Application of lipase to reduce ONP flotation rejects Part 1. Changes in hydrophobicity

JEONG-YONG RYU, BONG KEUN SONG, AND JAE KWANG SONG

ABSTRACT: Cleaner and cheaper deinking of old newspaper (ONP) is possible under neutral or low alkaline conditions. Yet excessive reject from froth-flotation is unavoidable under these conditions; reduction of alkali dosage sacrifices the yield of ONP recycling. Instead of alkali, deinking operations could use lipase as a biocatalyst for the selective hydration of some hydrophobic particles in deinking stock, such as cellulose fines and inorganic fillers covered by hydrophobic sizing agents, binders, or contaminants. Lipase from *Thermomyces lanuginosus* significantly affects ester linkage break down, which causes desizing of cellulose, deacetylation of PVAc, and dealcohol of SB latex films. We suggest that lipase is a better choice to change the hydrophobicity of ONP than conventional inorganic alkali.

Application: Lipase-applied flotation is effective in reducing flotation deinking rejects without sacrificing ink removal efficiency and may allow mills to control flotation selectivity by modifying the hydrophobicity of fine materials in deinking stock, reduce production costs, and reduce environmental impact.

Because of increased demand in developing countries, international trade of recovered paper has been growing yearly [1, 2]. Sustainable development of the paper industry will require sufficient supplies of raw material, particularly high quality recovered paper. Increasing the collection rate is part of the solution for the shortage of recovered paper, but increasing recycling yield is also important. Recycling yield of recovered paper is mainly influenced by two factors: the amount of contaminants and the removal efficiency of contaminants during the stock preparation process. Old newspaper (ONP) gives relatively low yield when recycled, compared with packaging grades, because of losses in the deinking process.

Deinking processes for recovered paper can be classified as washing and flotation. Selective segregation of ink by froth flotation is preferred because of reduced contamination and consumption of process water. Ink separation by froth flotation is based on the differences in surface properties between hydrophobic ink and hydrophilic fibers. Hydrophobic ink particles show a strong tendency to adhere to air bubbles. After attachment, they can be segregated from hydrophilic components, including hydrated cellulose fibers, fines, and inorganic fillers. The efficiency of the flotation deinking process depends on the surface physical-chemical properties and the hydraulic movement of suspended solids in the flotation cell. Ink particles are more efficiently removed when the hydrophobic ink particles are completely detached from hydrophilic fiber surfaces and when the detached ink particles collide with air bubbles in the flotation cell and are floated to the surface.

Using organic solvent extraction data, we estimated the amount of ink in deinking stock to be less than 2% (dry basis). However, the total reject loss during flotation deinking of ONP is usually higher than 10%. In addition to the hydrophobic ink particles, pulp fines and inorganic pigments are also floated and discharged during flotation. Although virgin pulp fines and unused inorganic pigments or fillers have hydrophilic surfaces, during the deinking process they have hydrophobic surfaces because of the adsorption of hydrophobic materials, including sticky contaminants or other chemicals intentionally added at the wet end. For this study, stickies include various polymeric contaminants, such as styrene-butadiene latex, polyvinyl acetate (PVAc), vinyl acetate (VA), polystyrene (PS), polyisoprene, and hot melts (EVA, polyethylene and waxes). Wet end chemicals include sizing agents, which adsorb mainly on fines because of their large specific surface area. These fines could be floated easily in deinking cells because of their physical size and surface hydrophobicity.

Fragmented stickies also adsorb on the surface of suspended solids, again, preferentially on the fines because of their higher specific surface area [3]. Most of the inorganic pigment particles originate from coating layers of recycled old magazines (OMG). Surfaces of inorganic pigments in deinking stock are usually covered by insoluble hydrophobic synthetic binder (SB latex). As a result, small particles, including fiber fines and inorganic pigments, are lost by rejection in the froth flotation step. The flotation loss includes simple loss of raw materials and waste of energy for stock preparation, including pulping, cleaning, and coarse screening. The flotation loss also results in unnecessary contamination of process water. These are all compelling reasons to optimize the flotation efficiency and reduce flotation loss. If we can control the flotation selectivity by modifying the hydrophobicity of fine materials in deinking stock, production costs and negative environmental effects could be reduced.

