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Development of Enzyme-Based Biotechnology for Removing Stickies and Regaining Fiber Quality in Paper Recycling

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DEVELOPMENT OF ENZYME-BASED BIOTECHNOLOGY FOR REMOVING STICKIES AND REGAINING FIBER QUALITY IN PAPER RECYCLING

Yun Wang, Ph.D.

Western Michigan University, 2024

Producing paper with recycled paper consumes about 30-70% less energy and emits less GHG than using virgin wood. However, with current recycling practices, more foreign matters are commingled with the recycled paper including hot-melt adhesives, food residues, inks, resins/sizing agents, and coating adhesives, which result in stickies issues in the paper remanufacturing process. On the other hand, recycled fibers inherently have lower quality due to mechanical treatment, heating, chemical processing, and aging in various types of application/use of paper products, limiting the production of high-quality paper grades from recycled fibers. The goal of this dissertation research is to address both the knowledge and technology gaps in contamination removal and fiber quality restoration in paper recycling.

Various recycled fibers including containerboard, newsprint, and residential wastepaper were analyzed using solvent extraction, FTIR, SEM, GC-MS and colloidal titration. The results indicate that the quantity and size and number of stickies vary among different paper grades. The wastepaper from curb side contains nearly 3 times more stickies than most of the wastepaper grades. Sticky contaminants, predominantly composed of polyvinyl acetate, styrene butadiene rubber, paraffin wax, resin, and polyamines, were found not only to create sticky issues on the paper machine and generate anionic trash (2-4.5 mmol/L), but also negatively impact paper strength.

Enzymatic technology was developed for stickies removal with three enzyme formulations. Critical factors influencing the enzymatic treatment process, including temperature, pH, residence time, and enzyme dosage, were systematically investigated. Enzyme treatment under optimal conditions, i.e., 65°C, 30-60 minutes, and pH 8.0, resulted in the removal of up to 93.4% of stickies. Microscopic analysis using SEM and AFM revealed that stickies deposits, appeared as tar-like materials, adhere to fibers and cover microfibrils on the fiber surface, and with the enzyme process developed, the stickies were effectively eliminated.

In fiber quality study, changes in both cell wall structure and chemical components were investigated with using SEM, FTIR, XRD, and with reducing sugars, WRV, and FQA analysis. The results indicate that enzymes preferentially attack the amorphous regions of cellulose and hydrolyzed cellulose into glucose. The fiber cell wall structure and inner layers were loosened, making the fibers more flexible and collapsible. As a result, the swelling capacity of recycled fiber was improved by up to 20%, and the physical properties of remanufactured papers were increased by 18-66% depending on the paper grades.

This comprehensive research identified and investigated the two most challenging technical issues facing the paper recycling industry. The enzyme-based technologies developed for both stickies removal and fiber quality restoration in this research will help the industry in using more recycled fibers in paper remanufacturing and produce more high-quality paper from recycled fibers, thus, promoting environmentally friendly industry practice for a sustainable future. The research work also reveals the fundamental mechanisms behind enzyme modification of wood fiber ultrastructure and the chemistry behind enzyme-assisted dissolution of stickies substance from fiber suspension system, providing an avenue for further development of enzyme-based green technologies for other industry applications.

DEVELOPMENT OF ENZYME-BASED BIOTECHNOLOGY FOR REMOVING STICKIES AND REGAINING FIBER QUALITY IN PAPER RECYCLING

by
Yun Wang

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Yun Wang

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
BHT	Butylated Hydroxytoluene
CI	Crystallinity Index
CSF	Canadian Standard Freeness
GC-MS	Gas Chromatography Mass Spectrometry
GHG	Greenhouse Gas
FC	Enzyme FiberCare
FQA	Fiber Quality Analysis/Analyzer
FTIR	Fourier-Transform Infrared Spectroscopy
MOW	Mixed Office Wastepaper
OCC	Old Corrugated Containers
ONP	Old Newsprints
PVAc	Polyvinyl Acetate
RES	Enzyme Resinase
RW	Residential Wastepaper
SA	Enzyme StickAway
SBR	Styrene-Butadiene Rubber
SEM	Scanning Electron Microscope
TAPPI	Technical Association of Pulp and Paper Industry
THF	Tetrahydrofuran
WRV	Water Retention Value
XRD	X-Ray Diffraction

CHAPTER I

INTRODUCTION

1.1 Background

Secondary fibers have become increasingly important as a raw material in the pulp and paper industry as one third of papermaking material is made from recycled fibers. In 2022, paper and paperboard recovery rate in U.S. rose to 68% [1]. Producing paper from recycled fibers recovers 30-70% of embodied energy and reduces fresh water use significantly in comparison with using virgin wood. However, among the 52.7 million tons of paper recovered in the US in 2018, only 32.5 million tons were remanufactured domestically, with the remaining materials being exported along with the tremendous energy and water saving potential. In addition, within the 32.5 million tons of paper remanufactured, 86% is boxboard; high quality and higher value paper grades from recycled fiber are very limited [2–4]. Contamination in recovered fibers, especially that from hot-melts, plastic films, food residues, inks, starch and gums, resins/sizing agents, is one of the major causes for manufacturing difficulties and paper quality downgrading [5–8]. On the other hand, fiber quality deteriorates naturally with repeated manufacturing cycles [9,10].

In current paper remanufacturing, processes are designed and implemented to specifically remove glass, metals, sands by cyclone separators and remove plastic films, shives, adhesives and macro-stickies by barrier screens. However, organics such as food residues, ink, starch, resins/sizing agents, wax and coating adhesives that form micro-size particles are not removed. They can also become dissolved in the process water forming “anionic trash” in the system. The micro-stickies or dissolved anionic trash also can re-agglomerate later in the process into macro-stickies, which adhere to paper processing machinery causing paper breaks and paper quality issues. Although efforts have been made in the industry to remove the stickies by chemicals and enzymes, the majority of the industry do not use the approach due to high cost and inefficacy.

The quality of recycled fibers is also deteriorated due to the prior papermaking process. The physical damage of fibers by mechanical forces and so-called hornification by heat in the papermaking and especially paper recycling process make the recycled fibers less desirable than virgin fibers and hence limiting their application in high grade paper. Current manufacturing process use mechanical refining or chemical additives to improve fiber quality; however, both of them make the fibers more deteriorated in the next recycling process.

This research aims to identify key technical barriers in contamination removal and fiber quality restoration and address the underlying knowledge gaps associated with them. This will include investigating the fundamental properties of the contaminants and reveal their behavior/pathway in the paper remanufacturing process, e.g., changes in size, quantity, chemistry, and their interaction with fibers, and fundamental understanding of stickies removal by enzymes. In addition, this dissertation seeks to reveal the mechanism of enzyme actions on recycled fibers by investigating the effects of enzyme-assisted mechanical treatment on fiber quality, ultrastructure and chemistry. Furthermore, based on the findings, this work expects to develop enzyme-based technologies for contamination removal and regaining fiber quality in lab-scale and pilot-scale.

1.2 Objectives of Research

The specific of this research are to investigate the fundamental properties of sticky contaminants present in recycled fibers and to develop new enzyme-based technologies for removing contaminants. Furthermore, enzyme-assisted mechanical refining technology is developed to improve the overall quality of paper made of recycled fibers. The new technologies developed will help paper recycling industry to produce much cleaner pulp and higher quality fibers so more recycled fibers can be used in place of virgin fibers in high grade paper. The new technologies developed based on new enzyme applications will also reduce the energy consumptions in both contamination removal and fiber refining process and increase the yield of the fiber recycling.

To achieve the objectives, this work first investigated the fundamental properties of the contaminants and reveals their chemistry and interactions with fibers; emerging enzyme technologies are evaluated to target specific contamination components and modify fiber properties as well. Additionally, a new approach with using enzymes to pretreat fibers prior to conventional mechanical refining to regain fiber physical properties and save electric energy in mechanical refining process is developed. The specific objectives of this research include:

(1) Identify the chemical and physical characteristics of the contaminants and their propagation through the paper remanufacturing process. The chemistry, binding/co-mingling, and penetration into the paper/fiber structure can vary markedly. Understanding the chemical and physical traits of contaminants throughout the entire process is critically important in designing strategies to tackle specific contaminants at the appropriate points of in the process.

(2) Fundamental understanding of stickies removal by enzymes, and develop new bio/enzymatic technologies for tackling multiple contamination components. Utilize mixtures of thermophilic enzymes to remove contaminants identified in recycled fibers, including adhesives, glues, wax, wet strength agents. Evaluate the factors that influence the performance of stickies removal.

(3) Investigate the impact of enzyme modifications on fiber quality, ultrastructure and chemistry, and reveal the mechanisms of enzyme interactions with fiber. In addition, develop and

evaluate the performance of developed enzyme-assisted mechanical refining process in conjunction with stickies removal enzymes in industrial paper remanufacturing process.

1.3 Organization of Dissertation

This dissertation, contains three major research projects, which include identification and characterization of organic sticky contaminants in multiple grades of wastepaper, investigation, and development of enzymes formulation towards highly efficient removal of sticky contaminants in secondary fibers, study, and development of enzyme-aided modification of cellulosic fibers for restoring fiber quality in paper recycling. To ensure that the developed processes and results can be transited into industrial technologies, a pilot scale trial using industrial facility and practices has been performed to validate the readiness of the developed methods.

This dissertation consists of six chapters. The first chapter provides the introduction to the contents presented in the rest of the dissertation. In Chapter 2, a comprehensive review on tacky contaminations and quality deterioration in fiber recycling are provided. Also, a review on the conventional methods for stickies removal and quality improvement, including mechanical methods, chemical additives, refining theories, and mechanisms are presented. In addition, enzyme technologies, their development and utilization in papermaking process is discussed in this chapter.

The first research project is related to the identification and characterization of organic sticky contaminants in wastepaper and is discussed in Chapter 3. In this project, wastepaper samples collected from local paper recycling mill, common workplace, and residential waste were extracted with water and organic solvent to identify the tacky stickies. Subsequently, multiple analytical techniques were employed to characterize the extracted stickies. Fourier-Transform Infrared Spectroscopy (FTIR) and Gas Chromatography Mass Spectrometry (GC-MS) were utilized to determine the chemical composition of the stickies. Optical microscope, Scanning

Electron Microscope (SEM), and colloidal titration were employed to characterize the physical properties of the stickies. Furthermore, the impact of the stickies on the physical strength of remanufactured paper sheets was evaluated using TAPPI standard handsheets.

The second research project is related to evaluation and development of enzyme formulations for stickies removal in wastepaper fibers and is discussed in Chapter 4. In this project, multiple enzyme formulations containing thermophilic enzymes were studied for the removal of tacky organics that were identified in Chapter 3. The factors that can impact the activities of enzyme formulations were determined, such as temperature, pH, reaction time, and enzyme dosage. The performance of two formulations containing multiple enzymes and one commercial lipase under extreme conditions was investigated and compared. In addition, the removal of stickies from fiber surface and the impact on paper strength was investigated as well.

The third research project involves with development and evaluation of enzyme-assisted mechanical process to restore the quality of recycled fibers and is presented in Chapter 5. This project explored the modifications of recycled cellulosic fibers when treated with enzyme formulation containing multiple enzyme species in combination with mechanical refining. The fundamental changes in fiber quality and chemistry such as fiber length, swelling capacity, and crystallinity were investigated using analytical techniques such as Fiber Quality Analysis (FQA), Water Retention Value (WRV), X-ray Diffraction (XRD), and FTIR. SEM images and the reducing sugar content provided insights into the mechanism of enzyme interactions with recycled fibers. Additionally, this enzyme-aided mechanical modification technology for restoring fiber quality was investigated on multiple wastepaper grades. Furthermore, the effectiveness of the developed technology was validated in pilot scale trial.

Finally, the conclusion for all three research projects along with suggestions for future work is presented in Chapter 6.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Secondary fibers have become increasingly important as a raw material in the pulp and paper industry. One third of papermaking material is made from recycled fibers. In 2022, making its third consecutive annual increase, the paper and paperboard recovery rate in the U.S. rose to 68% [1]. Paper recovery rate doubled in the following 32 years since 1990, and it is expected to exceed 70% in the near future. The consumption of recovered paper at U.S. paper and paperboard mills held generally stable at 30.8 million tons in 2016, while exports rose to 21.8 million tons [11]. Using recycled fibers not only saves space in landfilling but also saves substantial energy and water usage in paper making industries. It is estimated that 28-60% less energy is involved in paper recycling than that during the virgin paper making process because most of the energy employed in papermaking is used in pulping [12]. In addition, recycling paper preserves virgin wood resources and reduces greenhouse gas emissions as well.

However, the climbing trend of paper recycling plateaued in the past decades. Between 2012-2022, the paper recycling rate in the US was leveled at 65~68%. The growth of paper recycling is limited by the availability and quality of recovered fibers. In spite of the many advantages offered by paper recycling, several problems are associated with it: difficulties in deinking, poor drainage of recycled fibers on the web, stickies contamination, decreased wet-flexibility, and lower strength induced by unavoidable damage [13,14]. Innovative technologies with low energy consumption, low emissions, and low carbon footprint are needed to achieve a circular economy through paper recycling.

2.2 Contamination – Stickies

One of the major challenges that paper mills often face while producing papers using recycled fibers is the stickies – organic deposits that originate from adhesives, ink binders, and coating binders on various equipment of the paper machine, e.g. wire, press, drying cylinder, and calendar sections. Many significant operational and quality problems are caused by stickies in pulp and papermaking systems. Cleaning up fouled sections of the paper machine causes valuable machine downtime, which diminishes paper quality and reduces output, all costing millions of dollars per year. Furthermore, stickies will become a growing process problem in the years to come with the growing use of recycled fibers and the closing of the mill water loops [15]. Stickies are tacky, hydrophobic, pliable organic materials found in recycled paper systems [16,17] which can be pressure-sensitive adhesives, styrene‒butadiene rubber, vinyl acrylates, polyisoprene, polybutadiene, and hot melt adhesives (Fig 2.1). Stickies have a broad range of melting points and different degrees of tackiness depending on their composition. They can be classified into three categories:

- ***Macro-stickies***: Stickies cannot pass through a 100 micron slotted screen plate. This category of stickies is associated with the fibrous fraction of the pulp furnish.
- ***Micro-stickies***: The size of these stickies is below 100 micron and above 5 microns. That means that they pass through screen plates and can carry through the current paper recycling process. Micro-stickies are typically linked to the fine element fraction of the pulp.
- ***Colloidal stickies or dissolved stickies***: These are the smallest stickies, less than 5 microns. They belong to the dormant category of stickies. However, they can be potentially harmful if, owing to system upsets, imbalances can create agglomeration leading to their

precipitation. The perturbation of wet-end chemistry by a change in pH or ionic concentration could lead to a change in their state.

