EFFECT OF DIFFERENT HLB VALUE AND ENZYMATIC TREATMENT ON THE PROPERTIES OF OLD NEWSPAPER DEINKED PULP

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Current deinking processes use potentially environmentally damaging chemicals in large quantities. The use of enzymes could be an attractive alternative to certain other chemicals used in deinking. In this research, the effects of different HLB (hydrophile-lipophile balance) values and enzymatic treatments on the deinking of old newspaper pulp (ONP) was studied, and optical properties and mechanical strengths of deinked pulps (DIP) were determined. Enzymatic treatments of old newspaper pulps were performed at two temperatures, 20°C and 50°C. Nonionic surfactants with different HLB values were used as the flotation agent. The flotation was conducted for pulps with and without enzymatic treatment. The results showed that brightness values for the floated pulp without enzyme treatment were slightly greater than for the enzyme-treated deinked pulp. Also, dirt count for treated pulps with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 50°C was lower than that of other pulps. The mechanical strengths of the enzymatically deinked pulps, in terms of burst, tensile, folding endurance, E-MOD, and elongation, were increased, but tear strength for the floated pulps with ethoxylated fatty alcohol of HLB 12 was increased at 50°C without enzymatic treatment. Also, the deinking efficiency of handsheets made from treated pulps with commercial cellulase and ethoxylated fatty alcohol of HLB 12 was highest. The treated pulps with enzyme only, with a combination of commercial cellulase and lipase at 50°C, showed the lowest freeness value in comparison with other pulps.

Keywords: HLB; Enzymatic treatment; Old newspaper; Mechanical strengths; Cellulase; Lipase

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INTRODUCTION

The boundless growth of paper making industries in non-industrialized countries has resulted in serious problems for the forests as a main source of raw material for this industry. Waste paper recycling is an alternative that can alleviate this stress on the environment. But recycling has its own problems. One of the most important problems for producing printing and writing marketable papers from waste papers is the variation of printing processes and inks used in the printing industry (Technical annex. 2003). Consequently, when a mixture of waste paper is repulped, different kinds of ink particles having different sizes and qualities are released into the suspension. In this condition, the importance of the deinking method selection becomes more important.

Also, considering the increases in waste paper usage in the paper industry, the need for an efficient method with lower pollution, higher elimination of ink particles, and improvement of product quality level is being felt more than ever. So, it is imperative to have technology that deinks ink particles to an acceptable residual ink count in an economical and environmentally acceptable manner.

Deinking is the key process in waste papers recycling. Hydrophobic (water-repellent) ink particles are separated from hydrophilic (water-wettable) fibers. This process has been developed for offset and gravure inks, which are more than 95% of the current recovered paper mixture, on average (Jeffries et al. 1994). Preventing adsorption of detached ink particles onto fiber surfaces and entanglement of fiber bundles are essential for effective deinking (Jeffries et al. 1994; Sykes et al. 1998; Gleisner et al. 2003). The common industrial methods for deinking are costly and require high amounts of chemicals that increase environment pollution. Therefore, waste paper recycling mills have a motivation to apply lower chemicals and more environment friendly methods. Enzymatic deinking (bio-deinking) has been proven as an environmentally friendly solution for waste papers recycling. Enzymatic deinking uses enzymes to enhance the removal of inks from waste papers and can be more effective and less expensive than conventional deinking chemicals. Also, it tends to avoid some problems associated with alternative treatment technologies (Jeffries et al. 1994; Pala et al. 2006). The mechanism of enzyme deinking has not been clearly defined. Cellulase binding on pulp fiber may result in surface fiber alteration, sufficient to favor ink detachment during repulping. Nevertheless, most researchers agree that cellulase enzyme releases ink particles from fiber surface and that the main effects are hydrolysis and superficial degradation of cellulose, which implies ink removal from fibers (Jeffries et al. 1994; Heise et al. 1997; Sykes et al. 1998). Several authors have reported that removal of oil-carrier-based inks can be facilitated by treatment with lipases (Morkbak et al. 1999; Franks 2001), which can degrade vegetable-oil based inks. Additionally, enzymes can remove small fibrils from the surface of the ink particles, thus altering the relative hydrophobicity of the particles, which facilitates their separation in the flotation step (Heise et al. 1997; Sykes et al. 1998). The enzymatic treatment contributes to the improvement of the mechanical and optical properties of the treated pulps compared to the control pulp (Heise et al. 1997; Sykes et al. 1998; Pelach et al. 2003; Rutledge-Cropsey et al. 1998). One of the first reports on enzymatic deinking of old newspaper showed increases in tensile strength relative to conventional deinking (Kim et al. 1991). Prasad et al. (1992) reported that cellulases could also be effective in deinking and improving the brightness of color offset printed newsprint.

In this work, old newspapers (ONP) deinking was studied at the laboratory scale. Past studies of enzymatic deinking have focused on optical properties much more than mechanical properties (Pelach et al. 2003; Rutledge-Cropsey et al. 1994; Morkbak et al. 1999). Also, there has been limited research on the different HLB values of surfactants on enzymatic deinking. In this research, the role of enzymatic treatment, the influence of different HLB of nonionic surfactant, the simultaneous influence of enzymatic treatment and nonionic surfactant, and also the effects of different temperatures on mechanical strengths and optical properties of prepared handsheets have been determined. In addition, the influence of enzymatic treatment and nonionic surfactant are examined with respect to the freeness of deinked pulps, and their effect on mechanical strength.

EXPERIMENTAL

Materials

Newspaper and enzyme

A mixture of two newspapers (Hamshahri and Iran newspapers, which were printed by the offset method) was used in this study. The newspapers were cut into approximate 2×2 cm pieces. Commercial Celluzyme® (which was produced from *Humicola insolens*) and Commercial Lipolase™ (which was produced from *Aspergillus oryzae*), Novo Nordisk, Bagvard A/S, Denmark, were supplied from TAJ Co., (Tehran, Iran) and were added into the 1-kg pulper at 0.1% as solid form (based on oven dried weight of pulp).