DEINKING pH VERSUS FROTH FLOTATION LOSS

The surface hydrophobicity of fine materials might easily be reduced by increasing alkali chemicals in the pulping stage to increase alkaline hydrolysis of certain types of chemical linkages. Adding a sufficient amount of alkali at the pulping stage can promote wetting or hydration of hydrophobic suspended solids and reduce loss of fines and minerals. However, higher alkali dosage in pulping and deinking may indiscriminately dissolve or fragment inks and stickies. Therefore, a special method for the selective modification of valuable hydrophobic particles is required.

Reducing alkali in the deinking process of ONP has been considered. Neutral deinking of ONP has the primary benefit of significantly reducing chemical costs by eliminating caustic, peroxide, chelant, biocide for catalase control, and all or part of the sodium silicate from the pulper. As a related advantage, this would eliminate several chemicals that have serious safety and environmental implications [4]. However, one of the original purposes behind the development of neutral deinking technology was to reduce the breakup of stickies containing alkali-soluble lattices and adhesives that are readily dispersed when recovered paper is pulped with high alkali levels [5]. Although cleaner and cheaper deinking of ONP could be achieved at the neutral or low alkaline conditions, an excessive loss from flotation is unavoidable as the result of less wetting of fines [6,7]. The focus of this work is how to overcome this contradictory relation, getting the best of both. To achieve clean and high yield deinking of ONP, application of biocatalyst enzyme was considered.

Until now the use of cellulase, hemicellulose, or lipase-based enzymes has been an attractive alternative to chemicals in deinking. Enzymes could improve the deinkability of inks difficult to detach with the conventional deinking process. Using enzymes in neutral conditions yields a lower COD concentration than conventional alkaline deinking. In recent years, the application of enzymes in deinking has been studied in laboratories and at pilot plant scale, resulting in numerous patents.

Three approaches are available for the use of enzymes in deinking:

- The fiber surface can be attacked by enzymes such as cellulases, xylanases, or pectinases; this releases ink from fiber surfaces.
- The starch-based coating on paper can be solubilized by amylase, similarly promoting ink detachment from surface sized papers.
- Vegetable oil-based binders of the printing inks can be hydrolyzed by lipases (8).

However, so far enzymatic deinking has not been widely used commercially. We are not aware of previous use of lipase for the improvement of deinking yield.

LIPASES AND HYDRATION OF FINES

Lipase is an enzyme that catalyzes the breakdown of fats (triglyceride) into fatty acids and glycerol. If the lipase could cut the ester bond of chemically reacted internal sizing agents, such as AKD and ASA, lipase could promote the hydration of deinking stock and could reduce the loss of fiber fines during flotation deinking.

The major component of rosin size, abietic acid, is a partially unsaturated compound with three fused six-member rings and one carboxyl group anchored to the surface of fibers by forming a cationic precipitant with alum. The anchoring group of the cationic precipitant also could be cut by lipase.

Fine particles in flotation stock could be covered by adsorbed hydrophobic microstickies such as PVAc. If the enzymatic hydrolysis of the ester bond (deacetylation) could occur on the surface of PVAc, wetting of these fine particles would be increased and flotation deinking yield would improve.

Synthetic binders in the paper coating can provide hydrophobicity on inorganic pigments. As a major coating binder for paper coating, SB latex is usually a significant component of the coating formula and forms a binding layer or film between pigment particles. After reslushing of recovered paper such as OMG, SB latex-covered pigments show hydrophobic surface properties even though the dispersed pigments themselves are hydrophilic.

SB latex is made from monomers, comonomers, and modifiers. Methyl methacrylate (MMA) could be regarded as a common example of a comonomer having ester bond. Hydroxyethyl acrylate (HEA), used as a surface modifying monomer, also has an ester bond. These ester bonds could be hydrolyzed by lipase. Hence, the hydrophobicity of latex-covered pigments can be decreased by enzymatic hydrolysis of the ester bonds and alcohol generation by lipase.

This paper describes experimental evidence for enzyme-induced changes to the hydrophobic surfaces of these materials. The application of lipase to the froth flotation was successful and will be reported in the second part of this paper.

