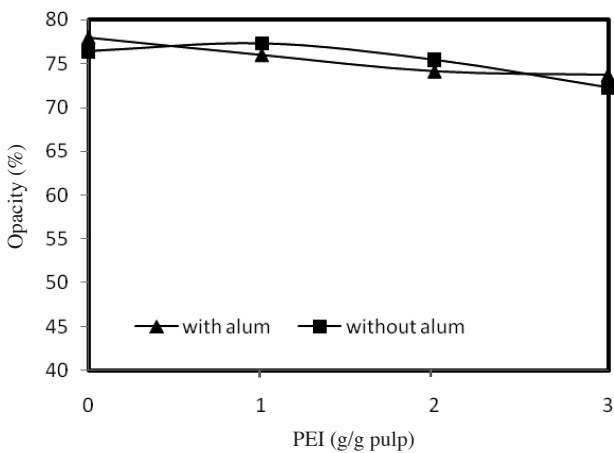


FIGURE 8. Opacity of paper from bleached mixed tropical pulp using PEI (0-3%) with or without alum

alum. Both the brightness and optical values decreased with increasing PEI treatment time. As PEI treatment time increased, more PEI was adsorbed onto pulp fibers and this will decrease the brightness and opacity values of paper.

Figure 9 shows the SEM micrograph of the cross-section of a pulp without loading. Figure 10 shows the micrograph of a cross section of bleached mixed tropical hardwood pulp loaded with PCC. The micrograph clearly shows that the filler particles have been loaded into the lumen of the fiber.

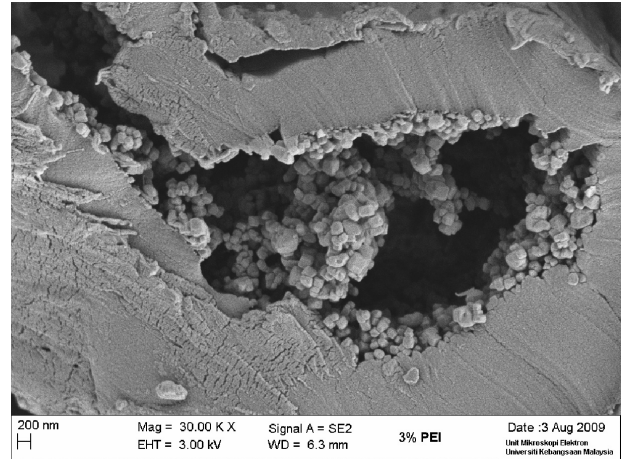


FIGURE 9. A scanning micrograph of cross-section of a pulp without loading

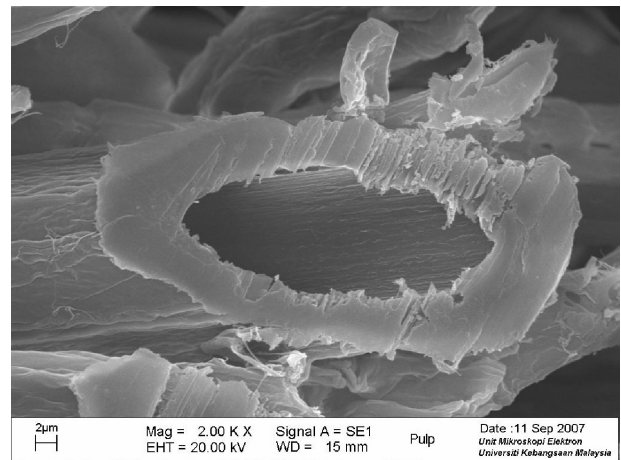


FIGURE 10. Scanning electron micrograph of cross section of unloaded pulp fiber and lumen-loaded pulp fiber with PCC

### CONCLUSION

PCC fillers were successfully loaded into the lumen of bleached mixed tropical hardwood pulp fibers using PEI and alum. The results showed that PEI enhanced the degree of loading of PCC into the lumen of fibers. The degree of loading can be further increased with the coexistence of alum and PEI. The mechanical strengths of the lumen loading paper increased with the PEI addition, while alum provided slight improvement on the mechanical strength of paper. The optical properties of the paper produced decreased with increasing addition of PEI. The scanning

electron micrographs indicated that the loading of PCC took place inside the lumen of the fibres.

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