Pulping and flotation step

Pulping was done at 4% consistency, using tap water at two temperatures 20°C and 50°C, with a laboratorial mixer at the low agitation setting. Pulping was continued for 2.5 min. After pulping, enzymatic treatment was continued for 30 min. using a Ben Mari water bath. The original pH of the paper furnish was approximately 7.9. For the flotation trial, four liters (containing 40 g oven dried fiber) of the pulped slurry were transferred to a 5-L capacity standard laboratory flotation cell and floated for 10 min. at 1% consistency, using 0.5% non-ionic surfactant (based on oven dried weight of pulp). The surfactant used in this study was Ethoxylated Fatty Alcohol with different HLB values obtained from Kimyagaran Emrooz Co. (Tehran, Iran). Froth was scraped off manually; flotation accepts were washed with tap water for 2 min and were drained over on 120-mesh laboratory screen. Finally, there were four kinds of pulp: control pulp (without any treatment), treated pulps with enzyme only, treated pulps with surfactant only, and treated pulps with combination of enzyme and surfactant. Note that the treated pulps with surfactant only and treated pulps with combination of enzyme and surfactant were deinked. Canadian standard freeness (CSF) of all pulps was measured. The characteristics of the surfactants used are listed in Table 1. For simplicity, 12.4 and 14.6 HLB was referred to as 12 and 15.

Table1. Specifications/Properties of Surfactants

Name	Composition	EO[a] (mol)	HLB[b]	PH (5% in water)
KELA-7	Ethoxylated Fatty Alcohol	7	12.4	5-7
KELA-12	Ethoxylated Fatty Alcohol	12	14.6	6-7

[a] EO: ethylene oxide, [b]HLB: hydrophile-lypophile balance

Handsheets

Handsheets were made for evaluation of mechanical strengths, optical properties, and image analysis measurement (by *LabTech Semi-Automatic Sheet Machine*) according to TAPPI Test Method 205 om-88.

Methods

Deinking evaluation methods

The mechanical strengths, physical, and optical properties of pulp and paper, before and after deinking treatment, were characterized as follows: burst index was measured according to TAPPI T 403 om-97, tear index according to TAPPI T 414 om-88, tensile index according to TAPPI T 494 om-96, folding endurance according to TAPPI T 511 om-96, and freeness according to TAPPI T 227 om-99.

Residual dirt count and ink area of all pulps were obtained on a commercially available image analyzer. Image analysis of the handsheets made from recycled old newspaper was performed using a PC, Konica Minolta Scanjet 3c Scanner Model C450 and LECIA QWEEN COLOR program. Scanning resolution was 600dpi, threshold was 140, and the analysed area of handsheets was 1cm^2 for each repeat. All of the handsheets were analyzed from the same side (opposite to the mesh side). Brightness of the handsheets was measured according to TAPPI test method T 452-om 98. In this study, the deinking efficiency was evaluated by the following formula:

$$\text{Deinking efficiency \%} = \frac{Dirt\ area\ of\ control\ pulp - Dirt\ area\ of\ treated\ pulp}{Dirt\ area\ of\ control\ pulp} \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Treated Pulps with Enzyme Only

Results for mechanical strengths and Canadian standard freeness (CSF) of the enzymatically treated pulps are summarized in Table 2. The freeness of pulps at 20°C in enzymatic treatment was increased compared with the control pulp. However, freeness of enzymatically treated pulps decreased at 50°C compared with the control pulp. The CSF of the pulps were 291, 324, and 294 mL for the control, treated pulp with commercial cellulase at 20°C, and treated pulp with combination of commercial cellulase and lipase at 20°C, respectively. The freeness measurements indicated an increase of approximately 30 mL CSF for treated pulp with commercial cellulase at 20°C compared with control pulp. Jeffries et al. (1994) stated that the CSF of enzymatic pulps could be increased. This can be due to eliminating microfibrils and fines particles from pulps in enzymatic treatment. In other words enzymatic treated pulps have lower specific surface area compared with control pulps (Jeffries et al. 1994; Sykes et al. 1998). Additionally, enzyme binding may also improve freeness (Jackson et al. 1994). Binding of cellulases could aggregate small particles much like what occurs when polymers are as used as retention aids. Also, Table 2 shows that tear index of treated pulps with combination of commercial cellulase and lipase at both temperatures produced a pulp with 6.0 mN.m^{2}g^{-1} compared with 5.3 mN.m^{2}g^{-1} for the control pulp. Removing fiber fines from enzymatic treated pulps resulted in improved tear strength because the mean of fiber length was increased, and increasing fiber length can increase tear strength. Prasad (1993) mentioned that enzymatic treatment changed fiber length by decreasing fines content. On the other hand, the enzyme can fibrillate the fiber wall. So, the possibility for fiber bonding was increased (Bajpai 1999). Because the tear strength is also affected by fiber bonding, increasing fiber bonding can improve tear strength. We can attribute the tear increase in relation to control pulp sample to this phenomenon. Some researchers suggested the improvement in strength properties is due to the changes in hemicellulose content and the breakdown of lignin-hemicellulose linkage (Tolan and Guenette 1997). Prasad et al. (1992) pointed out that strength properties respond to changes in hemicellulose composition and degradation of lignin-hemicellulose linkages.