MATERIALS AND METHODS

Three kinds of commercial lipases were evaluated in this study: Resinase A2X® (lipase 1) from Thermomyces lanuginosus (Novozymes); Lipex® (lipase 2) from Fusarium oxysporum (also Novozymes); and Optimyze® (lipase 3), from Magnaporthe grisea (Buckman). For verification of the desizing effect, AKD reacted filter paper was prepared. AKD wax was dissolved in dichloromethane (DCM) at 10% solids. Then, filter paper (Whatman No. 2) was soaked in the AKD solution for 1 min. After air drying, the filter paper was cured at 105°C for 1 hour. The cured filter paper was washed with DCM to remove the unreacted AKD. The AKD sized filter paper was soaked in the three lipase solutions (0.1% lipase) for 30 min at 45°C with stirring. Lipase treated filter papers were rinsed with 1N NaCl solution and distilled water and dried in the air for the analysis of hydrophobicity of its surface. Dynamic contact angle of a water drop was measured before and after the lipase treatment.

ASA-sized filter paper was prepared by exposing the filter papers in a chamber saturated with vaporized ASA at 105°C for

Ground calcium carbonate	85
American clay	5
Styrene butadiene latex (MMA 5 part, HEA 1.5 part)	8
Esterfied starch	2
Optical brightening agent	Trace
Violet dye	Trace
Ammonium hydroxide	Trace

I. Composition of the coating layer on the coated paper tested (%).

3 h [9]. ASA-sized filter papers were then soaked in the three 0.1% enzyme solutions for 30 min at 45°C with stirring. The lipase-treated papers were dried as described previously.

Unlike reactive sizing agents such as AKD or ASA, rosin does not form chemical bonds with cellulose. Rosin reacts with alum and forms aluminum resinate as a cationic complex, which usually sticks onto the hydrophilic fiber surfaces. To verify the desizing effect of lipase, the broke of highly rosin-sized wallpaper was disintegrated at the consistency of 2% for 5 min using a TAPPI Standard (T-205 om-88) disintegrator (0.1 % based on OD weight of stock) with and without lipase 1. A slurry of wallpaper broke was beaten by a Valley beater for 15 min and sampled from the beater at 5, 10, and 15 min to make pads of 100g/m^2. We also measured the water drop contact angle of the pads.

Besides sizing agents, adsorbed microstickies can cover the surface of fine materials and these hydrophobic fine materials are destined to be floated as rejects. To evaluate the use of lipase to modify microstickies through deacetylation, PVAc-coated plastic film was prepared. Commercial PVAc adhesives are produced by emulsion polymerization process and contain additives such as surfactants, emulsifiers, and stabilizers. To exclude the influence of the non-PVAc materials on surface properties of PVAc film, solution polymerization was used in this study.

The molecular weight of PVAc was significantly low. After homopolymerization of vinyl acetate, vinyl acetate monomer was dissolved in isopropyl alcohol at 20% solids. As an initiator, 0.3% azo-bis(isobutyro)nitrile (AIBN; $[CH_3]_2C[CN]N=N C[CH_3]_2CN$), based on monomer weight, was added and the temperature was maintained at 50°C for the polymerization. The polymerized PAVc had a number-average molecular weight (Mn) of 4430, a weight-average molecular weight (Mw) of 5710, and a molecular weight distribution (MWD) of 1.289. Plastic film was coated with PVAc and the coated films were soaked in the three 0.1% lipase solutions for 30 min at 45°C with stirring. Soaked films were rinsed with 1N NaCl solution and distilled water and dried as previously described.

To evaluate the surface modification of inorganic pigments from coated paper, the surface hydrophobicity of coated paper was checked before and after soaking in various lipase solutions. If lipase could decrease the contact angle of a water drop on coated paper, soaking in a lipase solution could be expected to promote the hydration of reslushed coating pigments in deinking stock. Coated paper (100g/m^2, ash 45%) having the coating layer composition shown in **Table I** was soaked in the three 0.1% lipase solutions for 30 min at room temperature with agitation by a magnetic stirrer.