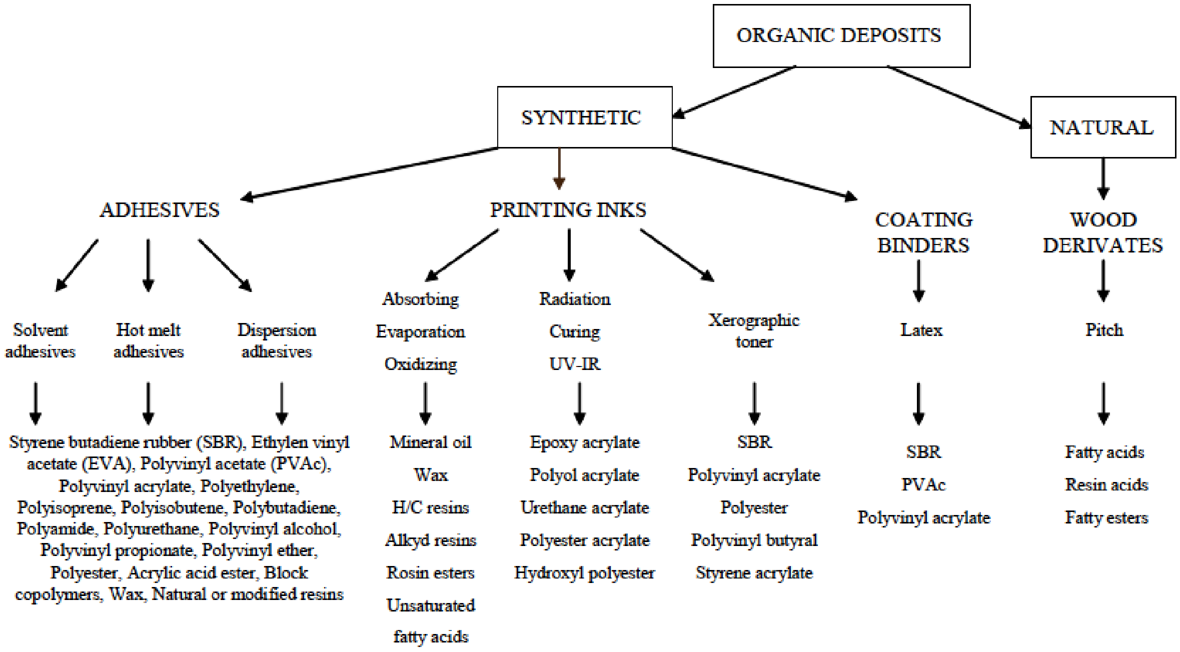


Figure 2.1. Sources of stickies in recycled fibers [18].

The problems caused by stickies are many, varied, and can occur at practically every stage in the papermaking and paper conversion chain including printing. Finding a suitable way to treat them can be difficult. The problem is complicated by the fact that there are two types of stickies:

- ***Primary stickies***: these are insoluble components that are tacky under normal conditions and are present in the incoming recycled paper and coated broke, for example, hot melts or pressure-sensitive adhesives, inks, waxes, plastics, synthetic adhesives, resin size, wet-strength resins, and binders.
- ***Secondary stickies***: composed of the soluble components of adhesives and chemicals used in papermaking and converting. Secondary stickies are formed because of sudden changes

in wet-end chemistry, temperature, or pH, when they react to produce insoluble or gel-like tacky particles. They can be more difficult to handle than primary stickies.

The problems caused by these tacky impurities are deposits. On the one hand, deposits on the paper machine can cause web breaks owing to weak spots and stickies to moving rolls; picking of fibers; lengthy non-productive cleaning times owing to build-up on wires, felts, rolls, and doctor blades. On the other hand, deposits in or on the paper can cause increased downgrades due to dirt counts; migration of stickies from inside of paper reaches outside the paper during converting processes at high temperature and pressure; converting problems owing to adhesion between sheets. Douek et al. provided a good discussion of the issues caused by stickies [19].

The control of stickies involves mechanical and chemical methods. Mechanical methods use screens, cleaners, dissolved air flotation (DAF), and washing stages to remove the stickies from the stock. Depending on the nature of the stickies, their size, melting point, conformability, etc., they may be removed by one or more of the various types of equipment. This variability means that although some stickies will be removed in one step of the process, there is not one piece of equipment, nor even a combination, that will remove all the stickies, all the time. Even with the best equipment and conditions, mechanical methods will not remove all the stickies. This is where chemical methods come in. Chemicals are the second line of defense used by paper mills to control stickies. Chemical control methods have mainly involved dispersants, polymers, and/or absorbents. The removal of a sticky material, particularly the specific point or piece of equipment where it is removed, depends on the nature of the sticky itself. For example, the size, melting point, and conformability of a particular material determine where removal occurs during the process. Factors such as process temperature and pH can be set or adjusted so that these unwanted materials are maintained in an optimum form for their removal by cleaners or screens.

Difficulties in controlling stickies with existing systems continue, they will remain a cause of paper quality problems and lost production. As mills increasingly close their water and fiber systems, there are fewer places where contaminants can be completely removed from the system. The trend towards increased mill closure is expected to continue, presenting additional challenges to the papermaker.

2.2.1 Control of Stickies by Mechanical Strategies

In addition to controlling the quality of wastepaper feedstock, control of stickies is typically achieved by mechanical method and/or chemical method. Depending on the mechanism, the goal is to either remove stickies to the maximum extent or to make the stickies less tacky or tie up the stickies so that they do not deposit [16–18,20–22]. Removal of stickies is usually the primary goal, and it is achieved by mechanical means. Removal of stickies may happen anywhere there is a reject system. Depending on the handling of the reject, stickies are either purged out of the system or recirculated. The true exit points are usually the pulper reject, dewatering screen, cleaner, flotation, internal water treatment reject, and wastewater.

2.2.1.1 Pulping

Pulping is not a removal step by itself. Nevertheless, pulping largely influences the removal of stickies and other contaminants in the following steps. The objective of pulping is to allow defiber recycled paper without significant disintegration of contaminants [23]. Most modern pulpers have supplementary equipment to remove contaminants before they are broken down into small pieces. This equipment includes a ragger to remove wire and string, a junker for large contaminants, and a secondary pulper. A stream is bled off at the secondary pulper and is subjected to mild defibering. High-density contaminants accumulate in a chamber with a double-valve arrangement while stock is sent back to the pulper or is screened in a rotary screen. Many older pulpers are being retrofitted with these accessories, and newer pulpers come equipped with secondary pulpers. The drum pulper is gaining in popularity, particularly for newsprint deinking [24,25]. The drum pulper does not have any cutting action, therefore many contaminants, such as plastics and book bindings, remain almost intact and are rejected by the associated rotary screen. Bouchette and Nagy proposed steam explosion pulping for defibering waste papers. Loose waste papers are subjected to steam at about 400psi and 400°F. When the pressure is released, the material explodes and defibers. Contaminants, stickies, and inks are also dispersed in this pulper.

2.2.1.2 Screening

Coarse screens with holes and fine screens with slots are used to remove contaminants, primarily based on their size [26,27]. The efficiency of the removal of stickies has increased with progress in screening technologies, which have occurred over several years. Contoured fine slot screens (with slots down to 0.15 mm and sometimes 0.10 mm) remove most adhesive particles. Unfortunately, some of them, mainly due to their small size and shape, still can go through the slots and contaminate the accepted pulp. In this respect, it is assumed by Heise et al. that 5 to 30% of primary stickies may pass through the screening slots [28]. As slot size decreases, contaminant removal increases but so does fiber loss [29,30].

Several factors influence the screening efficiency of sticky contaminants [22]. These include the following:

- Stock temperature
- Contaminant consistency
- Contaminant size
- Nature of the contaminant
- Slot or hole size of the screen basket

- Average stock velocity through the slot or hole
- Slot or hole profile
- Screen rotor type and speed

Most pressure screens operate with mass reject ratios of 15–30%. To reduce the fiber loss, there are second, third and sometimes fourth screening stages, and their arrangement is very important for contaminant removal efficiency. The elastic, deformable nature of stickies, especially pressure-sensitive adhesives (PSAs), allows them to extrude through fine slotted screens [31]. Mill data indicate that stickies in the screen accepts were significantly larger than the screen slot size, sometimes an order of magnitude larger.

Mechanical screening is the most efficient tool for sticky separation in the industrial process. However, only large enough stickies can be effectively removed. Thus, there is need of improvement in screening technology or equipment for stickies removal.

2.2.1.3 Cleaning

Cleaners are classified as high-, medium- or low-density cleaners. They remove the contaminants based on their density differences. Their use depends on the density and size of the contaminants they are removing. High-density cleaners, or forward cleaners, are used to remove nuts, bolts, paper clips and staples. They are usually located immediately after the pulpers. Smaller-diameter hydrocyclones are used for medium-density contaminants. As the hydrocyclone diameter decreases, it becomes more efficient at removing small contaminants. For practical and economic reasons, the 3 in. (75mm) diameter cyclone is the smallest cleaner used in the paper industry. Additionally, reverse hydrocyclones or through-flow cleaners are used to remove low-density contaminants. A disadvantage of reverse hydrocyclones is that 55% of the flow is in the reject stream, and secondary and tertiary stages are needed to recover the usable fiber

[32]. This problem does not occur in through-flow cleaners. The accepts and rejects come out at the same end in through-flow cleaners. The reject stream is only 10% by volume and 2% by mass [32] However, the contaminant removal efficiency of hydrocyclones is usually higher than for through-flow cleaners. Another problem with through-flow cleaners is that they are somewhat prone to plugging because of the narrow gap at the exit and the lower pressure drop.

Another lightweight cleaner, Gyroclean, functions as a rotating centrifuge and is effective at removing low-density contaminants [33]. The reject ratio of these cleaners is so low that the second or third stage is not necessary. Lightweight cleaners generally become inefficient as the particle density exceeds 0.95g/cm^3. A new design modifies the hydrocyclone's length, diameter, cone angle, etc. to increase the residence time [34]. Researchers claim this new design is 95% efficient in lightweight contaminant removal, compared with 63% for conventional through-flow cleaners under the same operating conditions.

In summary, the efficiency of stickies cleaners depends on the density of the particles to be removed. Unfortunately, a lot of stickies have a density close to 1 and are not removed effectively by cleaning.

2.2.1.4 Flotation

Flotation appears to be an interesting way to remove residual stickies from the pulp, which have been studied by several researchers [35–38]. Flotation efficiency depends on the shape, size, and surface properties of the stickies and on the hydrodynamic parameters of the flotation. Its main advantage, especially compared with screening, is its ability to remove micro-stickies from the pulp suspension [28,39]. Indeed, it is reported that small size stickies, which are not affected by screening, present the best removal efficiencies during flotation. Johansson et al. have reported that flotation may remove over 70% of micro-stickies in a wastepaper stream [38]. It is also reported that the removal of stickies in post flotation, performed after a dispersion step, must be more efficient than in the pre-flotation step where stickies are larger [28].

Doshi et al. and Hsu and Dauplaise have reported that the nature of the stickies plays an important role [36,40] . Wax and hot-melt adhesives are quite well removed by flotation, whereas waterborne PSAs are not. This is because these two types of adhesives represent different surface properties. The waterborne PSA has a more hydrophilic character than the hot-melt adhesive. Chemical additives may significantly change the ability of flotation to remove stickies. The removal of waterborne PSAs may be improved by the addition of cationic polymers [40]. These polymers may induce aggregation of the PSA particles into a size range more favorable for flotation removal. Polymer fixation may modify the surface properties, which could also favor interaction between the sticky particles and the air bubbles. Heise et al. reported that the concentration of surfactant also plays an important role [28]. High surfactant concentration can decrease stickies removal because the initial hydrophobicity of the stickies is reduced owing to high amounts of surfactant, which decrease the attachment force of stickies to air bubbles. Doshi et al. studied froth flotation to remove wax and stickies from re-pulped old corrugated container (OCC) [36]. Trials at a pilot plant used a conventional OCC stock preparation process with and without froth flotation. Additional washing and DAF were also evaluated. Including flotation in the OCC stock preparation system significantly improved stickies removal and promoted a decrease the area of wax spots in handsheets. Flotation was more effective in removing wax and stickies than through-flow cleaners. Analysis revealed that three stages of flotation in an OCC system was sufficient and there was no significant loss of yield.

2.2.1.5 Dispersion

Hot dispersion by low speed kneaders or high speed dispersers has been widely developed for the treatment of OCC containing waxes or hot-melts in order to avoid the formation of spots in paper. Most European suppliers recommend non-pressurized units (95–100°C). In contrast, American suppliers generally advocate dispersion under pressure at high temperature for more efficient dispersion of stickies. Fergusson and McBride studied the Shinhama kneader [41]. They found that no steam or pressure was needed for satisfactory stickies reduction. Reduction of the thermoplastic material from fiber was found to be more effective at low temperatures than at high temperatures, where the contaminants smeared onto the fiber. However, according to Mannes, hot dispersion is needed to ensure a high level of product quality and to avoid runnability problems on the paper machine [42]. He also reported that effective and reliable stickies treatment is possible with high-speed dispersers operating at high stock consistencies and high temperatures.

Kneading as a processing stage has been studied for its effect on stickies. Saint Amand et al. investigated shape changes of stickies during dispersion to improve their removal efficiency in subsequent processes [43]. They found that kneading caused stickies to become more spherical. The shape modification was more significant even on small particles, when kneading was done at high temperatures. This change in shape increased the removal efficiency of screening and improved the removal efficiency of cleaning and flotation, owing to the reduction in size of the stickies.

2.2.2 Chemical Additives for Stickies Control

Chemicals are the second line of defense used by paper mills to control stickies. Chemical control methods have mainly involved dispersants, polymers, and/or absorbents. The various chemicals used have two main modes of action:

- The first method is to tie up or passivate the stickie. These are stock applications.