Table 2. Effect of the Enzyme Treatment and Surfactant on the Pulp and Paper Properties of ONP

Assay[A]	Pulp and paper properties							
	CSF (mL)	Burst index ($kPa.m^2/g$)	Tear index ($mN.m^2/g$)	Tensile index (Nm/g)	Folding endurance	E-MOD (Gpa)	TEA (J/m^2)	Elongation %
Control	291	1.4	5.3	48.6	3.0	476.5	34.6	1.7
E								
C[a]	324	1.7	5.7	58.6	3.5	565.0	41.6	1.7
C[b]	260	1.7	5.8	59.1	4.2	508.4	46.0	1.9
(C+L)[a]	294	1.9	6.0	63.3	4.0	584.3	51.0	1.9
(C+L)[b]	258	1.7	6.0	62.2	3.8	561.8	54.5	2.0
S								
H12[a]	397	1.4	5.6	50.8	2.0	466.5	37.6	1.8
H12[b]	471	1.7	6.3	55.6	5.0	491.5	43.1	1.8
H15[a]	326	1.6	5.9	53.0	3.0	481.4	43.5	1.9
H15[b]	408	1.6	6.4	56.8	4.2	513.2	46.6	1.9
E+S								
(C + H12)[a]	399	1.8	5.9	61.8	3.8	557.3	54.0	2.0
(C + H12)[b]	340	1.8	6.2	62.3	3.8	539.8	52.7	2.1
(C + H15)[a]	382	1.8	6.1	62.5	4.2	575.0	52.9	2.0
(C + H15)[b]	343	1.7	5.7	57.2	4.0	533.2	43.7	1.8
(C+L + H12)[a]	407	1.7	5.8	56.1	4.2	511.7	49.6	2.1
(C+L + H12)[b]	349	1.8	5.8	68.9	4.3	620.7	56.0	1.9
(C+L + H15)[a]	364	1.7	5.6	57.5	4.3	516.8	48.9	2.0
(C+L + H15)[b]	332	2.0	5.6	64.4	5.3	570.5	54.7	2.0

[A] Fiber/ink particle sepration step: (C [a]) Cellulase at 20°c, (C [b]) Cellulase at 50°C, ((C+L) [a]) Cellulase+Lipase at 20°C, ((C+L) [b]) Cellulase+Lipase at 50°C, (H12[a]) HLB 12 at 20°C, (H12[b]) HLB 12 at 50°C, (H15[a]) HLB 15 at 20°C, (H15[b]) HLB 15 at 50°C
E: Treated pulps with enzyme only
S: Treated pulps with surfactant only

Regarding other kinds of mechanical strengths that are dependent to inter fibrous bonds, enzymatic treatment through developing internal fibrillation in fiber walls can enhance inter-fiber bonds (Sykes et al. 1996; Jeffries et al. 1995; Pala et al. 2004); therefore, the mechanical strengths of handsheets would be increased. Other authors mentioned in their previous work that pulp fibrillation by cellulases is recognized as a means to enhance strength properties (Pala et al. 2006; Jeffries et al. 1994). Cellulases were used to enhance fibrillation, thereby improving the strength of paper by increasing fiber-fiber contact. Similar improvement in physical and strength properties of enzyme treated pulps has been reported. Nomura (1985) reported that cellulase plus cellobiase added to pulps facilitated fibrillation without strength loss, and Jokinen et al. (1991) have also described the use of cellulases to improve fibrillation of pulps. Enzymatic treatment through hydraulic and mechanical reactions can promote the potential of fibrous connections (Sykes et al. 1998; Gleisner et al. 2003; Pala et al. 2006). It seems that this approach at both temperatures of 20°C and 50°C is not identical. Treated pulps with commercial cellulase at 50°C had better mechanical strengths. It can be pointed out that higher temperature had an impressive effect on the fibrillation of the secondary fiber. In addition, it was found that the mixture of commercial cellulase and lipase caused the highest mechanical strengths of pulp. The burst and tensile indices, folding endurance, TEA, and elongation for control pulp were 1.4 $kPa.m^2g^{-1}$, 48.6 Nmg^{-1}, 3.0, 34.6 J/m^2, and 1.7 %, respectively, whereas the values for enzyme treated pulp with combination of commercial cellulase and lipase at 20°C were 1.9, 63.3, 4.0, 51.0, and 1.9, respectively. Sykes et al. (1997) mentioned that mixture of cellulase and lipase at the neutral pH of mixed office waste paper removed the adhesives more effectively than did conventional alkaline pulping at pH 10. It can be pointed out that in addition to the effect of commercial cellulase in fiber fibrillation, the commercial lipase enzyme also has a significant role in increasing the mechanical strengths of handsheets (Kirk et al. 1996). In other words, commercial lipase enzyme is able to operate as an agent in eliminating hydrophobic agents (oil-based inks) in pulp (Nakano 1993). So it is expected that by eliminating hydrophobic agents, the possibility of connecting different parts of fiber walls to each other would be higher, and this would increase mechanical strengths of paper compared with pulp treated by commercial cellulase enzyme only. In fact, it can be pointed out that enzymatic treatment not only maintains the integrity of recycled fibers of old newspaper and prevents them from being damaged (Heise et al. 1997; Treimanis et al. 1999), but also it promotes the bonds between the fibers (more fiber-to-fiber) and so increases the mechanical strengths of paper. Also, the results of statistical tests show that except the folding endurance, other mechanical strengths of paper were increased meaningfully compared with control pulp sample.