Lipase-treated coated papers were rinsed and air dried to analyze the hydrophobicity of their surfaces. Dynamic contact angle of a water drop was measured before and after the lipase treatment. To confirm the effect of lipase on the modification of SB latex film, SB latex-coated plastic film was prepared. SB latex emulsion was coated on plastic film with a coating weight of 10g/m^2 and dried at 105°C. The latex-coated film was soaked in 0.1% lipase 1 solution for 30 min at 45°C with stirring.

To investigate the possible influence of additives in commercial lipase, coated plastic film was soaked in deactivated lipase 1. To deactivate the enzyme activity of lipase 1, NaOCl was added, 5% based on enzyme weight. Lipase-treated plastic films were rinsed with 1N NaCl solution and distilled water and air dried before analysis of the hydrophobicity of its surface.

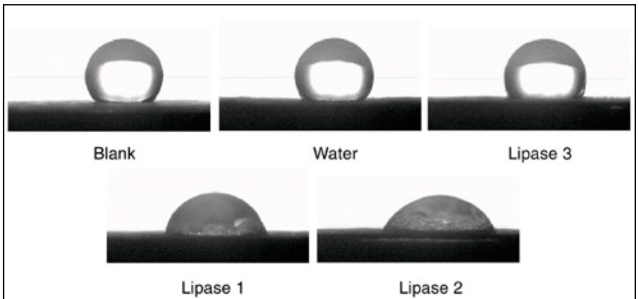
To obtain the direct proof of enzymatic modification of SB latex-coated plastic film, we investigated the surface variability of films before and after soaking in lipase solution using an attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectrophotometer. However, the latex film was not sufficiently thinner than the penetration depth of IR beams, so it was not possible to detect any difference between the ATR-FT-IR results of films before and after soaking in lipase solution.

RESULTS AND DISCUSSION

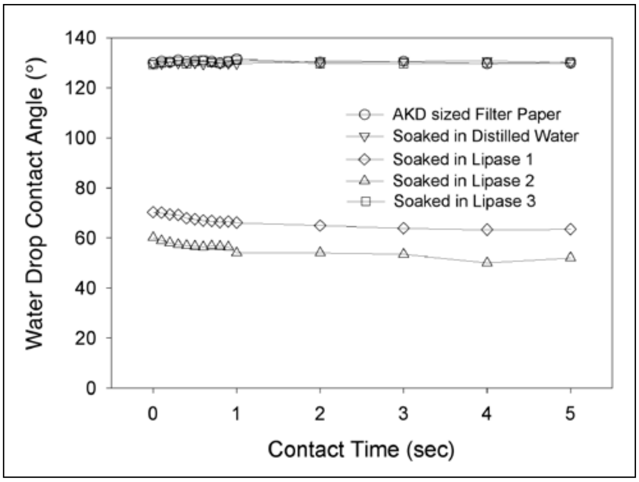
Lipase for desizing

The contact angle of a water drop on AKD sized filter paper before (blank) and after (water) soaking in water maintained at more than 120° as shown in **Figures 1** and **2**. Lipase 1 and 2 decreased the contact angle as much as 50° after 30 min of soaking. That means that the hydrophobicity induced by reacted AKD could be changed (reduced) by enzymatic hydrolysis, as illustrated in **Fig. 3**. The results show the possibility of using lipase to modify the AKD-reacted surfaces of fibers.

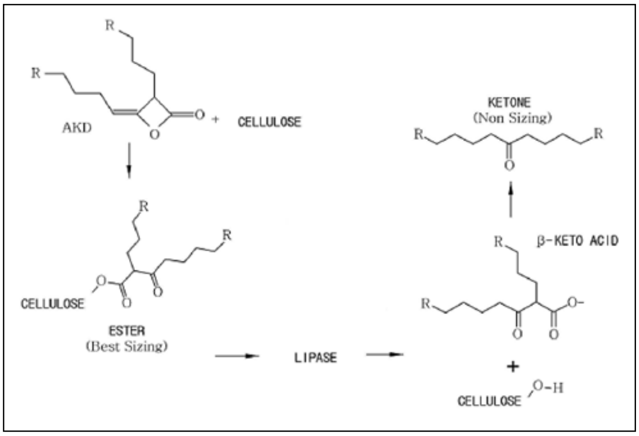
As shown in **Fig. 4**, lipase 1 and 2 changed the hydrophobic surface of the ASA sized filter paper into a more hydrophilic surface. Similar to the case of AKD, lipase 3 did not show any significant effect on the decrease of the contact angle of a water drop. Lipase 3 has been used as a stickies control agent and showed good efficiency for the surface modification of microstickies [10]. However, the activity of lipase 3