- The second mode of action is “point of problem” type applications. These passivate a surface or clean off the stickies after they have deposited on equipment.

2.2.2.1 Talc

Talc, a hydrous magnesium silicate, has a hydrophobic surface and hydrophilic edge [22]. The hydrophobic surface has an affinity for stickies whereas the hydrophilic edge allows easy dispersion of the talc in water. To be effective, it should be as pure as possible. Impurities will reduce the affinity of the surface for organic material. Talc is not effective on stickies that are not tacky at the headbox temperature but become tacky at the dryer temperature. Most of the talc should be retained in the sheet to avoid excessive concentration in the whitewater. Talc is often introduced at the inlet of the kneader or disperser to favor its mixing with the pulp components. Few strategies have been proposed to control stickies deposition with talc.

Maat and Yordan examined the effect of talc in removing stickies from a hot melt containing polyvinyl acetate [44]. In their experiment, the application of 0.5% talc (on an oven-dried pulp basis) gave a 77% reduction in the amount of tacky stickies detected using the Doshi microfoam method. The application of 2.5% talc reduced tacky stickies by 96%. Hayakawa and Williams have proposed modified talc in which the hydroxyl groups on the edges are modified by a cationic polymer for stickies control [45]. The cationic charge carried by this modified talc is believed to favor its attachment to negatively charged stickies and its retention in the paper sheet. Biza et al. have reported that when stickies become coated with talc, it increases their density so they can be removed more efficiently by high-density cleaners [46]. Stickies removal efficiency increased from almost zero (in the absence of talc) to more than 50% when 2% talc was added before the cleaning step. Stickies on the paper surface were passivated by spraying talc slurry onto the paper sheet in the forming section of the paper machine. Tests in three paper and pulp mills revealed that 1 tonne of recycled pulp treated with 9kg of talc has 70% fewer deposits in the final pulp product compared with the untreated pulp and no negative effects on the resulting paperboard quality. This talc treatment has a better cost performance than cationic polymer treatment. No stickies control can be achieved with the cationic polymer using the same budget as for talc treatment.

2.2.2.2 Cationic polymers

Cationic polymers have been used to control stickies. These polymers can be added to the thick stock chest, fan pump, or headbox. They help to avoid stickies building up in the whitewater system as the stickies leave the system in the paper sheet [16,18].

The function of these polymers is to act as fixing agents, helping stickies and the other colloidal particles in the pulp slurry to be adsorbed onto fibers [47]. Cationic polymer wire sprays are also used. A thin film of polymer attracts anionic materials, including stickies, which are then washed away when the paper machine wire is cleaned. The thin polymer film prevents stickies from coming into close contact with the wire. The polymer eventually ends up in the whitewater and serves as a retention aid. Proper use of showers to keep wires and felts clean will help maintain product quality and reduce downtime for the paper machine. Some products are also available for spraying on felts.

It has been reported that Hercules Inc. has combined an amphoteric, surface-active structured protein with a highly charged cationic polymer [48]. The structured protein increases the stability and reduces the tackiness of colloidal contaminants. This approach combines three different methods of control: stabilizing colloidal material; reducing the tackiness of the colloidal material; and removing contaminants from the system. It has been considerably more effective on commercial paper machines than conventional methods, according to laboratory measurements of zeta potential, contact angle after washing, and colloidal stability. The method was successfully applied to problems of stickies and pitch deposition at a mill producing 100% recycled corrugating medium, problems of wet- and dry-end breaks and a blue-tinted deposit in the stock chests and whitewater systems of an integrated alkaline fine paper mill, and problems of stickies at a mill producing 100% recycled bleached and unbleached towel and napkin grades.

Song and Rys used diallyldimethylammonium chloride (DADMAC) homopolymers and co-polymers [49]. These products have high fixation power for controlling pitch and stickies for improved runnability. They performed very well compared with the best products for pitch and stickies in furnishes of thermomechanical pulp (TMP), deinked pulp (DIP), coated broke and blends thereof. They include the high-molecular-weight structure poly-DADMAC as well as co-polymers of DADMAC and a co-monomer that can boost the polymer's fixation power, and terpolymers of DADMAC co-polymerized with two co-monomers that improve the fixation power. Vacuum drainage filtrate turbidity tests were conducted on the new polymers and the existing commercial fixatives. Their performance was validated on coated broke at a US paper mill, on a DIP recycled furnish at a UK newsprint mill, and on TMP, DIP and a TMP/DIP mixture at a Canadian newsprint mill. DADMAC gave significantly improved performance over existing commercial fixatives in removing turbidity for deposit control.

A joint study by Darmstadt Technical University and BASF showed that the effectiveness of fixative agents can be examined by the rotating wire mesh test and the pitch counter method [21]. Results from these two tests correlated well for coated broke. The tests showed that polyvinylamines with cationic charges of 3–5 milliequivalents per gram and molecular weights greater than 400kg per mole were the most effective, whereas poly-DADMAC and polyamines were less effective. Tests on coated broke showed that the molecular weight and linearity of a polymer had a greater effect on the polymer's fixative properties than its density or cationic charge.

2.2.2.3 Surfactants

Surfactants were initially developed to control pitch deposits in paper mills using virgin fibers as raw material but were later applied to reduce clogging by stickies in paper mills using recycled fiber. Passivators to reduce the tacky character of stickies have been based on non-ionic surfactants which modify the surface properties of sticky particles but do not favor their removal, so they are still free to accumulate in the circuits [50–53]. Non-ionic surfactants are ethoxylated alkyl phenol and ethylene oxide–propylene oxide block co-polymers. Surfactants may also be used to treat paper machine clothing such as felts or wires. Combined treatments based on dispersants and cationic fixing agents have also been studied. Dispersants are usually added at the pulping stage for dispersing and passivating the stickies. Cationic fixing agents are added near the paper machine to fix the dispersed stickies onto fibers, so they can be eliminated via the paper output. Another combined treatment involves dispersing the wax at low temperature using a formulation that includes a wax melting-point depressor and an anionic dispersant. The dispersed paraffin is then separated from the fibers by a washing or thickening stage. Finally, the resulting water, containing dispersed wax, is treated by microflotation with a specific chemistry that removes wax particles.

2.2.2.4 Bentonite

Several researchers have studied the use of bentonite to control stickies. A retention chemistry based on a combination of bentonite, enhancer and polyethylene dioxide was introduced by Tay et al. and had an incredibly positive effect on the paper machine [54]. This retention program was extended to the other two machines and had comparable results. Beaudoin et al. used bentonite with polyethylene dioxide and found an increase in retention, drainage and sheet solids content [55].

They also found lower turbidity of the whitewater and lower stickies deposits. Furthermore, the sheet quality and water removal characteristics could be more easily optimized, and the paper machine fabrics were cleaner.

2.2.2.5 Diatomite

Diatomite has been increasingly successful at controlling hardwood pitch, white pitch, stickies from recycling and other organic contaminants. Diatomite has worked successfully on various grades of paper and with various organic contaminants. In addition, because it is added in small amounts, there have been no detectable effects on paper properties or adverse effects on machine runnability. It is a unique mineral made from the skeletal remains of single-celled aquatic plants called diatoms. Diatomite powders used in the paper industry for stickies passivation have exceptionally high silica content. Case studies demonstrate how diatomite has improved machine cleanliness at a mill producing text and cover paper from virgin pulp, improved productivity at a mill producing coated and uncoated recycled paper, and improved converting efficiency at a mill manufacturing 100% recycled brown toweling.

2.2.2.6 Dispersants mixed with solvents

Mixing dispersants with appropriate solvents can help to defiber wet-strength papers. Environmental concerns such as toxicity, odor and flammability need to be addressed when selecting solvents and dispersants. Most dispersants are sensitive to pH, contaminants, temperature, and the presence of other chemicals. They should be selected to be compatible with the existing system. Non-ionic dispersants are generally long-chain molecules with one hydrophobic end and one hydrophilic end. When a secondary fiber slurry is mixed with a non-ionic dispersant, the dispersant’s hydrophobic end will attach to one of the stickies, leaving its hydrophilic end exposed to the water. The hydrophilic end has no affinity for stickies, which is how the stickies are prevented from agglomerating. Anionic dispersants keep small stickies suspended in a slurry by inducing a negative charge on them, which repels other negatively charged stickies.

2.2.3 Enzymes for Stickies

Enzymes esterases can hydrolyze ester bonds, which are the primary adhesive bonds in sticky substances, unlike chemical methods and essentially resolve the sticky adhesion issue while being ecologically friendly [56]. The formation and enzymatic degradation mechanisms of stickies are presented in Fig. 2.2. Lipolytic enzymes and pectinases are the two main enzymes currently used to control sticky situations. Commercial enzymes include Buckman’s Optimyze, Novozymes StickAway, and EDT’s Enzynk.

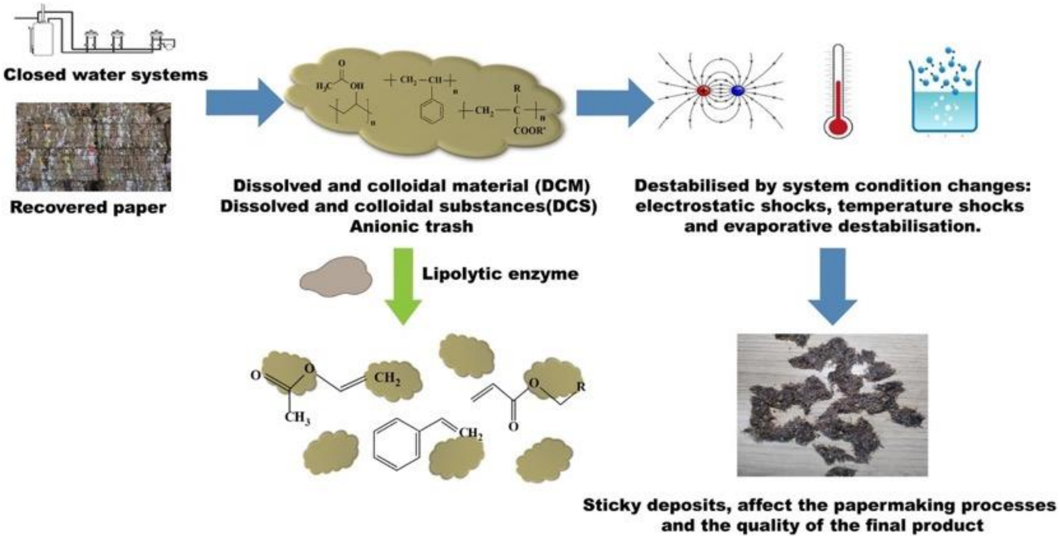


Figure 2.2. Formation and enzymatic degradation mechanisms of stickies in paper recycling processes [57].

Lipase and esterase were used to control pressure-sensitive adhesives in OCC at the laboratory scale, and it was discovered that enzyme treatment removed 70%–90% of the stickies while altering the surface adhesion of pressure-sensitive adhesives and reducing the adhesion strength [58]. In one study, a lab-scale mixture of esterase and cellulase was used to treat micro-stickies. The results showed that the enzyme treatment decreased the size of larger micro-stickies, and that this shift had an impact on the entire white water system and resulted in a new equilibrium between all particles [59]. In another investigation, three thermophilic esterases were combined with amylase, pectinase, and xylanase to treat stickies in wastepaper recycling, and under optimal conditions, 76.5% of the stickies were degraded and the pulp physical properties were improved[56].

The use of recycled fibers continues to grow. As demand increases, the quality of the recycled fiber will decrease, which will result in more stickies issues. Mechanical and traditional chemical control approaches have worked but they are not the complete answer. Enzymes are a new approach in the battle against stickies and have proved very effective. They will continue to play a major role in stickies control. The challenge is to fill the knowledge gap in understanding the mechanisms of enzyme actions and to develop new enzyme formulations that work in different temperature and pH ranges and on all types of stickies.

2.3 Low Fiber Quality

Another technical barrier that limits the further utilization of secondary fibers is their low quality due to loss of strength during recycling [60]. Detrimental changes in the structure and surface properties of fibers are unavoidable during conventional paper recycling practices leading to reductions in fiber strength such as tensile, burst, fold, and stretch, and also in density and drainage [61–63]. It is commonly accepted that the loss of strength during recycling is caused by repeated wetting and drying, leading to hornification, surface deactivation, and reductions in the wet flexibility and bonding properties of the fibers [64] . Many attempts have been made to explain the exact causes and mechanisms involved in hornification, and the most prevalent hypothesis is the formation of irreversible intra-fiber hydrogen bonds among the cellulose microfibrils, which restrict cellulose swelling and decrease its absorption capacity. In addition to drying, fiber morphology is also changed by other mechanical and chemical treatments such as pulping, refining, and bleaching. Mechanical refining is the most common approach to upgrade the properties of recycled fibers.

Refining creates fibrils, which improve the bonding ability. However, every reuse weakens the fibers and causes irreversible changes. These make the recycled fibers more sensitive to refining than virgin fibers. If not refined correctly, the result can be disastrous. Negative effects include high increases in the drainage resistance, a heavy fiber length, and a reduction in tear strength values. These can be avoided by choosing the equipment and conditions. Finally, recycled fibers often contain shives from the mechanical pulp components. Because these can be harmful, refining is needed to remove them when producing fine or coated paper grades. In most recovered papers, high-consistency re-pulping and refining are advantageous as these develop strength properties without reducing the drainage rates. High consistencies greatly reduce the amount of net energy that can be applied per unit of throughput in any pass through the system. Although this reduced refining intensity may cost more in energy, it is more than compensated for by the better drainage properties achieved.

Certain strength properties of recycled fibers are improved by refining, while some other paper characteristics are also affected. For instance, decreasing the freeness value decreases bulk and drainage. Optical characteristics such as brightness, opacity, light scattering coefficient, and tear strength are negatively influenced to a greater or lesser extent. An optimum compromise is therefore necessary between not only cost-effectiveness and quality but also between the various quality parameters. This compromise can occur by varying the refiner gaps, the energy input, the refiner type, and the processing stages before refining. Recycled pulp is mainly refined at low consistencies of about 3–6%. Sometimes high consistencies up to 30% and above have been used, such as in high-consistency refining.