Treated Pulps with Nonionic Surfactant Only

Table 2 also shows the results of freeness value and mechanical strengths of treated pulps with nonionic surfactant. The CSF of pulps in flotation process showed a meaningful increase compared with control pulp sample and treated pulps with enzyme only. The freeness values of the pulps were 291, 397, and 326 mL for the control, treated pulp with ethoxylated fatty alcohol of HLB 12, and treated pulp with ethoxylated fatty alcohol of HLB 15 at 20°C, respectively. Also, there was a significant difference between two different HLB values of ethoxylated fatty alcohol. As can be seen, treated pulps with surfactant with low HLB value showed a higher increase in freeness at both temperatures compared with treated pulps with high HLB value. Also, Canadian standard freeness measurements indicated an increase of approximately 70 mL CSF in both temperature for treated pulps with HLB 12 compared with HLB 15. This increase in freeness can be attributed to elimination of fine particles and microfibrils, and this phenomenon increases the CSF of the pulps. Also, all of the mechanical strengths of handsheets were increased compared with control pulp. It seems that in a flotation process, with elimination of fine fibrous particles (Pèlach et al. 2003; Sykes et al. 1997; Kim et al. 1991), the mean of fiber length of deinked pulps increases compared with the control pulp sample, and this leads to a meaningful increase in tear strength. On the other hand, the flotation process results in elimination of non-fibrous (inorganic or ash) particles in pulp, and possibly this would lead to an increase in the potential of inter-fibers bonds. Therefore, the strengths related to inter-fiber bonds such as burst and tensile indices showed a significant increase. Regarding the results of mechanical strengths of handsheets, compared with deinked pulps with ethoxylated fatty alcohol of HLB 12, the deinked pulps with ethoxylated fatty alcohol of HLB15 had higher strengths at both temperatures. Of course, at 50°C higher increases were obtained, and results of statistical tests for burst, tear and tensile indices and TEA confirmed these results. The burst, tear and tensile indices, folding endurance, E-MOD, TEA, and elongation for treated pulp with ethoxylated fatty alcohol of HLB 12 at 20°C was 1.4 $kPa.m^2g^{-1}$, 5.6 $mN.m^2g^{-1}$, 50.8 Nmg^{-1}, 2.0, 466.5 Gpa, 37.6 J/m^2, and 1.8%, respectively, whereas the values for ethoxylated fatty alcohol of HLB 15 at 20°C were 1.6, 5.9, 53.0, 3.0, 481.4, 43.5, and 1.9, respectively. Also, statistical results of the research showed that though E-MOD of floated pulps with ethoxylated fatty alcohol of both HLB value had no meaningful difference compared with control pulp sample, but TEA and elongation in floated pulps with ethoxylated fatty alcohol of both HLB value showed a significant increase compared with control pulp sample.

Treated Pulps with Enzyme and Surfactant

Results of this deinking trial are summarized in Table 2. The freeness of deinked pulps at both temperatures was increased compared with control pulp. However, freeness of treated pulp with combination of commercial cellulase and lipase and floated with ethoxylated fatty alcohol of HLB 12 at 20°C was highest compared with control and other pulps. The CSF of the pulps were 291, 399, 382, 407, and 364 mL for the control, treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 20°C, treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 15 at 20°C, treated pulp with combination of commercial cellulase and lipase and floated with ethoxylated fatty alcohol of HLB 12 at 20°C, and treated pulp with combination of commercial cellulase and lipase and floated with ethoxylated fatty alcohol of HLB 15 at 20°C, respectively. The freeness measurements indicated an increase of approximately 120 mL CSF for treated pulp with a combination of commercial cellulase and lipase and floated with ethoxylated fatty alcohol of HLB 12 at 20°C compared with control pulp. Also, results reveal that treated pulps with a combination of enzyme and surfactant had higher mechanical strengths than control pulps, treated pulps with enzyme only and treated pulps with surfactant only. The results obtained from simultaneous enzymatic treatment and flotation showed that all of the mechanical strengths of deinked pulps were increased compared with control pulp. In other words, in simultaneous enzymatic and flotation process, enzymatic treatment results in improve fiber fibrillation (Heise et al. 1997; Rutledge-Cropsey et al. 1998; Pala et al. 2004) and the non-fibrous particles removed by the flotation process. So, it seems that combining the enzymatic treatment and flotation process can improve potential of inter-fibers bonds (Pala et al. 2004). Therefore, all of the mechanical strengths of enzyme-atically deinked pulps were increased compared with control pulp significantly. The burst, tear, and tensile indices, folding endurance, E-MOD, TEA, and elongation for treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 15 at 20°C were 1.8 $kPa.m^2g^{-1}$, 6.1 $mN.m^2g^{-1}$, 62.5 Nmg^{-1}, 4.2, 575.0 Gpa, 52.9 J/m^2 and

2.0 %, respectively, whereas the values for treated pulp with combination of commercial cellulase and lipase and floated ethoxylated fatty alcohol of HLB 12 at 50°C were 1.8, 5.8, 68.9, 4.3, 620.7, 56.0, and 1.9, respectively. Generally, regarding results obtained from measuring the mechanical strengths of handsheets, it can be seen that using commercial cellulase in pulp samples which were floated by ethoxylated fatty alcohol of HLB 15 at 20°C, and higher handsheet strength properties were obtained. Also, in pulp samples treated by commercial cellulase and lipase mixture, floated by ethoxylated fatty alcohol of HLB 12 at 50°C, higher paper strength properties were found.

Brightness

According to Fig. 1, the treated pulps with surfactant only and treated pulps with a combination of enzyme and surfactant showed higher brightness compared with control pulp. It seems that applying surfactant in flotation leads to elimination of more ink particles and ash from the pulp suspension, so the brightness increased, especially at 50°C. In fact, separating ink particles by flotation could make them easier to remove from pulp, resulting in increased brightness. Besides, based on the figure and according to investigations made for statistical results, it was observed that there was no meaningful difference between the two HLB values of ethoxylated fatty alcohol. Regarding the higher brightness of treated pulp with combination of enzyme and surfactant compared with control pulp, it can be pointed out that enzymatic treatment through a peeling mechanism would cause the ink particles to be taken off the surface of cellulose (Sykes et al. 1998; Heise et al. 1997; Sykes et al. 1997), and in the next step, i.e., a flotation step the efficiency of ink removal would be improved by adding ethoxylated fatty alcohol.