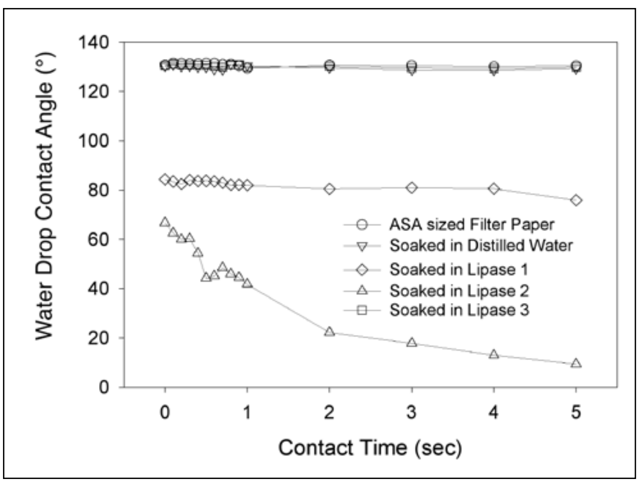
1. Contact angle of a water drop on AKD-sized filter paper before and after lipase treatment.



2. Dynamic contact angle of a water drop on AKD-sized filter paper after soaking in various lipase solutions.



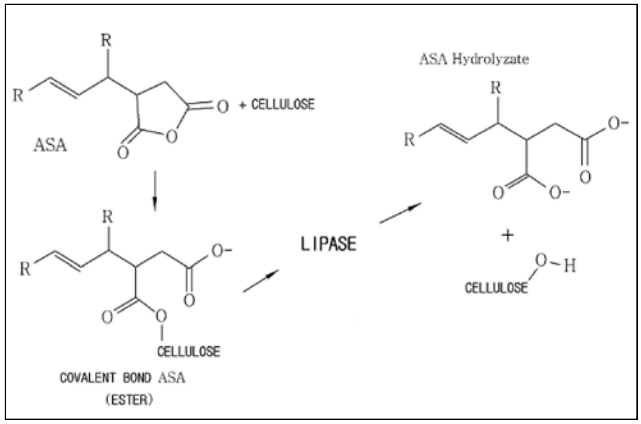
3. Lipase applied desizing mechanism of AKD.



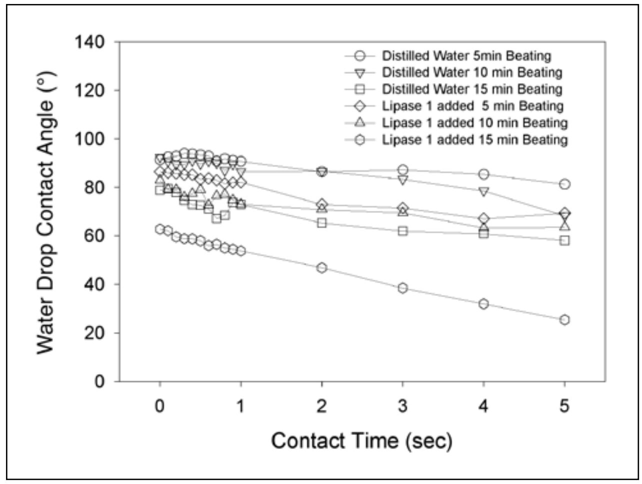
4. Dynamic contact angle of a water drop on ASA-sized filter paper before and after soaking in various lipase solutions.

was too low compared with the other lipases and so the efficiency of desizing was believed to be insignificant because of this.

The enzyme activity of lipases 1, 2, and 3 were 35,056, 14,974, and 187 units/mL, respectively, judging from the decomposition rate of *p*-nitro phenyl myristate [11]. **Figure 5** shows the desizing mechanism of ASA by lipase.



5. Desizing of reacted ASA by lipase.



6. Water drop contact angle of pads of rosin-sized wallpaper slurry with or without lipase treatment after varied disintegration times.

