Morphological and Mechanical Properties of Old Newspaper Deinked with Cellulase and Laccase Combination

Noni Oktari[1], Saharman Gea[2*], Andriayani[2], Sri Rahayu[1], Reka Mustika Sari[1] and Khatarina Meldawati Pasaribu[1]

[1]*Postgraduate Chemistry Study Programme, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan, Indonesia*
[2]*Department of Chemistry, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan, Indonesia*

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Abstract: The utilization of enzyme in deinking process of recycle paper is still in development phase since it was known that conventional deinking use large amount of chemicals such as sodium hydroxide, sodium silicate, and hydrogen peroxide which are environmentally damaging. In the present study, cellulase combined with laccase was used for deinking process of old newspaper pulp. The first step was repulping the old newspaper, and then the pulp slurry at 10% consistensy was treated with cellulase and laccase with different concentration from 0-2%. After washing process, the pulp was reforming in to the handsheet. The tensile strength of the handsheet was tested and the morphological changes was analyzed using scanning electron microscopy (SEM). The result showed that handsheet treated with 1% cellulase and 1% laccase had the highest tensile strength (2.1 MPa) with 1493 MPa Young's modulus. From the images of SEM, showed that fiber surface pulp turned rough and microfibril also appeared on the fiber surface after enzymatic treatment with cellulase and laccase, which indicated delignification process and facilitated the release of ink particle entrapped.

1 INTRODUCTION

Paper is one of important materials which is inseparable from human life and used for various purposes in life. Based on survey conducted at 2014, the global production of paper was 407 million metric tons (Pandharipande & Ingle, 2018). The demand of paper is continuously increase year by year. This causes high demand of green plant as a basic raw material for paper production. Recycling of waste paper is an alternative process to preserve the green plant. Old newspaper is one of waste paper that has a potential amount especially in urban area in Indonesia, because it was produced and consumed every day (Saputra & Sagala, 2017).

Recycling of waste paper requires the removal of ink from the paper by a process called deinking (A. Singh et al., 2012). Deinking process involves ink particle dislodgement from the fiber surface and the separation of dispersed ink from fiber suspensions (Muryeti et al., 2015). During chemical deinking or also called conventional deinking, large quantities of chemicals such as sodium hydroxide, sodium silicate and hydrogen peroxide were used, which are not environmentally friendly (Bajpai, 2014; K. C. Lee et al., 2016; Liu et al., 2017). On the other hand, enzyme mediated technologies are getting vast popularity due to their potential to replace the use of chemicals and also limit the wastage of water, save energy and result helps to improve the product quality (G. Singh & Arya, 2019).

Many researchers have reported the studies on deinking process using various enzymes. As compared to the conventional deinking, pulp treated with enzymes reduce the load on waste water treatment system due to reduced use of chemicals. Enzymatic deinking has high efficiency and low environmental impact. Moreover, enzymatically deinked pulp also displays improved drainage, lower residual ink, higher brighness and superior physical properties (Saxena & Chauhan, 2016). Cellulase-free xylanase preparation of Aspergillus niger DX-23 could cause efficient deinking of old newspaper pulp and considerably reduce the use of chemicals (Desai & Iyer, 2016). The use of cellulases and hemicellulases mixtures has been described to be able to deink high quality waste paper (C. K. Lee et

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al., 2013). Treatment with laccase indicates several characterictic and prominent changes including degradation of the guaiacyl group and a high degree of deformation of methyl group in lignin (Shankar et al., 2018). Combining hemicellulase with laccase mediator system on old newsprint deinking process shows that surface coverage lignin of pulp is lower than the control (Xu et al., 2011). Laccase is capable to deink old newspaper where the mechanical pulp contains a huge of lignin (Saxena & Chauhan, 2016). Waste paper pulp was deinked effectively using laccase and xylanase without mediator supplementation for laccase activity. It was the first report on deinking of old newspaper pulp using a bacterial laccase without the need of mediator, resulting the process cost effective (Virk et al., 2013).

This study was carried out to deink old newspaper pulp using combination between cellulase and laccase without any mediator. Conventional deinking method was also done as the comparison. The morphological and physical properties of enzymatically and conventionally deinked pulp were investigated.