2.3.1 Refining Mechanisms

The goal of refining theory is to predict changes in fiber properties from known refining conditions. Prior to discussing theories, the mechanism of refining is explained in this section. In a typical disk refiner, fibers are treated between two parallel grooved plates: stator and rotor. The three dominant refining stages are illustrated in Fig. 2.3. The first one is the pick-up stage where fibers are accumulated and trapped between the edges of bars. In the next stage, the trapped fibers are compressed by the surfaces of the moving and stationary bars. In the final stage, the fibers are affected by the shear forces. In this stage, the fibers also hit the bars on the surface to edge and again edge to edge. During the bar crossing, two different forces act on the fibers, one of them is due to the contact of fibers to bars while the other force is caused by the contact of fiber to fiber [65,66].

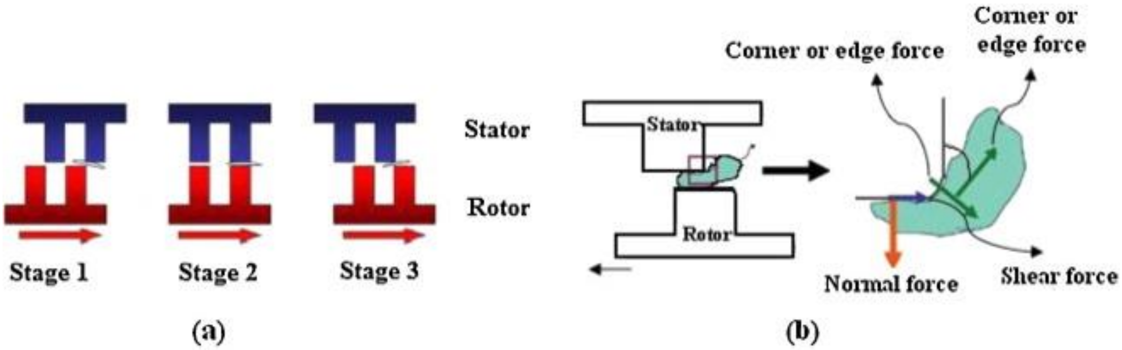


Figure 2.3. (a) Refining mechanism [66]. (b) Forces acting during refining [67].

2.3.1.1 Specific edge load (SEL) theory

The goal of refining The SEL theory is a well-known and a most reliable theory in papermaking industries [68–72]. The SEL is the amount of effective energy spent per unit edge length of bar crossing and rigorously is presented as “machine intensity”, meaning it represents the energy expenditure at bar crossings without reference about the pattern of energy distribution [70,73]. SEL can be obtained from equation (2.1): (Ws/m or J/m)

$$SEL = \frac{P_{net}}{CEL}, P_{net} = P_{tot} - P_{noload} \qquad (2.1)$$

where P_{tot} is the total power consumed, P_{net} is the net power (kW) consumed to change the pulp properties. P_{noload} is the initial power or no-load power which is defined as the power needed to rotate the rotor in the refiner. It is noticeable that this power has no contribution in pulp refining, and it is only consumed to overcome the losses, including loss due to shaft and bearings friction (mechanical losses), required energy to rotate the refiner plate in pulp suspension close to the stationary plate (hydraulic) and required energy consumed by refiner when pumping pulp suspension from inlet to outlet of refiner (pumping). Different studies have been reported to explore the no-load power in LC refining both experimentally and computationally [74,75].

As it can be seen in equation (2.1), another parameter contributed in the SEL is the cutting edge length (CEL) which is calculated by equation (2.2).

$$CEL = BEL \times \omega \qquad (2.2)$$

where BEL is bar edge length and ω is rotational speed. Plate designs are typically characterized by BEL and BEL/CEL is given to paper makers by suppliers of refiner plates.

Typical SEL for softwood and hardwood is 1.5–3 J/m and 0.2–1.0 J/m respectively [66]. The SEL theory works quite well with coarse fillings when bars are wider than the length of the fiber flocs [65].

One parameter that contributes to the study of different theories is the specific refining energy (SRE). SRE is used for calculating how much energy is given from the refiner to the fibers, and it can be obtained by dividing the net power by the fiber mass flow rate. Typical SRE for chemical pulps is between 80 to 250 kWh/t [76,77]. The higher the SRE, the more refining is happening to the fibers. Nugroho found that at constant refiner speed, flow rate, and pulp consistency, the specific refining energy and refining intensity are influenced by net power only, so it makes a linear correlation between specific refining energy and refining intensity [66]. In this case, the specific refining energy is proportional to refining intensity.

2.3.1.2 Specific surface load (SSL) theory

Though SEL is widely used theory in industries, it is quite simple. For instance, in SEL theory, the width of bars has not been considered. To eliminate this issue, Lumiainen proposed SSL theory which considerate should be last name, years the impact length of the bars (IL) in SEL theory [78]. SSL (Ws/m^2 or J/m^2) is calculated by equation (2.3).

$$SSL = \frac{SEL}{IL} \qquad (2.3)$$

IL can be calculated from the width of rotor (W_r) and stator bars (W_{st}), and from the average intersecting angle α of the rotor and stator bars.

$$IL = \frac{W_r + W_{st}}{2} \times \frac{1}{\cos\left(\frac{\alpha}{2}\right)} \qquad (2.4)$$

SSL theory seems to work quite well when bars are narrow. If bars are much narrower than the fiber floc, then they heavily cut the fibers [65].

2.3.1.3 C-factor theory

Several scientists have described the SRE into two parameters which are the number of impacts (N) and the intensity of each impact (I) [79–81]. To provide a relationship among the new power and fiber mass flow rate with N and I, Kerekes has proposed the C-factor theory (equation (2.5)) [79].

$$SRE = \frac{P_{net}}{\dot{m}} = N \times I = \frac{C}{\dot{m}} \times \frac{P_{net}}{C} \qquad (2.5)$$

Where C is described as the capacity of a refiner to inflict impacts on fibers. C has been given for different refiners (disk, conical, and PFI mill) as a function of fiber length, coarseness, plate geometry, rotation speed, and pulp consistency [76,79,82]. For example, C for a disk refiner is calculated by equation (2.6)

$$C = \frac{8\pi^2 GD\rho C_F l_A n_b^3 \omega(1+2tan\phi)(R_2^3-R_1^3)}{3w(l_A+D)} \tag{2.6}$$

Although C-factor is a more precise theory than SLE and SSL, it is not yet a widely used theory in the papermaking process. One important factor that makes some difficulties in the use of C in the industry, is the measurement of the initial pulp dimensions (length and coarseness). Another factor refers to the basic effects of refining, the length of the fibers is subjected to change during refining, so C is not constant [72,83].

2.3.1.4 New concept in refining theories

By reviewing the theories (SEL, SSL, and C-factor) mentioned above, it is found that all of them are energy-based intensities and energy is the commonly used variable in paper mills. However, it is stated that force not energy is responsible for changing the fiber properties during refining. In the new concept, the attempts are focused on using force in characterizing refining action [73,84]. To understand such theories, detailed knowledge of the applied forces, the fiber distribution in refiner gaps, and the amount of fibers are needed [76]. In pulp refining, the typical gap is 0.1–0.2 mm which is as big as the thickness of several single fibers. Therefore, fibers are trapped between the stator and rotor bars as the flocs and the forces act on the flocs rather than single fibers [85,86]. The forces that are transmitted to the flocs are normal force, shear force, and corner or edge force (Fig. 1(b)). The normal force is due to the compression of the floc between bars, the shear force is produced by the movement of bar surface on the floc and the corner force appears at the bar edge [87–89]. To estimate the number of flocs trapped between bars, Batchelor et al. proposed that the number of fibers trapped under any segment of bar will determine the point at which the net refining power begins to rise and the net refining power is fitted with a negative exponential function [86]. Kerekes proposed a force based theory that the refining intensity is based on the forces on bars which are linked to the forces on fibers through fiber distribution over bars and gap size [72]. It should be noted that in Kerekes theory, the forces are predicted on the individual fibers. To develop such a concept, more studies are needed.

2.3.2 Refining Effects

2.3.2.1 Fiber cell wall structure

The fiber cell wall structure of different species is generally composed of cellulose, hemicellulose, and lignin. Cellulose is a linear polysaccharide solely consisting of D-glucose units joined by $\beta(1\rightarrow4)$ glycosidic bonds. The cellulose molecule with several chains organizes into elementary fibrils, which are the narrowest fibrils (diameter 3.5 nm). Each cellulose chain consists of a reducing end with an aldehyde group and a non-reducing end with a hydroxyl group [90]. The aggregation of elementary fibrils forms the microfibrils having diameters between 10 and 35 nm [91]. Finally, aggregations of microfibrils shape the units of macrofibrils [92,93]. Cellulose has crystalline structure while hemicellulose has amorphous structure. Hemicellulose surrounds cellulose microfibrils. Hemicellulose has a lower strength than cellulose and can be easily hydrolyzed. It is a polymer of neutral polysaccharides present in the plant cell wall matrix and can be divided into xylans, mannans, β-glucans with mixed linkages, and xyloglucans. The third component of the cell wall is lignin. Lignin is a complex polymer within the fiber cell wall which acts as glue and binds the different layers of cell wall. It is a hydrophobic substance which is normally removed in chemical pulping and bleaching. Unlike cellulose and hemicellulose, lignin is not a polysaccharide, but a polymer produced from aromatic structures, with fenylpropane unit as a building block. Aromatic alcohols are aromatic lignols or phenylpropane units, i.e., guaiacyl propanol, p-hydroxyphenyl propanol, and syringyl propanol. The lignin components are then cross-linked together by β-O-4 linkages and C-C linkages with a number of additional functional groups, including methoxy groups, phenolic hydroxyl groups, and side terminal aldehyde groups [94,95]. It is these linkages between the lignol groups and the various functional groups that give lignin a unique and complex structure.

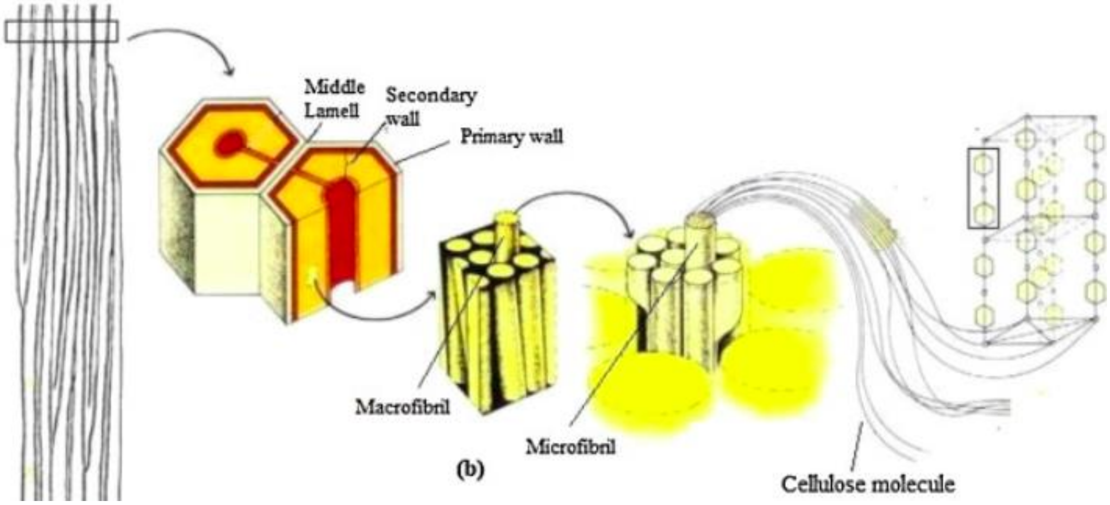


Figure 2.4. Fibrillar structure of wood cell wall **[96]**.

The fiber cell wall is produced from layers of microfibrils (Fig. 2.4). Microfibrils within the fiber cell wall are arranged within sheets or lamella, each of which consists of one single layer of elementary fibrils and is approximately 4 nm thick. These lamellae are then layered together to produce the cell wall. Fig. 2.5 illustrates the organization of the fiber cell wall layers. The fiber consists of two main layers, a thin primary cell wall (P) and a relatively thick secondary cell wall (S), along with a hollow center known as the fiber lumen. The S cell wall is further divided into three parallel arrays, based on the orientation of microfibrils and chemical composition: S1 is the outer most secondary cell wall; S2 is the middle secondary wall sub layer; and the S3 or tertiary wall is the most inner portion of the fiber cell wall. The thickness of the P, S1, S2, and S3 cell wall layers are 0.05-0.1, 0.1-0.3, 1-8, and <0.1 μm, respectively. Surrounding the primary wall, middle lamella (ML) acts as a cementing substance between the cells and has highest concentration of lignin. Since it is often difficult to distinguish between the ML and P layers, they are often described as one term known as the compound middle lamella (CML).

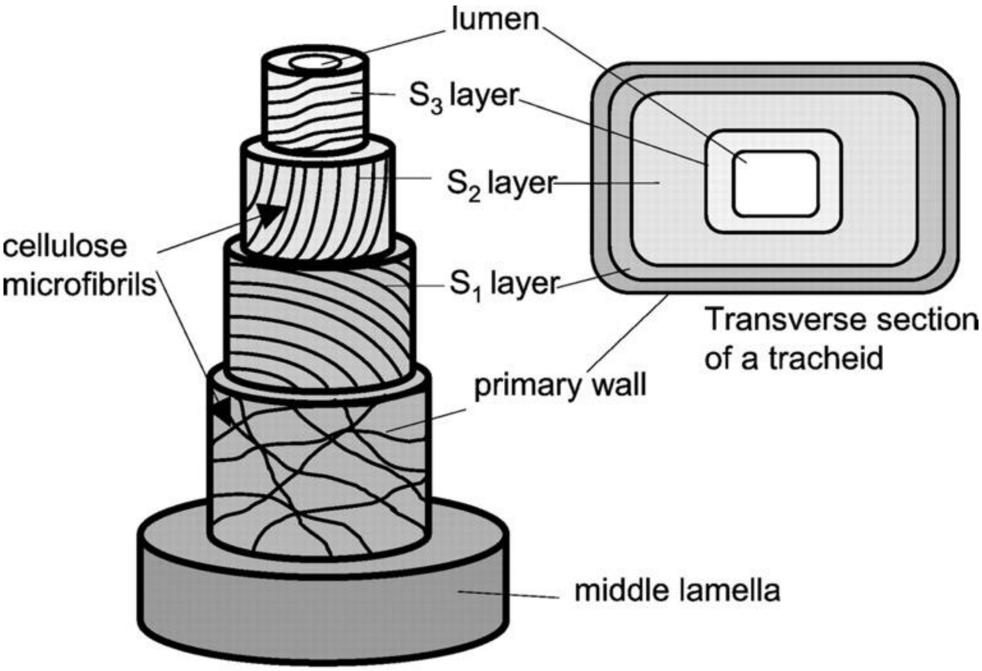


Figure 2.5. Structure of a tracheid cell wall **[97]**.