After disintegrating and beating, a slurry of wallpaper broke decreased its hydrophobicity (**Fig. 6**). Paper from this rosin-sized broke became significantly more hydrophilic surface by the application of lipase and prolonged beating time. Lipase 1 showed good efficiency in desizing of rosin alum added paper. **Figure 7** illustrates a desizing mechanism for rosin size by lipase.

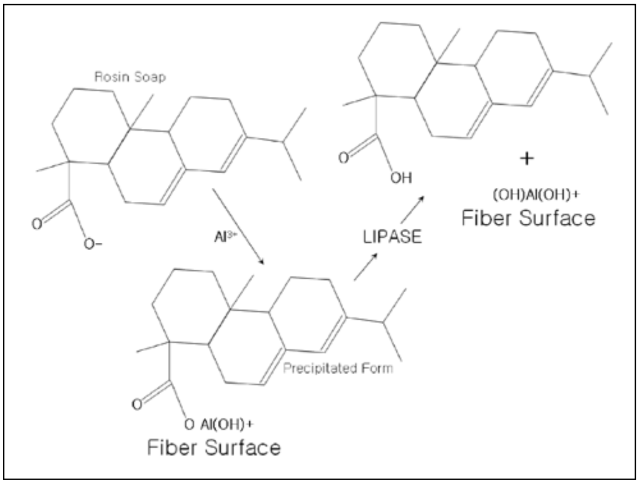
The investigation confirmed the desizing effect of three major sizing agents, so that surface modification of hydrophobic-coated cellulosic materials in deinking stock is anticipated.

Lipase for deacetylation of stickies

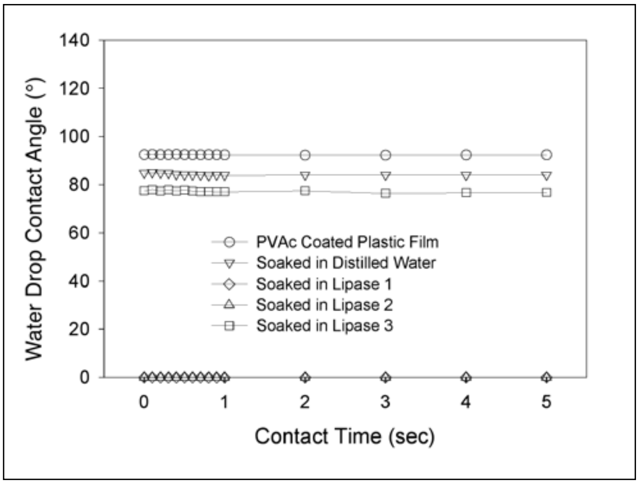
Data in **Fig. 8** confirm the effect of enzymatic hydrolysis on PVAc. Lipase applied to PVAc should make the surface less hydrophobic through the mechanism depicted in **Fig. 9**.

Lipase for dealcohol of SB latex films

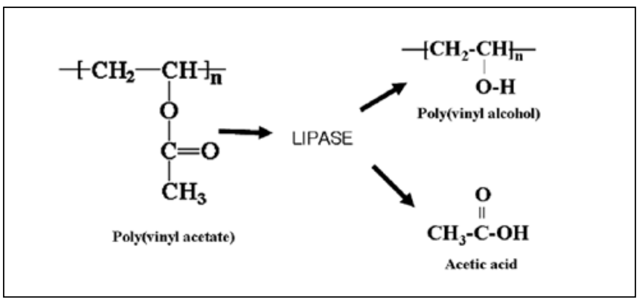
As shown in **Fig. 10**, the contact angle of a water drop on coated paper soaked in distilled water remained at more than 80° over time while the contact angle of coated paper soaked in lipase 1 and 2 solutions decreased to below 60°. This means the hydrophobicity of components such as MMA or HEA could be reduced by lipase catalyzed reactions. Although lipase 1 and