2 MATERIALS AND METHODS

2.1 Materials

Cellulase from Aspergillus sp. (Carezyme 1000 L) with an activity of 1000 S-CEVU/g and laccase from Aspergillus sp. (Novozym 51003) with an activity 1000 LAMU/g were purchased from Sigma Aldrich. All the reagents used are analytical grade chemical. The old newspaper used was collected from the same publisher by a local supplier.

2.2 Methods

This study consists of 3 main stages, which are repulping, deinking and reforming process.

2.2.1 Old Newspaper Pulp Preparation

The old newspapers were manually cut into length size 2-3 cm^2 and then soaked overnight in distilled water at room temperature. After that, the soaked newspapers were washed and then disintegrated using a mechanical stirrer until pulp slurry obtained. The pulp slurry then squeezed to remove absorbed water and after that oven dried at 50ºC. The dried pulp was used for further experiments.

2.2.2 Chemical Deinking

The amount of 15 g dried old newspaper pulp was soaked in 150 mL distilled water for 30 minutes to obtain pulp with 10% (w/v) consistency. After that, pulp was added with 2% NaOH, 2% Na_2SiO_3 and 2% H_2O_2. The treatment was carried out at 70ºC for 2 h. The treated pulp was then washed with distilled water until the pH to be neutral.

2.2.3 Enzymatic Deinking

The amount of 15 g dried old newspaper pulp was soaked in 150 mL phosphate buffer (pH 7.5) for 30 minutes to obtain pulp with 10% (w/v) consistency. Cellulase was added to the pulp and incubated at 40ºC for 30 minutes in inkubator shaker with 150 rpm. After 30 minutes reaction, laccase was added and allowed to react for 30 minutes at 30ºC with 150 rpm in inkubator shaker. The enzymes were inactivated by placing the pulp in a boiling water bath for 15 minutes. The treated pulp was then washed with distilled water until the pH to be neutral. Cellulase and laccase enzymes used with 5 different variations of concentration (0%; 0.5%; 1%; 1.5% and 2% of dry weight old newspaper pulp).

2.2.4 Handsheet Formation

The treated pulp (chemically and enzimatically treated) were suspended in distilled water in an erlenmeyer flask, mixed and filtered using buchner funnel under suction using whatman filter paper. Pulp was recovered using 200 mesh wire and pressed between two plates using napkin to remove extra water and then oven dried at 50ºC.

2.2.5 Handsheet Characterization

The handsheets obtained were analyzed for morphological properties using scanning electron microscopy (SEM) (ZEISS) at an accelerating voltage EHT of 20.00 kV, probe = 101 Pa and signal A = SE1.

Mechanical properties was carried out using a tensile test tool GOTECH AL-7000M under ambient temperature and humidity (25ºC, 65 RH) with a tensile speed 5 mm/min and 1 kN load.

3 RESULTS AND DISCUSSIONS

3.1 Scanning Electron Microscopy Analysis

The analysis on newspaper pulp using SEM was carried out to analyze the surface morphology of untreated, enzimatically and chemically treated newspaper pulp.

Surface morphology of handsheet on 500x magnification can be seen in Figure 1, it shows that the fiber surface was significantly changed after enzymatic deinking process.

The smooth fiber surface was observed on untreated newspaper pulp (A). On contrary, fiber surface on enzymatically treated pulp was turned to be rough. As can be observed, more fibrillation was appeared on fiber surface, which indicating delignification process was occured (Xu et al., 2011). This fiber surface change which facilitated the release of high amount of lignin molecules and the ink particles entrapped (Kumar et al., 2019). Moreover, the change of the fiber surface had a significant role increasing the strength of the recycled pulp. Deinking process using cellulase resulted two types of changes in pulp surface, it was modification on internal structure and surface roughening (Efrati et al., 2013). Laccase treatment alone did not generated in rupturing of the fibers and deform the structure of the cellulose fibers (Shankar et al., 2018).

Fiber surface of chemically deinked pulp (conventional deinking) can be seen in Figure 2, it shows rupturing after the deinking process. The rupturing increase with increasing the concentration of the chemicals, which indicated that high concentration on chemical deinking deforms the structural integrity of the cellulose fibers (Shankar et al., 2018). On the other hand, combine enzimatically deiked pulp did not show any rupturing. It is clearly observed that the detachment of the ink particles from the surface of the fibers was more prominent in case of pulp treated with cellulase and laccase combination as compared to conventional deinking.