The cellulose microfibrils within the cell wall are generally measured at an angle from the cell axis, known as the microfibril angle (MFA) [98,99]. Microfibrils can be wrapped around the axis in two different directions, either to the right (Z helix) or to the left (S helix). Microfibrils of the P wall form a loose, irregular network that is generally oriented somewhat along the fiber axis. The S1 wall contains microfibrils presented in both the Z helix and S helix, with an MFA of about 50-70°. Microfibrils of the S2 layer have an MFA of approximately 10-30°, almost parallel to the wood fiber. The thickness and angle of the S2 layer provides strength along with other characteristics of wood fibers such as flexibility. In the S3 layer, microfibrils are oriented in the Z and S helix, with an MFA of about 50-90^o [100,101].

Microfibrils within the cell wall are made up of crystalline cellulose, which is embedded in a matrix of hemicellulose and lignin. Cellulose is in immediate contact with hemicellulose which is bonded to the lignin component. The CML layer has a very high lignin and hemicellulose content, consisting of about 50-100% lignin, while the S wall layers have a much lower lignin content, consisting of about 15-25% lignin [102]. More recently the relative distribution of lignin has been investigated by Fromm et al., indicating the lignin-saccharidic complex in the CML is high in lignin and S1 has relatively little lignin compared to all other cell wall layers [103].

In the process of fiber refining, several changes in fiber structure take place. The major effects of refining that result in fiber structural changes are extensively studied by researchers, and are typically categorized as internal and external fibrillation, fines formation, fiber shortening and fiber straightening [77,104,105].

2.3.2.2 Internal fibrillation

The first effect of refining on fiber layer is internal fibrillation. This is the delamination of the P and S1 layers, caused by the cyclic compression action of forces inside the refiner (Khalil El-Sharkawy et al., 2008; Nugroho, 2012b). Internal fibrillation has been extensively studied since it is considered to be the most important effect of refining.

Internal fibrillation is also known as “swelling”. The breakage of inner bonds which are between cellulosic fibrils, between fibrils and hemicellulose, between cellulose and lignin, and between hemicellulose and lignin causes the pore structure inside the cell wall to expand and swell [108]. Swelling is an evidence of internal fibrillation during refining and can be evaluated by the fiber saturation point (FSP) test [109,110]. Hardwood and softwood pulps swell inwardly and this behavior is confirmed by the decrease in the lumen size [111]. Bamboo pulp was found to swell toward the outside of the cell wall, which is due to the small size of the lumen in bamboo [112].

Internal fibrillation also makes the fiber more flexible or conformable [68]. Loosening of the fiber wall or delaminating of wall layers reduces the bending stiffness of the fiber wall and thus makes fiber flexible or collapsible as a result of the internal fibrillation [113]. Flexibility is a key factor as it governs the most physical and optical properties of pulp and paper, including paper formation and paper strength. The flexible and collapsible fibers give more close contact which leads to strong bonding between fibers [114]. Rusu et al. showed that fiber bendability increases with internal fibrillation [114].

2.3.2.3 External fibrillation

Peeling off the fibrils from the fiber surface is associated with exposing the S2 layer which is defined as an external fibrillation [95]. This phenomenon can be observed in the microscopic images as the fibrils are attached to the fiber wall (Fig. 2.6). The most significant effect of external fibrillation is the increase in the specific surface area of fibrils on the fiber surface [106,115]. During the fibrillation process, hydrophilic compounds from the cell wall are released which produce gel-like layers [116]. And these gelatinous layers can significantly improve the fiber-fiber bonding.

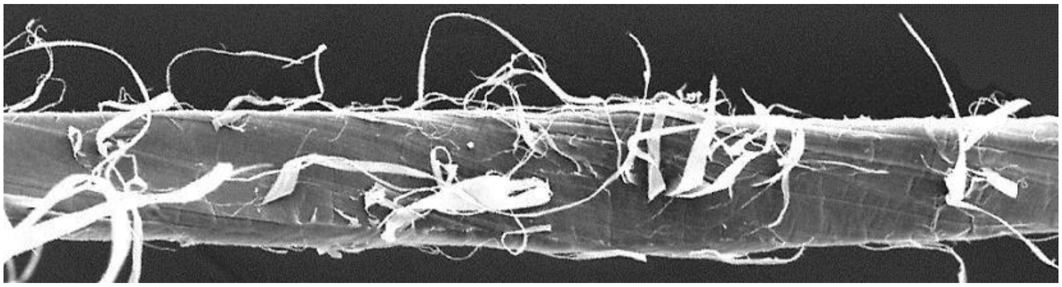


Figure 2.6. SEM image showing surface ultrastructure and highlighting mechanisms of external fibrillation **[117]**.

It is claimed that external fibrillation is the main reason for improving the bonding, however, the role of external fibrillation on pulp and paper properties is a controversial subject [115]. In comparison with internal fibrillation, the external fibrillation has been subjected to less interest because during refining it is associated with internal fibrillation and fine formation and these simultaneous changes made it difficult to judge the role of external fibrillation.

2.3.2.4 Fines formation

Two types of fines are present in pulp: primary fines and secondary fines. Primary fines are present in unrefined pulp and come from ray cells and parenchyma cells [62,118]. While secondary fines are produced during the refining, as a result of external fibrillation or fiber shortening [119]. These fines consist of fragments of primary and secondary walls with a size of less than 0.3 mm [76]. Usually, a 200 mesh screen (75 μm opening) is used to remove fines [118]. Fines have high surface area and can improve the fibers bonding, though, they have negative effect on pulp drainage [62]. The primary fines content of chemical pulp is typically less then 2%, but refining can increase the total fines content to 15% [120]. An increase of refining time or shear rate also increases the amount of fines [121].

Different behaviors of fine formation based on different consistencies have been reported by researchers. An increase in fine content has been observed by increasing the specific energy consumption of LC refining [116]. Kang et al. reported that HC refining causes fewer fines formation, while LC refining tends to produce more fines. However, Wistara and Young have reported the different results [122,62]. They showed that there is no significant decrease in the production of fines, by refining of never dried pulps at 5% versus 10% consistency, although higher consistency refining (30%) results in a higher amount of the fines in comparison with the refining results, at the lower consistencies (5% and 10%). The effect of gap clearance on fines formation by ultra-fine friction grinder has been reported by Kang et al. [122]. It is stated that the generation of fines is reduced by increasing the gap.

2.3.2.5 Fiber shortening

Another change in fiber quality is a reduction in fiber length which usually has an undesirable impact during the refining [123]. Breaking of fiber happens when the strain on a fiber is great enough. The mechanical effects of refining will cause transverse subdivision of the fibers. Accordingly, fibers may be cut by direct shearing forces of the passing refiner bars, or they may fail when pulled from a network of other fibers [79].

It was described above that fines generation also occurs because of excess force during external fibrillation. Since there is a relationship between fiber cutting and fine generation, accurate measurement of the fiber length changes during refining is difficult [83]. Practically, the reduction of the fiber length was calculated based on the length weighted average before and after refining. It is notable that the changes in the length-weighted fiber length did not completely reflect the changes in the number of long fibers per unit mass, due to the fact that the measured average fiber length is affected by the generation of fines during refining [83]. Chen et al. reported that the fiber weight length of the first cycle and second cycle of refined eucalyptus pulps cellulose was reduced by 8% and 8.16%, respectively, in comparison to the first cycle and second cycle unrefined pulps, and showed that at consistency of 6%, refining has no significant effect on fiber cutting [124].

In some rare applications, the reduction of fiber length is a desired effect to improve formation, by decreasing the crowding number [125]. The shortening of fibers improves sheet formation considerably due to a decrease in the crowding number which leads to the lowering of flocculation tendency and smaller sizes of flocs, thus, contributing to paper uniformity and smoothness [82,120,124].

Various results of refining influence on the fiber shortening by using the different refiners have been reported. Zeng et al. treated the bleached pine kraft pulp with a conventional Valley beater and showed that the fiber length first increased due to fiber straightening and then decreased gradually with refining [120]. Beg and Pickering refined the fiber by using a Sprout-Waldron disc refiner with a SEL of 0.89 Ws/m and indicated that fiber length decreases with increased refining time [126]. The average fiber length for virgin fiber was 2.36 mm with a fiber distribution from 0.2 to 5.8 mm and after 8 min, the fiber length was reduced to 1.84 mm.

2.3.2.6 Fiber straightening

Chemical pulp fibers are initially curly, and refining causes the fiber straightening [127]. Shape factor and curl index are two common parameters to determine the curl index. Page, Jordan and Barbe introduced the curl index (equation (2.7)) as the relationship between the fiber "contour length" and the "projected length" (Fig. 2.7) [128]. Shape factor is defined as the ratio of the shortest distance between the fiber ends and the true (contour) fiber length [120]. There also exists a relationship between shape factor and curl index as indicated by equation (2.8) and (2.9).

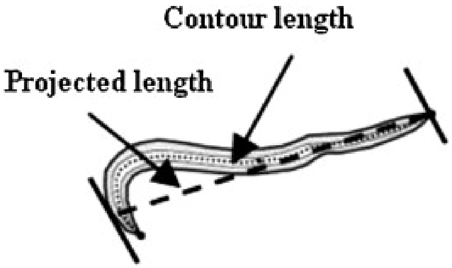


Figure 2.7. Definition of contour length and projected length **[129]**.

$$Jordan\ and\ Page's\ "Curl\ Index" = \left(\frac{fiber\ contour\ length}{projected\ length} - 1\right) \qquad (2.7)$$

$$Shape\ factor = \frac{1}{curl\ index + 1} \times 100 \quad (2.8)$$

$$Curl\ index = \frac{1 - shape\ factor}{shape\ factor} \qquad (2.9)$$

During pulping process, the pulp is subjected to the varieties of mechanical and chemical treatments which introduce the curl to the fiber. Curl affects the drainage resistance of most pulps. A reduction in curl index results in a reduction in freeness value [128]. The average curl index for straight fiber and curly fiber is 0.1 and 0.2, respectively. Fiber straightening plays an important role in the development of paper properties. Straightening of fibers improves the load carrying ability as well as the stress distribution in the fiber network and mostly increases the elastic modulus and tensile strength of the paper [107].

The curl is generally reduced upon LC refining while the HC refining increases the curl because of the stresses transferred between fibers. This is often a disadvantage, as it changes the properties of paper, for instance, the tensile strength is reduced [128,62]. The analysis of the fiber straightening in the Valley beater, commercial refiner, PFI mill, and an ultra-fine friction grinder showed that the curl index decreases with the enhancement of refining and the fibers treated in the Valley beater in comparison to the ultra-fine friction grinder, are more straightened under compressive and shear forces [122,128,130,131]. It has been shown that the amount of fiber curl decreased sharply at the initial refining with the Valley beater and later decreased more gently [120]. Haavisto et al. examined the effect of different plates on the fiber straightening of two types of fibers [107]. He presented that at the same refining condition, the conical filling has more influence on the straightening of pulps than wide bar disk filling and this effect is more significant in the case of a mixture of softwood and hardwood pulps.

In summary, mechanical refining can improve the overall quality of recycled furnish. It can affect fiber structure and its properties through some simultaneous changes. However, these changes are not all desirable, fiber shortening, and the formation of fines can deteriorate recycled furnish. Therefore, alternative methods and innovative technologies are being investigated not only to improve the recycled fiber quality while minimizing the negative effects associated with mechanical refining but also to decrease the high energy demand required by the mechanical refining process. Bio-modification of cellulosic fibers with enzymes has attracted growing interest for this purpose.

2.3.3 Enzyme-assisted Refining

The strength loss of secondary fibers is caused by hornification (decrease of swellability and conformability of fibers) and loss of bonding areas [132]. The strength of fibers can be recovered to a certain degree by beating. However, the generation of fines during the beating process decreases the runnability of the paper machine. The decrease of drainage properties of pulp caused by the fines becomes an important limiting factor for recovering paper strength by beating. Mechanical pulp content in wastepaper grades used for the corrugated medium is an additional source for generating more fines during the beating.

The use of enzymes in upgrading secondary fibers has been an interesting topic in recent years. In most of the studies, commercial mixtures of different cellulases and hemicellulases were used to treat recycled fibers, and the treatment resulted in improved drainage properties. Stork et al. used isolated cellobiohydrolases and endoglucanases of *Penicillium pinophilum* to treat recycled pulps and measured the effects on the water retention value. They concluded that endoglucanases are necessary for improving the dewatering of pulp [133]. Pulp fibrillation by cellulases for enhancing strength properties was reported. The effect of different hydrolases on the improvement of the refining process by reducing energy consumption has been a matter of intensive research in the past two decades. Different cellulases and hemicellulases have been proven to have a beneficial effect on refining and on surface fiber morphology, giving rise to better bonding properties and a closer structure of paper. Furthermore, cellulase-free xylanase application has improved pulp fibrillation and water retention, shortened the time of refining in virgin pulps, enhanced the restoration of bonding, and increased both the freeness in recycled furnish and the selective removal of xylan from dissolving pulps.

Some basic effects of the enzymatic treatment were studied by Jackson et al with a preparation made of xylanases and two different mixtures of cellulases and xylanases on a softwood kraft pulp [134]. With cellulases, pulp drainability improved and it was verified that fiber hydrolysis occurs because of the treatment. Low enzyme doses produced a reduction in fines content, which was related to a possible effect of flocculation produced by the enzyme, similar to that of polymeric drainage aids. The highest enzyme doses led to increased fines contents, which were attributed to the fiber disintegration produced by cellulases.

Pala et al investigated refining, refining plus enzymatic treatment, enzymatic treatment plus refining, and enzymatic treatment of recycled fibers [135]. The physical and mechanical properties of pulp and paper were measured to evaluate the effectiveness of the methods. They found that the most suitable method for upgrading recycled pulps was refining plus enzymatic treatment. Refining increases burst and tensile resistance, whereas enzymatic treatment produces better drainage under certain conditions. Fiber that has been recycled more than once has lower papermaking qualities than virgin or once-recycled fiber. By using an enzyme blend with recycled furnish, some of the lost freeness can be restored.