7. Desizing of precipitated rosin size by lipase.



8. Dynamic water drop contact angle of PVAc-coated plastic film with varied lipase treatment.

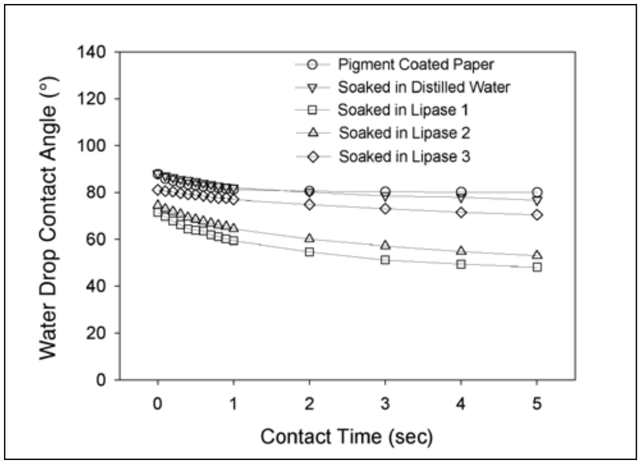


9. Lipase applied de-esterification or deacetylation of PVAc.

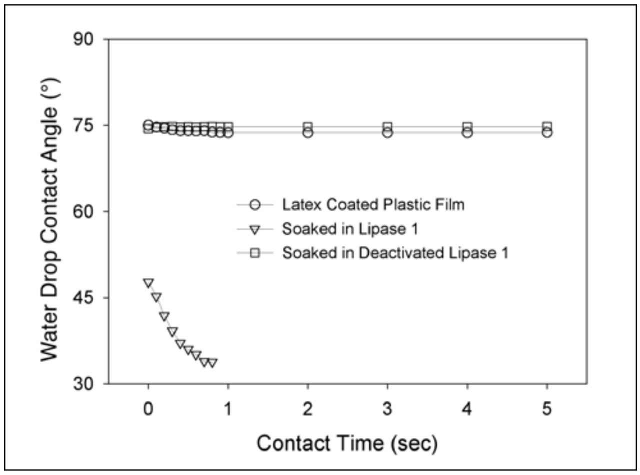
2 reduced the hydrophobicity of the surface, similar to the case of AKD and ASA, lipase 3 did not give any significant effect.

Figure 11 shows the dynamic contact angle of water drops on latex coated plastic film soaked in normal and deactivated lipase 1. Lipase 1 decreased the hydrophobicity of the surface while deactivated lipase 1 did not cause any change. The contact angle of the plastic film soaked in deactivated lipase 1 was similar to that of distilled water. This means the lipase solution changes the surface chemical properties of SB latex film without any significant influence from additives in enzyme solution such as surfactants, salts, or other stabilizers.

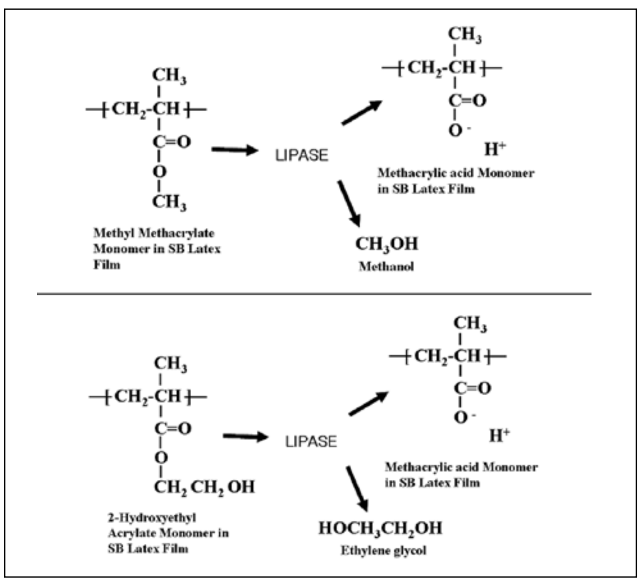
The de-esterification or dealcohol mechanism of MMA and



10. Dynamic water drop contact angle of pigment coated paper with various lipase treatments.



11. Dynamic water drop contact angle of SB latex-coated plastic film with lipase 1 and deactivated lipase 1 treatment.



12. Lipase catalyzed de-esterification or dealcohol of MMA and HEA.

HEA by lipase could be as suggested as **Fig. 12**. With the hydrolysis of ester bonds in methyl methacrylate and hydroxyl ethyl acrylate and the generation of carboxylic acid, the hydrophobicity of latex-covered pigments is expected to be reduced.