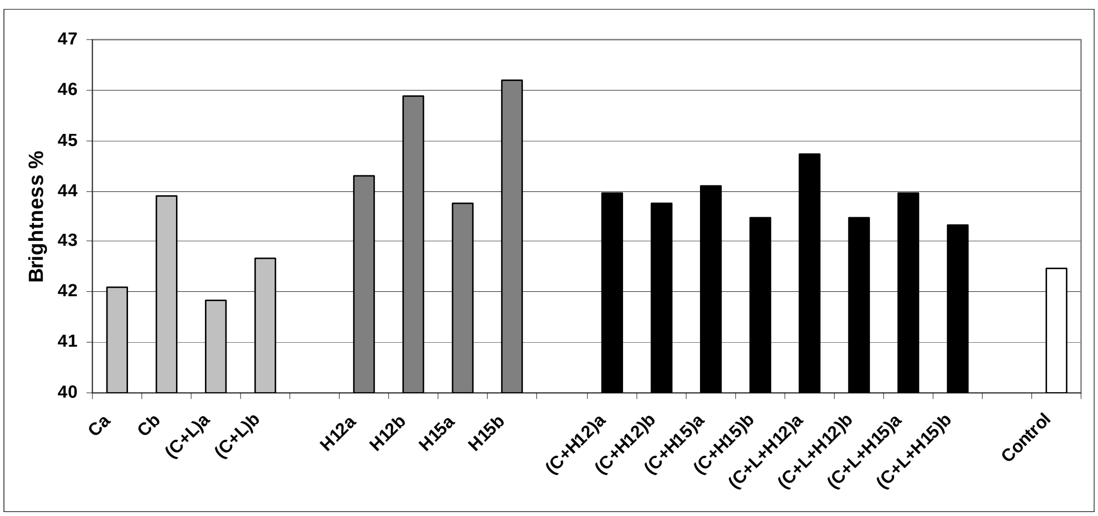

Figure 1. Brightness of handsheets made from control, enzyme treated, surfactant treated, and combination of enzyme and surfactant treated pulps

As shown in Fig. 1, the highest brightness of the pulps was 46.19 % for the treated pulp ethoxylated fatty alcohol of HLB 15 at 50°C and 42.46 % for control pulp. In contrast, the lowest brightness of the pulps was 41.82 % for the enzyme treated pulp with a combination of commercial cellulase and lipase at 20°C. It seems that for treated pulps with enzyme only, enzymatic treatment had no positive effect on brightness of pulps except at 50°C. Also, the results obtained from enzymatic treatment showed that brightness of pulps decreased at 20°C compared with control pulp, presumably due to reduced ink particle size. The brightness of the pulps were 42.46, 42.09, and 41.82% for the control, treated pulp with commercial cellulase at 20°C, and treated pulp with combination of commercial cellulase and lipase at 20°C, respectively. The quality, size, or tackiness of organic contaminants, or stickies can be reduced in recycled pulps and papers through the use of enzyme compositions according to Glover et al. (2002). The enzyme compositions contain lipases and esterases. The compositions are said to reduce the size of contaminants. Also, Kim et al. (1991) speculated that enzyme treatment allowed finely dispersed ink particles to re-adhere to fiber surfaces or to penetrate into porous parts of fibers, thereby limiting effectiveness of flotation. As an example, reductions in particle size in the presence of cellulases for newspaper, and overall reductions were greater than those noted in conventional deinking (Kim 1991). In fact, we can point out that enzymatic treatment with a surfactant typically results in residual ink areas and dirt count (Table 3) significantly lower than those produced by enzyme only or surfactant only. Besides, pulps with enzymatic treatment often giving brightness less than with conventional deinking (Rushing et al. 1993). This differential outcome has been observed repeatedly, and may result from the tendency of enzymes to reduce ink particles to much smaller sizes than other methods.

Deinking Efficiency, Ink Area, and Dirt Count

The results of image analysis showed that deinking efficiency was improved in enzymatically treated pulps (Figures 2 and 3) relative to treated pulps with surfactant. Also, dirt count and ink area decreased steadily with enzymatic treatment (Table and Fig. 3). However, the statistical tests for dirt count indicated that there was no significant difference between enzymatic treated pulps relative to treated pulps with surfactant only. In general, a combination of enzyme and surfactant process was more effective than enzyme only or surfactant only treatment; however, the greatest enhancement of ink elimination was obtained with the combination of enzyme and surfactant treatment for the treated pulp with commercial cellulase and ethoxylated fatty alcohol of HLB12 at 50°C which was 78% (Fig. 2).

In contrast, it must be highlighted that the treated pulps with surfactant only, which showed the higher brightness in the deinking process, showed lower improvement in deinking efficiency, which was 47%. In an enzymatic process, a flotation process, and a combination of enzymatic and flotation processes, the number of the ink particles were less than in the control pulp sample (Table 3).

It seems that in a combined process consisting of enzymatic treatment and flotation, the number of ink particles compared with enzymatic treatment and flotation process are decreased. As can be seen in Fig. 2, the deinking efficiency in combined process was better than the other two treatments (as in Jeffries et al. 1995). On the other hand, as it is clear from Table 3, in combined process the average size of ink particles was higher than treated pulps with enzyme only and treated pulps with surfactant only.