Moran reported that the addition of enzymes before refining has a very different effect compared with post-refining treatment [136]. Pre-refining applications result in improved refining efficiency, whereas post-refining treatment results in increased furnish freeness. A combination of the two can provide optimized strength and drainage benefits. Pre-refining treatment involves the addition of the enzyme to the stock that feeds an unrefined stock chest. In this application, the enzymes begin to hydrolyze the outer walls of cellulose fibers. This surface treatment prepares the fiber surface for improved refining efficiency. Strength properties can be developed with fewer refining energy requirements. This application has the following benefits:

- lower refining energy to meet strength specifications;
- improved strength properties at equivalent refining energy.

The improvement of secondary fiber properties through enzymatic pretreatment has been demonstrated by many studies. However, the detailed mechanism of the enzyme effects is still not sufficiently understood. Without fully understanding the fundamentals of how enzymes work on recycled fiber cell wall structure, a wider range of applications of this green technology is limited.

2.4 Enzymes Used in the Pulp and Paper Industry

The use of enzymes in the Pulp and Paper Industry was reported from 1970’ s. However, paper-related enzymes have been shown to be relatively expensive, poorly recyclable and unstable [137]. Since then, the performance and competitiveness of enzymes have significantly improved with the development of enzyme-centered industrial biotechnology in the last few decades, and many enzyme treatments have been developed and applied in various pulp and paper processes (Fig. 2.8). The application of enzymes in the pulp and paper industry has tremendously improved the green and sustainable development of this industry, not only by increasing the pulp yield and physical properties of paper but also simultaneously reducing energy consumption in a more environmentally friendly way [138–141].

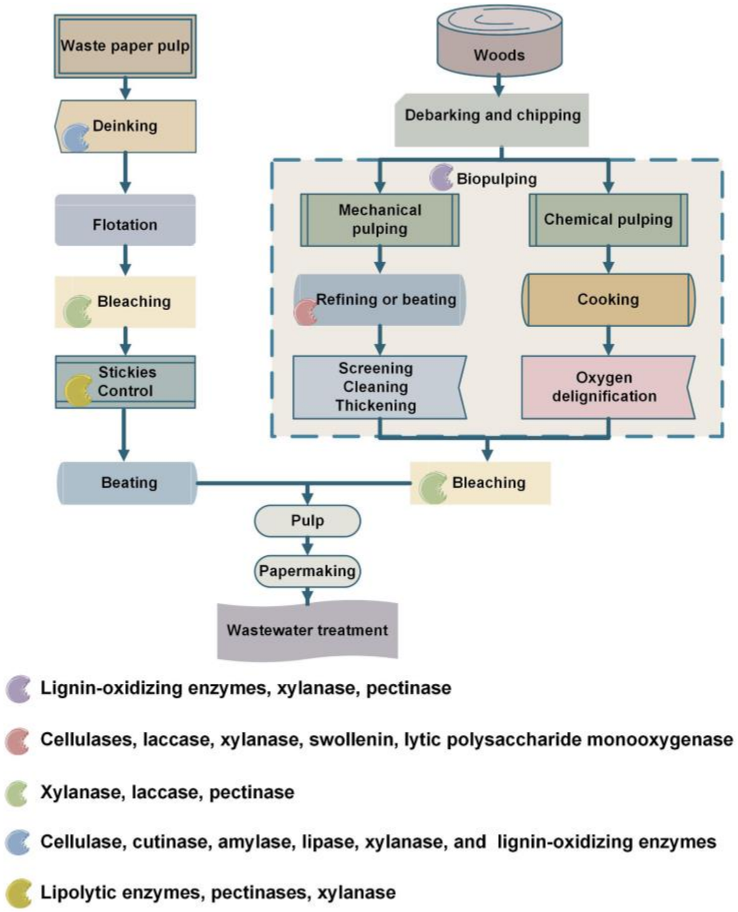


Figure 2.8. Schematic graphic of enzyme applications in the pulp and paper industry [57].

It should be emphasized that the papermaking process occurs in a complex environment in which enzyme efficiency depends on a variety of factors, including reaction pH, temperature, residence time, pulp properties, and enzymes concentration. In particular, the interactions between enzymes and substrates, including different pulp fibers, a variety of chemical additives, and various contaminants in the recovered paper, are of great importance [138,141–143]. Depending on the process, different types of enzymes were employed because the goal and substrates differ. Hydrolases and oxidoreductases are frequently utilized enzymes. Cellulases, hemicellulases, pectinases, lipolytic enzymes, and amylases are examples of hydrolytic enzymes; lignin-degrading enzymes and auxiliary enzymes like lytic polysaccharide monooxygenases (LPMOs) are examples of oxidative enzymes [141,144]. Given the complexity of the application environment, no single enzyme has been able to completely and independently resolve the issues of all papermaking processes to date. As a result, there has been a lot of interest in the precise formulations of enzyme cocktails for different processes, and competitive formulations have been created. In the following section, the research and development of enzyme applications in the pulp and paper process are discussed.

2.4.1 Cellulases

Cellulases are complex enzymes, whose enzymes act synergistically and are subdivided into at least three different activities. In this way, endo-β-1,4-glucanases or endoglucanase (EG) act randomly in breaking internal molecular bonds in the amorphous regions of the fibers, producing a rapid decrease in the length of the chain and a slow increase in the quantity of free reducing groups. The exo-β-1,4-glucanases or cellobiohydrolases (CBH) remove glucose or cellobiose units from the end of free non-reducing cellulose chain, resulting in a rapid increase in reducing sugars and little change in the size of the polymer. Finally, β-1,4-glucosidase or cellobiase (CB) hydrolyzes the cellobiose produced by the above activities, giving D-glucose as an end product. Fig. 2.9 displays the catalytic diagram of cellulases reactions. Cellulases are mostly employed in the refining/beating process. Cellulases act on the surface and inner layers of cellulose fibers in an efficient enough way to allow the production of special paper with reduced energy consumption [145]. Cellulases effects on fiber morphology lead to improved fiber–fiber bonding in the refining process and hence to increased fiber cohesion in the final paper [146–148]. Lecourt et al. treated softwood bleached kraft pulp with commercial cellulases prior to the refining stage and observed increased intense fibrillation, higher conformability and flexibility, and higher bonding potential [149]. Consequently, the pulps had a higher breaking length and lower bulk, and the resulting energy saving reached 15%. Studies have also demonstrated the effectiveness of cellulases in pulping, deinking, and other processes where energy use were reduced, and physical qualities and drainage of the pulp were enhanced [150,151].

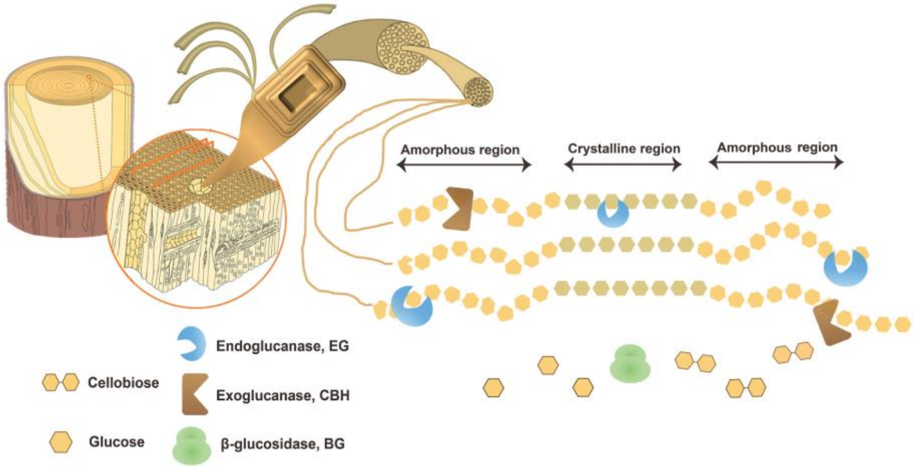


Figure 2.9. Conceptual graphic of cellulase catalysis of wood cellulose [57].

2.4.2 Xylanases

Xylan, which is the dominating component of hardwood and annual plants hemicelluloses, is one of the most abundant organic substances on earth, and its biodegradation is performed by xylanolytic complex (enzymes) produced by fungi and bacteria. Xylanases (endo-1,4-β-xylanase) are glycoside hydrolases catalyzing the endolytic hydrolysis and break down hemicellulose by hydrolyzing the β(1,4)-linkages of xylan backbone structures without environmental pollution [152–154]. Sathiva et al. studied the effects of xylanases on biobleached wastepaper pulp properties and observed, in comparison to conventional chemical bleaching, a significant increase in pulp brightness and improvement in thickness and bulkiness [152]. In addition, based on pore size distribution, it has been demonstrated that xylanases can easily penetrate inside the cell wall and, therefore, alter the dewatering properties of the cell wall. Blomstedt et al. reported xylanases treatment could improve dewatering properties of bleached hardwood kraft pulp. The time to reach 95% dry solids content was reduced by 15% by xylanases treatment, which can lead to significant energy consumption reduction in paper drying section [155].

2.4.3 Laccases

Laccases (EC 1.10.3.2, p-diphenol, dioxygen oxidoreductase) belong to the so-called blue-copper family of oxidases. They are glycoproteins, which are ubiquitous in nature. Laccase enzymes are expressed by white-rot fungi and other organisms that play a crucial role in the terrestrial carbon cycle by helping to degrade lignocellulosic material. They act on phenolic substrates by catalyzing the oxidation of their phenolic hydroxyl groups to phenoxy radicals while dioxygen is reduced to water; this initiates the depolymerization process [156]. Laccase is a large molecule (MW ~70,000) which cannot penetrate deep into wood; moreover, due to its rather low redox potential (~0.5–0.8 V), it is unable to oxidize non-phenolic (C4- etherified) lignin units, which have a high redox potential (>1.5 V). Because of these limitations, laccase alone can only oxidize phenolic lignin units (<20 % of all lignin units in native wood) at the substrate surface. Therefore, laccase is often applied with an oxidation mediator, a small molecule such as 2,2'-azinobis(3-ethylbenzthiazoline-6-sulfonate) (ABTS) or 1-hydroxybenzotriazole (HBT) among others, able to extend the effect of laccase to non-phenolic lignin units and to overcome the accessibility problem. This association is named laccase mediator system (LMS). In these so-called LMS, the mediator is first oxidized by the laccase and then diffuses into the cell wall, oxidizing lignin inaccessible to laccase [157,158]. Camarero et al. observed increased pulp delignification (25% decrease of lignin compounds) in their study where unbleached pulp was treated with laccase mediators [159]. The LMS enabled over 15% increase in final brightness. Petit-Conil et al. treated spruce chips with laccases obtained from fungi with a mediator (HBT) prior to

TMP [160]. Laccase/HBT saved refiner energy by up to 20%. The effect on pulp properties in terms of mechanical strength and brightness of handsheets was mostly positive. A decrease of 15% in peroxide consumption during subsequent bleaching to equal brightness was achieved compared to bleaching without laccase pretreatment.

2.4.4 Manganese Peroxidases

Lignin peroxidases (LiP) are generally considered the primary catalysts for the fungal cleavage of non-phenolic lignin structures. Manganese peroxidase (MnP) oxidizes Mn^{2+} to Mn^{3+}, which oxidizes phenolic structures to phenoxyl radicals. The product Mn^{3+} is highly reactive and complex with chelating organic acid, as oxalate or malate, which is produced by the fungus. The redox potential of the Mn peroxidase system is lower than that of lignin peroxidase and it has shown capacity to preferably oxidize in vitro phenolic substrates. On the other hand, studies indicate that, contrary to LiP, MnP may oxidize Mn(II) without H_2O_2 with decomposition of acids and concomitant production of peroxyl radicals that may affect lignin structure [161].

2.4.5 Amylases

Amylases hydrolyze starch. Starch contains about 15–30 % amylose and 70–85 % amylopectin. Amylose is a long linear polymer of α-1,4-linked glucose residues. Amylopectin is a branched polymer having both α-1,4 and α-1,6 linkages. Three types of amylases are involved in starch bioconversion: endo-amylase (α-amylase), exo-amylases (glucoamylase or glucan 1,4-α-glucosidase, β-amylase), and debranching enzymes (pullulanase or isoamylase). α-Amylase cannot act on α-1,6 linkages and hydrolyzes internal α-1,4-glycosidic bonds of starch randomly and produces maltooligosaccharides of varying chain lengths. Glucoamylase cleaves glucose units from the non-reducing end of starch, and it can hydrolyze both α-1,4 and α-1,6 linkages of starch. β-Amylase hydrolyzes the α-1,4-glycosidic bonds in starch from the non-reducing ends.

Pullulanase (pullulan α-1,6-glucanohydrolase) or isoamylase (glycogen α-1,6-glucanohydrolase) cleaves the α-1,6-linked branch points of starch and produces linear amylosaccharides of varying lengths.

2.4.6 Pectinases

Pectin is a main component of the middle lamella and primary cell wall of the cellulose fibers. The term pectin is used for a group of components comprising rhamnogalacturonans, galactans, and arabinans. Rhamnogalacturonan is a main component of pectin and has a backbone of α-(1,4)- linked D-galacturonic acid units and α-(1,2) or α-(1,4)- linked L-rhamnose. Pectinases are a group of enzymes involved in depolymerization of the pectic polymers. This group of enzymes mainly consists of polygalacturonases (PG), pectin methyl esterases, and pectin lyases polygalacturonases that cleave the bonds between galacturonic acids of the pectin chain. It is a hydrolytic enzyme and exists in two forms: endo-PG and exo-PG. Endo-PG acts randomly on the α-(1,4)-polygalacturonic backbone, whereas exo-PG acts at the non-reducing end of the chain. Pectin methyl esterase provides demethylation of pectin and decreases the amount of esterified pectin.