In this study, lipase 3 was not so effective in changing the surface of hydrophobic contaminants. Although lipase 2 showed better efficiency compared with lipase 1, lipase 1 was chosen for the flotation trial on the basis of enzyme price versus its efficiency.

Lipase modification of hydrophobic materials chemically reacted or adsorbed on the surfaces of suspended solid particles in deinking stock seems to have potential as a method of reducing the flotation reject rate.

CONCLUSIONS

Instead of an inorganic base, a novel catalyst for the promotion of hydration is urgently required in low alkaline or neutral deinking of ONP to reduce the unwanted loss from the flotation deinking process. Model experiments verified the significant efficiency of lipase for the hydration of hydrophobic contaminants commonly found in ONP. Lipase from *T. lanuginosus* is effective in breaking down the ester linkage (desizing, deacetylation, and dealcohol effects) and could be applied to promote hydration. The ability to adjust the degree of hydrophobicity of contaminants commonly adsorbed onto fine particles in flotation deinking suggests that yield loss during deinking at lower pH could be reduced through the use of lipase. We further explore this in Part 2 of this series. **TJ**

Received: October 18, 2006
Accepted: January 28, 2008

LITERATURE CITED

1. Korea Paper Manufacturers Association (KPMA), Annual report 2005, KPMA, Seoul, Korea, p. 35.
2. Jain R.K., Singh K., and Kulkarni A.G., *Pulp Paper Intl.* 47(3): (2005).
3. Delagoutte, T., *KRICT-KTAPPI RTM 2005 Proceedings*, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea, p. 200.
4. Morrow, H., Horacek, B., Hale, K., et al., *PaperAge*, September/October 121(5): 34(2005).
5. Sykes, M., Klungness, J., Gleisner, R., et al., *TAPPI 1998 Recycling Symposium Proceedings*, TAPPI PRESS, Atlanta, Georgia, USA, p. 291.
6. Carre, B., Vernac Y., Galland G., et al., *2003 5th CTP Recycled Fibres Forum Proceedings*, Centre Technique du Papier (CTP), Grenoble, France, vol. 2. p. 18.
7. Moe S.T. and Røring A., *Preprints of the 6th Research Forum on Recycling*, Pulp and Paper Technical Association of Canada (PAPTAC), Montreal, Quebec, Canada, 2001, p. 55.
8. The European Commission, *Enzymatic deinking as an environmentally friendly solution for recovered paper recycling (bio-deinking), FAIR-CT96-1492, final report*, Brussels, Belgium, 2000.
9. Shin D.S. and Ryu J.Y., *J. Korea TAPPI* 26(2): 5(1994).
10. Patrick, K., *PaperAge* 120(6): 22(2004).
11. Gupta, R., Rathi, P., Gupta, N., et al., *Biotechnol. Appl. Biochem.* 37: 63(2003).

INSIGHTS FROM THE AUTHORS

Results from a mill trial in a Korean newsprint paper mill demonstrated that an excessive loss from flotation is unavoidable because of less wetting of fines under neutral or low alkaline conditions. We decided to test lipase as a biocatalyst to possibly improve ONP recycling results.

We are not aware of previous use of lipase for the improvement of deinking yield. Although three different approaches use enzymes, including attack on fiber surfaces, starch-based coating, and vegetable oil-based binders of the printing inks, so far enzymatic deinking has not been widely used commercially.

Lipase was shown to be effective in promoting hydration by desizing, deacetylation and dealcohol reactions. Lipase applied flotation process is effective in reducing flotation deinking rejects without sacrificing ink removal efficiency.

By controlling the flotation selectivity by modifying the hydrophobicity of fine materials in deinking stock, mills could reduce production costs and negative environmental effects.

As a next step, we should verify the significant efficiency of lipase for the hydration of hydrophobic contaminants commonly found in ONP. It was verified by model experiments. Next it should be evaluated through mill trials of lipase applied ONP deinking, especially in terms of economic and environmental effects.

J.Y. Ryu

B.K. Song

J.K. Song

Ryu, Song, and Song are with the Center for Chemical Biotechnology Research, Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea; email Ryu at jyryu@krict.re.kr.