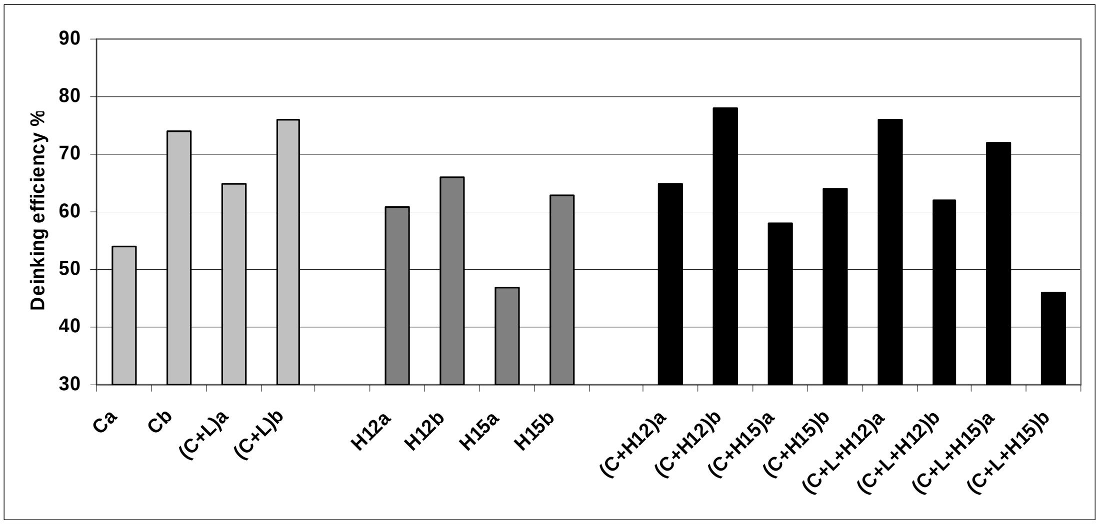

Figure 2. Deinking efficiency of handsheets made from enzyme treated, surfactant treated, and combination of enzyme and surfactant treated pulps (deinking efficiency, expressed as % of ink area reduction relatively to control pulp)

The ink particle size average values of the pulps were 0.0198, 0.0163, 0.0162, 0.0210, and 0.0237 cm^2 for the control pulp, treated pulp with combination of commercial cellulase and lipase at 50°C, treated pulp with ethoxylated fatty alcohol of HLB 15 at 50°C, treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 50°C, and treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 15 at 50°C, respectively. Cellulases were reported in 1991 to be effective in removing inks from newsprint, in research done in Korea (Kim et al. 1991). Also, we can mention that a combination of surfactant and enzyme had a strong effect on the deinking efficiency (Table 3). The dirt counts of pulps were 51, 16, 15, 22, 23, 11, and 20 for the control pulp, treated pulp with commercial cellulase at 50°C, treated pulp with combination of commercial cellulase and lipase at 50°C, treated pulp with ethoxylated fatty alcohol of HLB 12 at 50°C, treated pulp ethoxylated fatty alcohol of HLB 15 at 50°C, treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 50°C, and treated pulp with combination of commercial cellulase and lipase and floated with ethoxylated fatty alcohol of HLB 15 at 50°C.

The results showed that ink elimination was highest in the case of a combination of enzyme and surfactant, compared with enzyme treated pulps and surfactant treated pulps (Table 3); nevertheless brightness was even slightly decreased by the enzymatic treatment compared with treated pulps with surfactant only. The ink area values of pulps were 1.008, 0.467, 0.357, 0.388, 0.529, 0.348, and 0.238 cm^2 for the control pulp, treated pulp with commercial cellulase at 20°C, treated pulp with combination of commercial cellulase and lipase at 20°C, treated pulp with ethoxylated fatty alcohol of HLB 12 at 20°C, treated pulp with ethoxylated fatty alcohol of HLB 15 at 20°C, treated pulp with commercial cellulase and floated ethoxylated fatty alcohol of HLB 12 at 20°C, and treated pulp with combination of commercial cellulase and lipase and floated ethoxylated fatty alcohol of HLB 15 at 20°C.