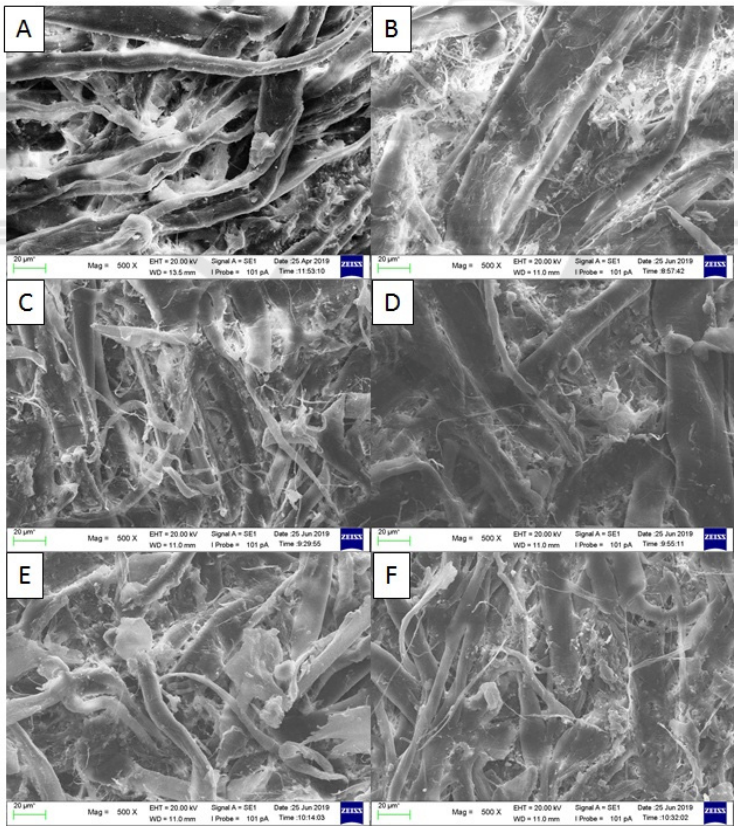

Figure 1: Scanning Electron Micrographs of A) Untreated newspaper pulp B) Laccase 2% C) Cellulase 0.5%; laccase 1.5% D) Cellulase 1%; laccase 1% E) Cellulase 1.5%; laccase 0.5% and F) Cellulase 2%.

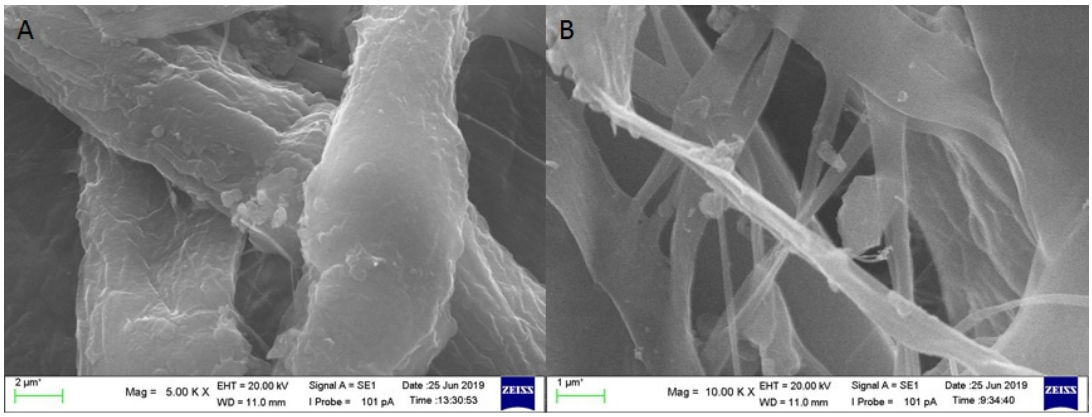

Figure 2: Scanning Electron Micrographs of A) Chemically deinked pulp and B) Combined cellulase and laccase deinked pulp.

3.2 Mechanical Properties Analysis

In this study, the mechanical properties of recycled paper was analyzed. The specimen was cut into 80 x 25 mm^2 and then test with tensile test tensometer. Stress (MPa) vs strain change curve can be seen in Figure 3.