2.4.7 Lipolytic Enzymes

Lipolytic enzymes belong to a large α/β-hydrolase superfamily comprising structurally related but functionally diverse enzymes, all of which share the same catalytic Ser-Asp/Glu-His triad typical of all serine hydrolases, including lipase, cutinase, and esterase [162]. Lipolytic enzymes are widely used in the paper industry for deinking and sticky control processes. Long-chain ($C > 10$) water-insoluble acyl esters are hydrolyzed by lipases, short-chain ($C < 10$) water-soluble acyl esters are catalyzed by esterases, and short- and medium-chain (C2–C12) acyl esters are catalyzed by cutinases [162]. The primary distinctions between these three lipolytic enzymes pertain to their substrate (type, solubility) and mechanism of action (interfacial effect) [163,164].

Lipases, also known as glycerol ester hydrolases, are a special class of ester bond hydrolases that can function independently without the use of cofactors. Triglyceride molecules, such as linolenic, linoleic, and oleic acids, which are frequently employed in printing inks and adhesives, are the substrates of lipase. Lipases can partially break down the aforementioned substances to remove ink groups from fibers, decompose pigments and resins, and lessen pulp viscosity. The resulting byproducts can also act as surfactants to prevent the re-agglomeration of stickies [165,166]. Lipase, cellulase, and xylanase were coupled to deink pulp and achieved approximately 14.5% improvement on brightness [167].

Cutinases, which are produced by fungi and several bacteria, hydrolyze ester bonds and can degrade aliphatic and aromatic polyesters. Cutinases also are binders for synthetic toners or inks, and can hydrolyze polyvinyl acetate and polyacrylate during the deinking process [166]. Based on substrate and catalytic complementarity, Liu et al. designed a chimeric lipase-cutinase, which boosted the activity of the original enzymes by 127% and 210%, respectively [168].

Esterases can hydrolyze ester bonds and can be classified as lipases, carboxylesterases, and sterol esterases. By severing ester bonds in a variety of adhesives, esterases can dissolve sticky materials, significantly reducing sticky deposits and prevent re-agglomeration [169]. Polyvinyl alcohol (PVA) is a common adhesive used in pulping; Yin et al. isolated a novel esterase, that can deacetylate PVA and has the potential to be used for sticky control [169].

Although the use of enzymes in papermaking processes has been around for many years and has gained greater attention, indicating a promising future for the development of this industry, there is still a need to think about how enzymes, particularly enzyme mixtures, might be used with greater efficiency [140,143]. Each paper mill must systematically decide the viability of using different enzyme preparations in its various processes because there is no patent recipe for creating the ideal enzyme cocktail for all pulp mills. As a final point, it should be noted that before any conclusions can be drawn, a thorough life cycle assessment of the process and the consideration of environmental impacts are also necessary to build a complete system within the circular economy with recyclable resources, low energy consumption, low emissions, and connections to nature's carbon cycle.

2.5 Summary

This chapter provided a comprehensive review of the technical challenges in secondary fibers faced by the pulp and paper industry, and present and emerging technologies for tackling these challenges. Initially, an introduction to paper recycling and the limitations of recycled fibers were provided. After that, the contaminations and related removal processes were discussed. In this section, the organic sticky contaminants especially macro- and micro-stickies were highlighted as the most problematic contaminants in the remanufacturing process. The development of mechanical processes, chemical additives, and enzyme-based biotechnologies for the removal of such problematic contaminants was discussed in the section as well. Following this, low fiber quality, as another major challenge in fiber recycling, was reviewed. The mechanical refining process that has been determined as the most common approach to restore recycled fiber quality is discussed, as well as the refining mechanism and changes in fiber structure. Additionally, enzymes that can facilitate mechanical refining and reduce energy consumption were introduced. Finally, the research and development of enzyme applications in pulp and paper process were discussed.

CHAPTER III

IDENTIFICATION AND CHARACTERIZATION OF STICKY CONTAMINANTS IN MULTIPLE RECYCLED PAPER GRADES

3.1 Introduction

Recovered paper plays an increasingly important role in global paper industry as paper recovery rates continue to increase each year in most parts of the world. As a great substitute for virgin fibers, it provides savings on energy consumption and reductions on GHG emissions during papermaking process. However, the use of recovered paper is limited by its low quality due to the presence of a variety of contaminants, which can be classified according to their sources, i.e. organic, inorganic and microbiological contaminants [170]. Although cleaning techniques are implemented in the papermaking process, some contaminants can carry through or even build up during the manufacturing process. The term "stickies" is commonly used to describe these tacky substances.

Stickies represent one of the biggest problems in the paper recycling process. These contaminants inhibit inter-fiber bonding which directly impacts the physical strength of the recovered paper products [19]. In addition, the presence of stickies in the paper machine also causes plugging of wires and felts, leading to a reduction in the water drainage of the fiber suspension. Furthermore, the contaminants stick to process equipment, such as the press rolls and the dryers, causing mechanical problems of the runnability [50,171]. Ultimately, all these problems lead to low quality products and higher costs for the paper manufacturers. Therefore, the efficient removal of these sticky contaminants has become increasingly critical to paper industry. To improve the removal of sticky contaminants and eventually extend the utilization of recovered paper, the nature of these stickies and their characterizations need to be investigated.

The sticky contaminants are commonly classified based on particle sizes as "macro-stickies" and "micro-stickies" [172]. This classification defines "macro-stickies" as solid contaminants that are retained on mesh and have a diameter of about 100–150 um. This kind of contaminant is generally monitored to determine the contamination removal efficiency of the process units. On the other hand, contaminants with a diameter of less than 100 um are defined as "micro-stickies". Micro-stickies can be further classified into suspended and dispersed (5–100 um), and colloidal and dissolved stickies (<5 um). However, this classification by size is not enough. From a chemical point of view, stickies consist of a very broad range of components including high and low molecular weight organic compounds, and natural and synthetic polymers. They are typically derived from a combination of contaminant sources, e.g. adhesives, coating materials, ink residues, processing chemicals, and wood derivatives [173]. Adhesives are generally considered to be the most detrimental source for the formation of deposits during papermaking process [21,174]. The predominant polymers used for adhesives include polyvinyl acetate (PVAc), polyacrylates, styrene butadiene rubber (SBR), ethylene vinyl acetate (EVA), polyamide, polyvinyl alcohol, styrene butadiene styrene (SBS), synthetic resins, etc [20,175]. Coating binders are a secondary source for the generation of stickies. One of the most predominant compounds is SBR latex; while PVA and polyvinyl acrylate are also commonly used [176,177]. As tacky contaminants from printing inks, toners using SBR, and polyvinyl acrylate contain the same chemical components as adhesives. Wood extractives, rosins, and wet strength additives are other possible causes of stickies deposits.

The heterogeneous nature of sticky contaminants makes their identification and characterization very difficult using simple methods [178,179]. The determination typically requires complex multi-step procedures starting with fractionation of stickies, and solvent extraction for quantification, followed by characterization using several analytical techniques [173,179–181]. Gravimetric extraction with an organic solvent is commonly used to isolate hydrophobic substances from the fibers. It is the basis of the stickies measurement method, the result is, however, very dependent on the solvent used. Most commonly used solvents include dichloromethane (DCM), dimethyl formamide (DMF), trichloroethane (TCE), acetone, and tetrahydrofuran (THF) [182–187]. Among them, THF and DCM have been demonstrated to be more selective to stickies which obtain higher yields, but DCM was reported also dissolve the non-sticky components such as the lignin components, e.g., dimethylformamide [188,189]. Therefore, THF was selected in this study. Subsequently, multiple analytical techniques have been applied for the characterization of stickies including Fourier-transform Infrared Spectroscopy (FTIR), Gas Chromatography/Mass Spectrometry (GC/MS), Gel Permeation Chromatography (GPC), Thermogravimetry (TGA), Differential Scanning Calorimetric Analysis (DSC) and Scanning Nuclear Resonance (NMR) [179,190–193]. Fourier Transform Infrared spectroscopy (FTIR) is commonly used in identification of sticky substances in many studies [35,182,194]. Johansson et al. were able to quantify stickies with IR analysis and multivariate data analysis of the spectra [38]. Gas Chromatography (GC) combined with Mass Spectrometry (MS) can detect and quantify organic components, and it has been used for quantifying wood extractives (Guo and Douek, 1995; Orsa, 1994). For investigating stickies, a pyrolysis unit is needed on GC/MS. In pyrolysis, stickies are decomposed into individual compounds and are then identified and quantified. Py-GC/MS has been used by many authors [185–187,197–199]. In addition, Sjöström et al. used HPLC for separating stickies from other substances with a Size Exclusion Column (SEC), where substances are separated based on molecular size [187]. They used IR and Py-GC/MS for the polymeric fraction and

GC for the low molecular size fractions. Holmbom also separated polymers from other hydrophobic substances with HPLC-SEC and quantified these polymers with Py-GC/MS [185].

Although multiple methods have been proposed for the characterization of stickies, the establishment of a universal method is not completed, making it difficult to study the evolution of stickies content along the process and the removal efficiency of the different stages [172,180,200]. Additionally, these methods mainly focus on the analysis of macro-stickies, but no generally accepted standard method for the determination of micro-stickies is available. Furthermore, being the main origin of potential deposits in the paper recycling process, micro-stickies constitute 70-90% of the total stickies while remaining recalcitrant in the paper recycling process and not being removed effectively [16,35,38,201]. In this sense, the identification and characterization of the most problematic contaminants is the key for reducing contamination [202,203]. Therefore, in this research, an integrated chemical approach by solvent extraction and subsequent characterization of the extracted stickies is proposed which allows the analysis of stickies at all dimensions. In this case, multiple analytical techniques are applied for the characterization of stickies, including FTIR, GC-MS, colloidal titration, etc. Through full characterization of sticky contaminants in multiple recycled paper grades, it is expected that the findings of this research will provide information to address the knowledge gaps in understanding the nature of stickies and their behavior and eventually develop highly efficient technologies for contamination removal.

3.2 Experimental

3.2.1 Materials

Multiple grades of recycled paper feedstock are obtained from local paper recycling mills and from residential curbside collection. These include residential wastepaper (Residential), old corrugated containerboard (OCC), recycled boxboard cuttings (Box), recycled kraft linerboard (Kraft Liner), printed bleached kraft paper (Bleached Kraft), used office paper (Mixed Office), and old newsprint paper (ONP). Residential mainly consists of food containers such as burger boxes, pizza boxes, food wrapping papers, etc. These papers are highly contaminated with oil and grease. OCC includes mostly post-consumer packaging materials, such as containerboards obtained from wholesale stores. The box consists of cuttings of multiple paperboards that are used in the production of folding paper cartons such as cereal boxes. Kraft Liner is sorted paperboard with Kraft liners, which are mainly from postal packaging boxes. Bleached Kraft is heavily printed sheet with a high calliper, made of bleached sulfite pulp. They are typically used as feedstock for converting mills to make high-grade packaging boxes. Mixed Office is common printing and writing paper, which can be found in typical workplace. ONP is a mixture of used newspaper and old grocery store flyers. Photos of these wastepaper are shown in Fig. 3.1.

Figure 3.1. Recycled paper raw materials collected from local paper mill and curb-side stream.

Table 3.1. Ash content in as-received wastepaper samples.

Wastepaper grades	Ash content (wt%)
Residential	6.20
OCC	2.15
Kraft Liner	6.04
Bleached Kraft	7.88
Box	13.92
ONP	13.56
Mixed Office	17.63

The recycled papers were used as received, and the “as received” moisture content of all grades was determined following TAPPI standard method T412. The ash content of each wastepaper grade is determined following TAPPI standard T211, and the results are shown in Table 3.1. All chemicals used in this study such as tetrahydrofuran (THF) and poly-DADMAC were purchased from Fisher-Scientific.

3.2.2 Physical Characterization of Sticky Contaminants

Dried recycled fibers were ground to pass a 0.4mm (40 mesh) screen following TAPPI T257. Ground fibers were utilized to perform solvent extraction of sticky contaminants using conventional laboratory Soxhlet extractor following TAPPI T204 (Fig. 3.2). Deionized water (DI water) and tetrahydrofuran (THF) were used as extraction solvents. The fibers were extracted with DI water first and then with THF. Extraction process was maintained for 4 hours (predetermined), and the heat was controlled to provide a boiling rate which cycles the solvent at least 6 times per hour. Solvent was partially evaporated to 20ml in the extraction flask using rotary evaporator, and then transferred to a weighing dish with a small amount fresh solvent. The weighing dish and content were dried in an oven for 1 hour at $105^{o}C \pm 3^{o}C$, cooled in a desiccator, and weighed to the nearest 0.1mg.

The content of sticky contaminants was calculated using equation (3.1):

$$Content\ of\ sticky\ contaminants\ (wt\%) = \frac{W_f - W_e}{W_f} \times 100\% \qquad (3.1)$$

where

W_f = oven-dry weight of recycled fibers prior to extraction, g

W_e = oven-dry weight of recycled fibers post extraction, g

The size and number of sticky contaminants in recycled paper were determined by a modified “pick-up” method following TAPPI T277. Handsheets which were made from wastepaper samples were placed between two coated papers. The three sheets were heated and pressed under controlled conditions (7 tons, $177^{o}C$) for 5min. Once the coated papers were removed from the handsheet, the coating were picked up by the stickies and a contrast was created on the handsheet, which readily allowed the measurement of area and number of heat-set stickies.

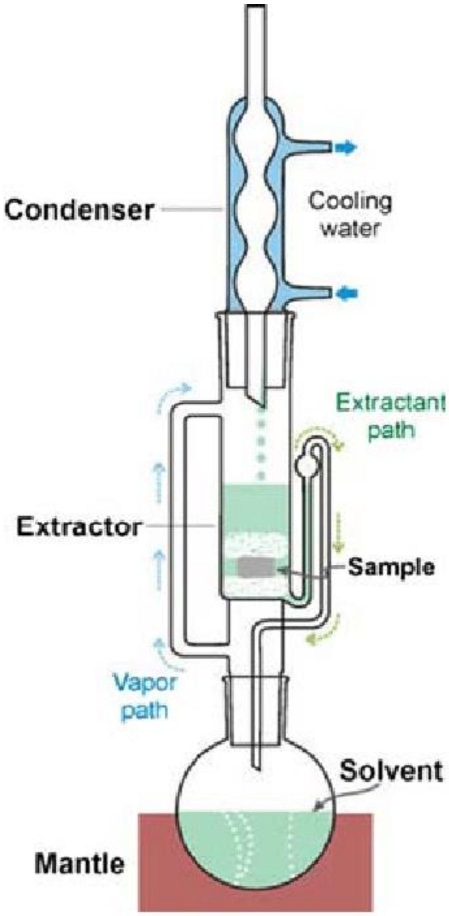


Figure 3.2. Experimental setup of solvent extraction procedure.