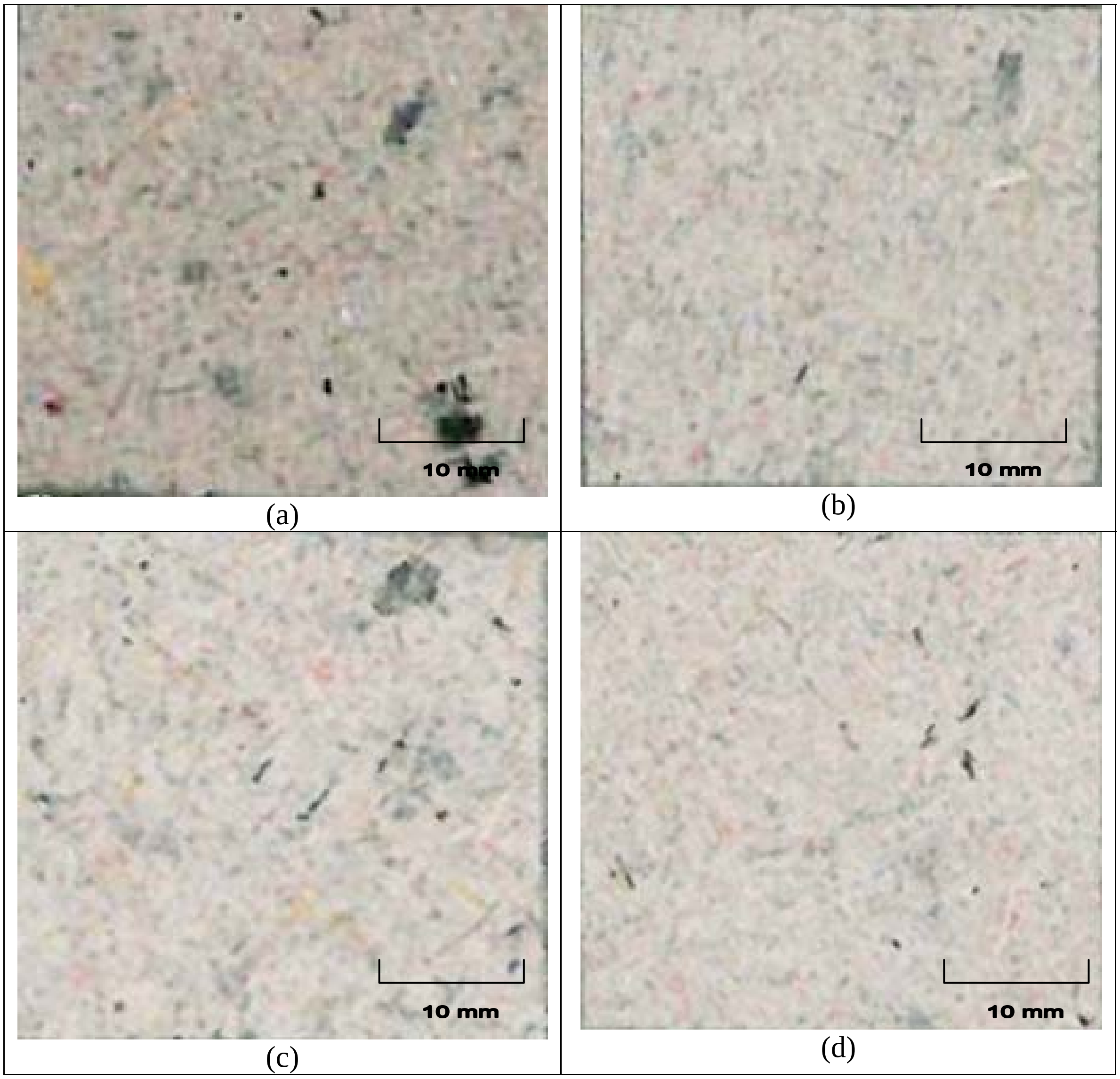

Figure 3. Image analysis images of control pulp (a); treated pulp with enzyme only (b); treated pulp with surfactant only (c); and treated pulp with enzyme and surfactant (d). Additional information: b: treated pulp with commercial cellulase and lipase at 50°C, c: treated pulp with ethoxylated fatty alcohol of HLB12 at 50°C, d: treated pulp with commercial cellulase and floated with ethoxylated fatty alcohol of HLB12 at 50°C.

According to Fig. 3 and Table 3, it can be pointed out that enzyme treated pulps had lower dirt count compared with surfactant-treated pulps, but ink areas of these pulps were greater, and due to this, deinking efficiency of treated pulps with enzyme only was more but showed lower brightness compared to treated pulps with surfactant only. Also, we can mention that there was a significant difference between two different HLB values of ethoxylated fatty alcohol. As can be seen, treated pulps with surfactant of HLB 12 showed a meaningful decrease in dirt count and ink areas compared with HLB 15, especially at 50°C. According to Table 3, it seems that ethoxylated fatty alcohol of HLB 12 had a strong effect on ink removal, especially at 50°C.

Table 3. Effect of the Enzyme Treatment and Surfactant on the Optical Properties of ONP

Assay[A]	Image analysis results		
	Ink area (cm^2)	Dirt count	Ink Particle size average (cm^2)
Control	1.008	51	0.0198
E			
C[a]	0.467	28	0.0167
C[b]	0.262	16	0.0164
(C+L)[a]	0.357	23	0.0155
(C+L)[b]	0.245	15	0.0163
S			
H12[a]	0.388	25	0.0155
H12[b]	0.355	22	0.0161
H15[a]	0.529	35	0.0151
H15[b]	0.372	23	0.0162
E+S			
(C + H12)[a]	0.348	17	0.0205
(C + H12)[b]	0.221	11	0.0201
(C + H15)[a]	0.425	19	0.0224
(C + H15)[b]	0.357	17	0.0210
(C+L + H12)[a]	0.238	12	0.0198
(C+L + H12)[b]	0.386	20	0.0193
(C+L + H15)[a]	0.285	15	0.0190
(C+L + H15)[b]	0.546	23	0.0237

[A] Fiber/ink particle sepration step: (C [a]) Cellulase at 20°c, (C [b]) Cellulase at 50°c, ((C+L) [a]) Cellulase+Lipase at 20°c, ((C+L) [b]) Cellulase+Lipase at 50°c, (H12[a]) HLB 12 at 20°c, (H12[b]) HLB 12 at 50°c, (H15[a]) HLB 15 at 20°c, (H15[b]) HLB 15 at 50°c
E: Treated pulps with enzyme only
S: Treated pulps with surfactant only

Enzymes also remove small fibers from the surface of the detached ink particles (Kim et al. 1991), thus allowing their smooth passage to the top during the flotation process. Once the ink particles are floating on the water surface, they are removed by a skimming action. In other words, in the combined process, the number of ink particles remaining in the paper was lower, but the size of the particles was larger. It seems that in combined process due to increased CSF, removal of ink particles would be facilitated (Sykes et al. 1997; Jeffries et al. 1994), although the average of particles size was higher in the combined process.

CONCLUSIONS

In this study, optical properties and mechanical strengths of enzymatic deinked pulps of old newspaper in presence of a nonionic surfactant were determined and the following conclusions can be obtained:

1. Generally, when the HLB value of surfactant becomes lower, ink particles adsorption to surfactant increases.

2. The results showed that freeness of treated pulps with ethoxylated fatty alcohol (nonionic surfactant) increased significantly more compared with enzyme-treated pulps and enzyme/surfactant treated pulps, especially at 50°C.
3. We conclude that mechanical strengths of enzymatically deinked pulps were higher than control pulp and treated pulps with enzyme only and surfactant only.
4. The tear index of the hand sheets made from treated pulps with surfactant only showed the highest increase compared with treated pulps with enzyme treatment.
5. Compared with control pulp, enzymatic treatment of pulp with commercial cellulase and combination of commercial cellulase and lipase can improve the mechanical strengths of pulp. The mechanical strengths of treated pulps with combination of commercial cellulase and lipase treatment were higher than commercial cellulase treatment only. However, there were no significant differences between pulps subjected to two temperatures of enzyme treatment.
6. As noted in this report, the results of mechanical strengths and optical properties of enzymatic deinked pulps with ethoxylated fatty alcohol of HLB 12 were better than HLB 15, especially at 50°C.
7. The highest brightness of pulps was seen in pulp treated with ethoxylated fatty alcohol of HLB 15 at 50°C.
8. The deinking efficiency of pulps made from treated pulps with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 50°C was increased significantly compared with other pulps.
9. Image analysis indicated that the treated pulps with commercial cellulase and floated with ethoxylated fatty alcohol of HLB 12 at 50°C had the lowest ink area and dirt count.
10. The results showed increasing temperature of enzymatic treatment and flotation trial can improve the optical properties and mechanical strengths of handsheets made from deinked pulps.