Tensile strength (MPa), elongation at break (%) and Young's modulus (MPa) of untreated and reated newspaper pulp are shown in Table 1. As can be seen, tensile strength increased significantly for enzymatic treated pulp. Tensile strength for untreated pulp was 0.42 MPa with Young's modulus 714 MPa, whereas the highest tensile strength was 2.78 MPa with Young's modulus 743 MPa which obtained in 2% cellulase treated. Young's modulus is the ratio between stress and strain.

Pulp given an enzymatic treatment with 1% cellulase and 1% laccase combination had the highest Young'a modulus, it was 1493 MPa with 2.1 MPa tensile strength value. This indicated that there was a synergestic deinking effect between cellulase and laccase.

While compare with conventional deinking, enzymatic deinking had a better tensile strength with a significant difference. This results are in accordance with the use of chemical that caused damage during the deinking process which can also observed from the morphology of pulp fibers. Conventional deinking method even decreases the

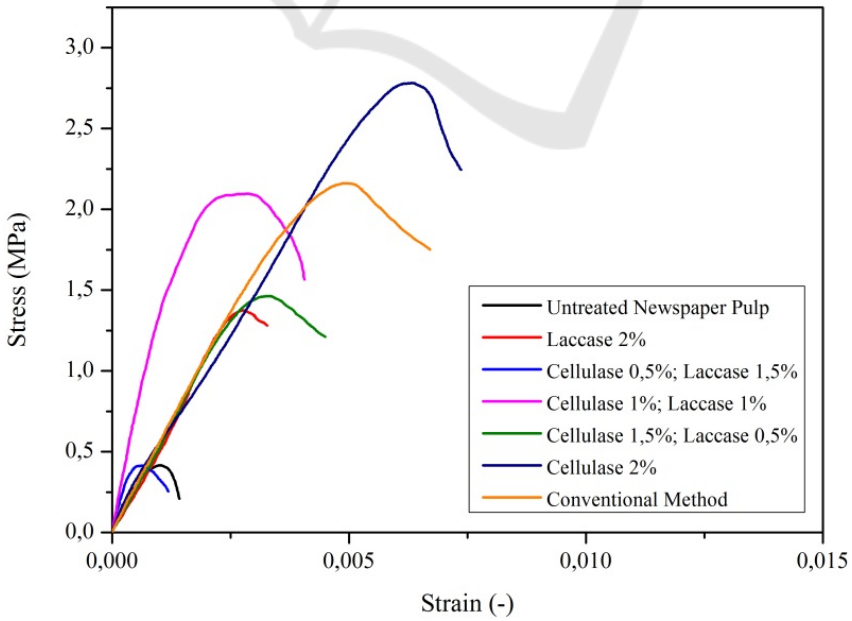

Figure 3: Stress-strain curve of untreated and treated handsheets of newspaper pulp.

Table 1: The Mechanical properties of untreated and treated newspaper pulp.

No	Treatment	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
1	Untreated Newspaper Pulp	0.42	0.1	714
2	Laccase 2%	1.38	0.3	572
3	Cellulase 0.5%; Laccase 1.5%	0.41	0.07	1041
4	Cellulase 1%; Laccase 1%	2.1	0.3	1493
5	Cellulase 1.5%; Laccase 0.5%	1.46	0.3	523
6	Cellulase 2%	2.78	0.6	743
7	Conventional Method	13	0.4	459

Young's modulus compared to untreated newspaper pulp. This study also in accordance with Shankar et al. (2018) who reported the increasing of chemical concentration caused substantial decrease in tensile strength. The use of large concentration of chemical may have reduced the tensile strength owing to high degree of depolymerization of cellulose content of the fibers (Shankar et al., 2018).

4 CONCLUSIONS

Cellulase combining with laccase effectively deinked old newspaper pulps without mediator supplementation for laccase activity. Morphological properties of enzymatic treated pulp show that the detachment of the ink particles from the surface of the fibers is more prominent in case of pulp treated with cellulase and laccase combination as compared to conventional deinking. Tensile test observed pulp treated with cellulase 1% and laccase 1% has the highest mechanical properties with 1493 MPa Young's modulus and 2.1 MPa tensile strength.

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