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REFERENCES CITED

Anon. (2003). "Draft document, description of the printing processes," Technical Annex 1, http://ec.europa.eu/environment/ecolabel/ecolabelled_products/categories/pdf/technicalannex1_nov03.pdf

Bajpai, P. (1999). "Application of enzymes in pulp and paper processing," *Biotechnol. Prog.* 15, 147-157.

Franks, N. E. (2001). "Methods for deinking and decolorizing printed paper," *US Pat.* 6,241,849.

Gleisner, R., and Blankenburg, J. (2003). "Semiannual patents review," In: *Progress Paper Recycling* 12(3), 26-33.

Glover, D., Jaques, P., and Fitzhenry, J. (2002). "Methods to control organic contaminants in fibers," *US Pat.* 6471826.

Heise, O. U., Unwin, J. P., Klungness, J. H., Fineran, W. G., Sykes, M. S., and Abubakr, S. (1997). "Industrial scaleup of enzyme-enhanced deinking of nonimpact printed toners," *Tappi J*. 79(3), 207-212.

Jackson, L. S., Heitmann, J. A., and Joyce, T. W. (1993). "Enzymatic modifications of secondary fiber," *Tappi J*. 76(3), 147-154.

Jeffries, T. W., Klungness, J. H., Sykes, S., and Rutledge-Cropsey, K. (1994). "Comparison of enzyme-enhanced with conventional deinking of xerographic and laser-printed paper," *Tappi J*. 77(4), 173-179.

Jeffries, T. W., Sykes, M. S., Rutledge-Cropsey, K., Klungness, J. H., and Abubakr, S. (1995). "Enhanced removal of toners from office waste papers by microbial cellulases," In: *Sixth International Conference on Biotech. Pulp and Paper Industry*, 141-144.

Jokinen, O., Kettunen, J., Lepo, J., Neimi, T., and Leine, J. E. (1991). "Method of producing fluff pulp with improved defibration properties," *US Pat*. 5,068,009.

Kim, T.-J., Ow, S. S.-K., and Eom, T.-J. (1991). "Enzymatic deinking method of wastepaper," In: *TAPPI Pulping Conference Proceedings*, 1023-1031.

Kirk, T. K., and Jeffries, T. W. (1996). "Roles for microbial enzymes in pulp and paper processing," Institute for Microbial and Biochemical Technology, Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, 1-14.

Morkbak, A., Degn, P., and Zimmermann, W. (1999). "Deinking of soy bean oil based ink printed paper with lipases and a neutral surfactant," *J. Process Biochem*. 67, 229-236.

Nakano, J. (1993). "Recent research trends of pulping chemistry," *Appik J*. 25(1), 85-91.

Nomura, Y., (1985). "Digestion of pulp," *Japanese Pat*. 126,395.

Pala, H., Mota, M., and Gama, F. M. (2004). "Enzymatic versus chemical deinking of non-impact ink printed paper," *J. Biotechnol*. 108(1), 79-89.

Pala, H., Mota, M., and Gama, F. M. (2006). "Factors influencing MOW deinking: Laboratory scale studies," *J. Enzyme Microb. Technol*. 38, 81-87.

Pèlach, M. A., Pastor, F. J., Puig, J., Vilaseca, F., and Mutjè, P. (2003). "Enzymic deinking of old newspapers with cellulase," *J. Process Biochem.* 38, 1063-1067.

Prasad, D. (1993). "Enzymatic deinking of laser and xerographic office wastes," *Appita J*. 46(4), 289-292.

Prasad, D. Y., Heitmann, J. A., and Joyce, T. W. (1992). "Enzyme deinking of black and white letterpress printed newsprint waste," In: *Progress Paper* Recycling. 1(3), 21-30.

Rushing, W., Joyce, T. W., and Heitmann, J. A. (1993). "Hydrogen peroxide bleaching of enzyme deinked old newspaper," In: *Seven International Symp. on Wood and Pulping Chemistry*, Beijing, China, 233-238.

Rutledge-Cropsey, K., Jeffries, T., Klungness, J. H., and Sykes, M. S. (1994). "Preliminary results of effect of sizings on enzyme-enhanced deinking," In: *TAPPI Recycling Symposium*, 103-105.

Rutledge-Cropsey, K., Klungness, J. H., and Abubakr, S. (1998). "Performance of enzymatically deinked recovered paper on paper machine runnability," *Tappi J.* 81(2), 148-151.

Sykes, M. S., Klungness, J. H., Abubakr, S., and Tan, F. (1996). "Upgrading recovered paper with enzyme pretreatment and pressurized peroxide bleaching," In: *Progress Paper Recycling* 5, 39-46.

Sykes, M. S., Klungness, J. H., Gleisner, R., and Abubakr, S. (1998). "Stickie removal using neutral enzymatic repulping and pressure screening," In: *Tappi Recycling. Symposium Notes*, p. 291-297.

Sykes, M. S., and Tan, F. (1997). "Enzymatic removal of stickie contaminants," In: *TAPPI Pulping Conference Proceedings*, 687-691.

Tolan, J. S., and Guenette, M. (1997). "Using enzymes in pulp bleaching: Mill applications," In: *Advances in Biochemical Engineering/ Biotechnology*, Vol. 57, 288-310.

Treimanis, A., Leite, M., Eisimonte, M., and Viesturs, U. (1999). "Enzymatic deinking of laser-printed white office wastepaper," *J. Chem Biochem Eng.* 13(2), 53-57.

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