The specific stickies area, specific stickies number, and average stickies size were calculated using the following equations (3.2), (3.3), and (3.4), respectively:

$$S_a = \frac{A}{M} \qquad (3.2)$$

$$S_n = \frac{N}{M} \qquad (3.3)$$

$$D = \frac{S_a}{S_n} \qquad (3.4)$$

where

Sa = Specific stickies area, mm^2/kg

Sn = Specific stickies number, kg^{-1}

D = Average stickies size, mm^2

A = Total area of stickies, mm^2

M = Total O.D. mass of handsheet, kg

N = Total stickies count.

3.2.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of sticky contaminants were identified using a Perkin Elmer Spectrum 100 instrument with attenuated total reflection accessory. The sticky samples were placed in close contact with the internal reflection element to perform the characterization. The acquisition of each spectrum has provided 20 scans in the range 600-4000 cm^{-1}, with a resolution of 4 cm^{-1}. FTIR spectra were compared with those of the electronic library of the instrument and with ones reported in the literature.

3.2.4 Gas Chromatography – Mass Spectrum (GC-MS) Analysis

Extracted stickies samples were analyzed using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 Mass Spectrometer. Analyte separations were accomplished in an Agilent J&W HP-5MS Ul column (5% phenyl methyl siloxane, 30M x 0.25 mm x .25 um) using the following temperature program: 50ºC, hold 3min, 10ºC per minute to 310ºC, and hold for 9 minutes. The split less injector was held at 300ºC, carrier gas was helium at a constant flow rate of 1 ml/min. The MSD transfer line temperature was held at a constant 310°C, the MSD ion source at 230°C and the MSD quadrupole at 150°C. After a 3-minute solvent delay, full scan mass spectra were collected from 35 to 750 m/z. Peak identification was accomplished by comparison with a

NIST (National Institute of Standards and Technology) 2008 library.

3.2.5 Scanning Electron Microscope (SEM) Analysis

The recycled fibers and sticky contaminants were observed by Field Emission Scanning Electron Microscopy (FE-SEM) (Jeol JSM-IT200, Japan). Dried wastepaper samples were immobilized on conductive tape and coated with a thin gold layer. A low acceleration voltage 10 kV was used to prevent degradation of cellulose [204]. The images were observed a with resolution of 0.1 nm.

3.2.6 Colloidal Titration

The water-soluble sticky contaminants typically possess negative charges. These dissolved colloidal substances (DCS) also known as anionic trash, were quantified through colloidal titration The capability of DSC to absorb polyelectrolyte of opposite charge, which in this case, is the amount of cationic polymer required to neutralize the sample, was determined using a Mütek PCD-03 charge detector. The streaming current method was followed to determine the endpoint of the colloidal titration.

Recycled papers were disintegrated into 0.1% fiber suspension and denoted as total stock (total charge). Clear liquid samples, taken from the centrifuged total stock, were denoted as dissolved substances (dissolved charge). The volume of poly-DADMAC (cationic titrant) consumed to achieve zero potential was recorded. The specific charge quantity (mmol/L or mmol/kg) was calculated using equation (3.5):

$$\boldsymbol{q = \frac{(V - V_b) \times C}{wt}} \qquad (3.5)$$

where

q = specific charge quantity of sample, mmol/L or mmol/kg

V = consumed titrant volume, ml

Vb = consumed titrant volume in blank test, ml

C = specific charge quantity of titrant, mmol/L

wt = volume of tested pulp suspension sample, ml

3.2.7 Mechanical Properties of Remanufactured Paper Sheets

As-received wastepaper samples were repulped using a British Disintegrator following TAPPI standard T205. Solvent extraction has been applied on the repulped fibers to remove organic sticky contaminants. TAPPI standard handsheets were made using the repulped fibers with and without solvent extraction following standard T205. The mechanical properties of handsheets were investigated following TAPPI standards including T403 bursting strength, T494 tensile strength, and T414 tearing resistance.

3.3 Results and Discussion

3.3.1 Observations of Sticky Contaminants

Pictures of the recycled paper raw materials collected from local paper mills are shown in Fig. 3.1, and pictures of the visible contaminants are shown in Fig. 3.3. It is noted that these recycled papers contain multiple sources of sticky contaminants, including but not limited to food residue (oil/grease), tape and label residue (adhesives), hot melt adhesives, and printed ink (chemical substances). These contaminants vary in size, shape, and chemical compositions, and thus are difficult to remove through mechanical process.

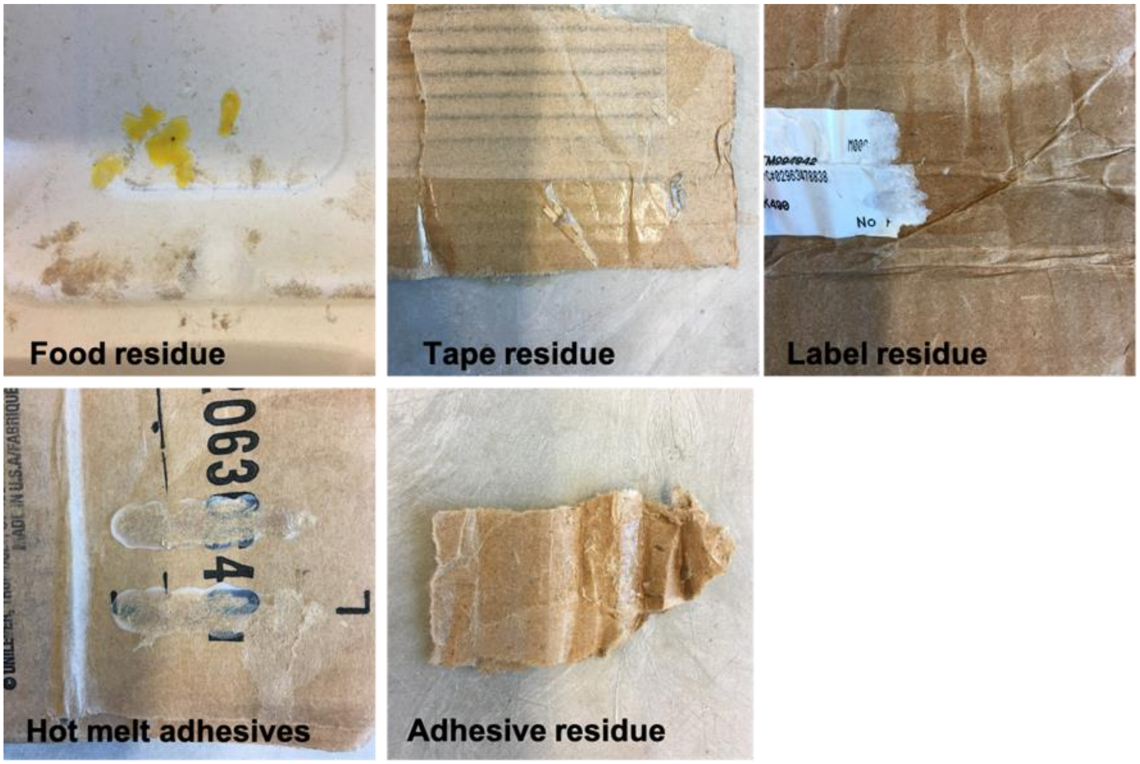
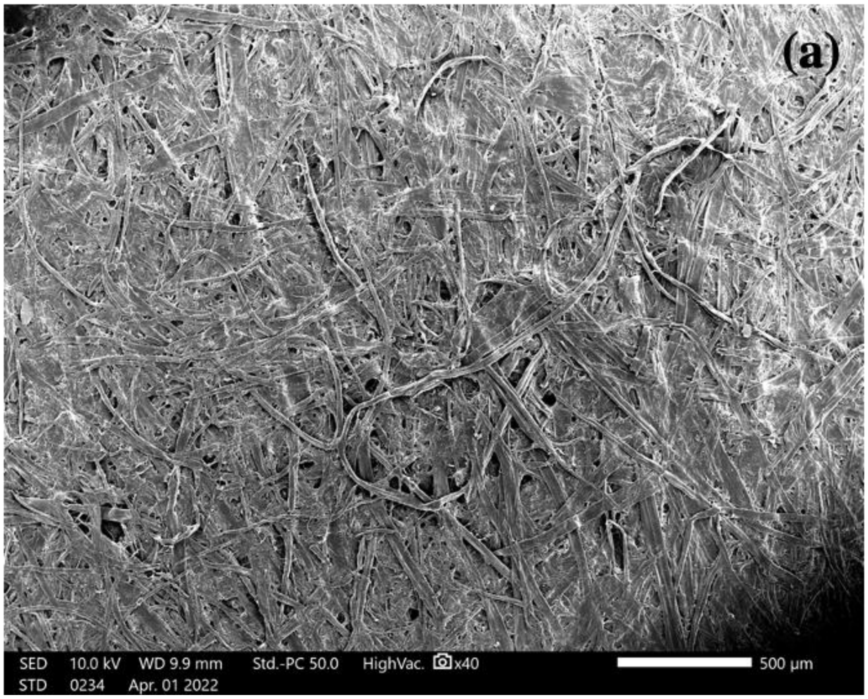
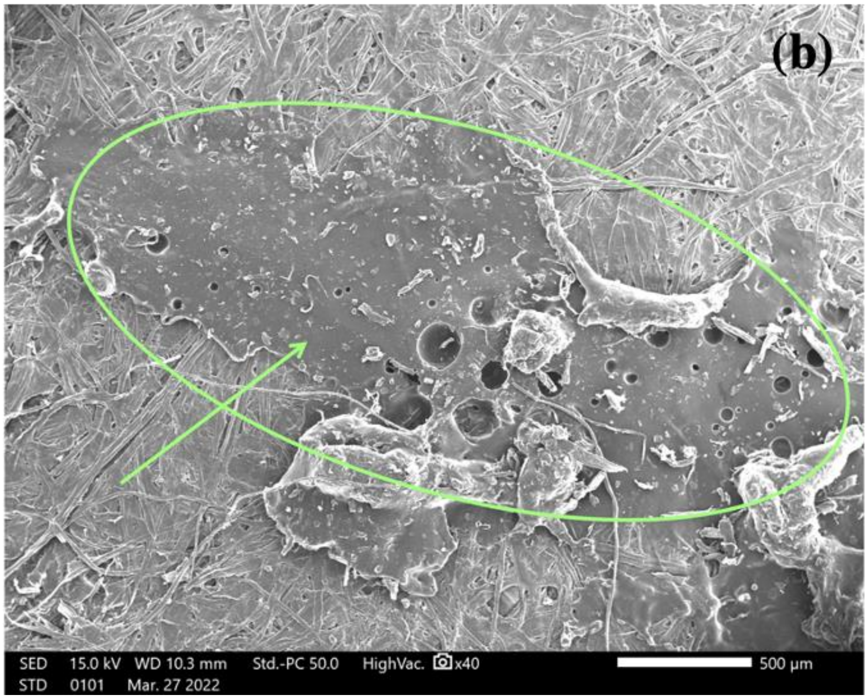


Figure 3.3. Examples of visible sticky contaminants on wastepaper.

Field Emission Scanning Electron Microscopy (FE-SEM) was utilized to further observe the sticky contaminants attached on paper surface. Each sample was analyzed with 20-30 images, and the most representative images are presented in this section. Recycled OCC materials were analyzed to observe adhesives attached on fiber surface. The SEM images are shown in Fig. 3.4. In Fig. 3.4(a), on the surface of a clean recycled OCC paper, the fibers are clearly visible without any major contaminant. The fiber wall structure and some microfibrils can be clearly observed even with paper coating pigments and fillers attached to fiber surface. In the contrary, at lower magnification in Fig. 3.4(b), recycled fibers are completely covered by a layer of tar-like substance which is the adhesive polymer. At high magnification in Fig. 3.4(c), fiber wall structure, microfibrils, and coating particles are completed blocked by contaminants.


(a)
SED 10.0 kV WD 9.9 mm Std.-PC 50.0 HighVac. x40
500 µm
STD 0234 Apr. 01 2022


(b)
SED 15.0 kV WD 10.3 mm Std.-PC 50.0 HighVac. x40
500 µm
STD 0101 Mar. 27 2022

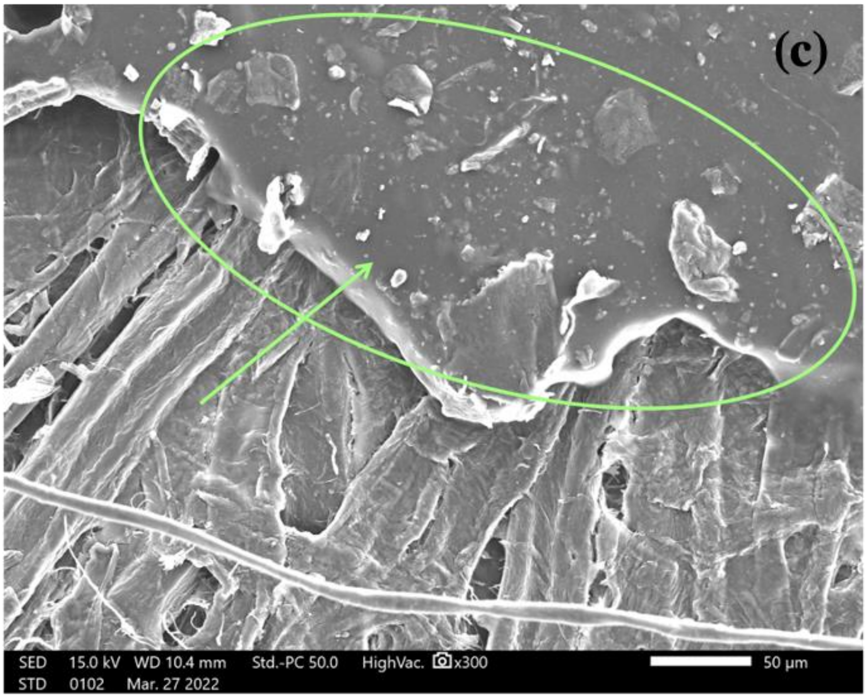


Figure 3.4. SEM images of adhesive contaminants on recycled OCC, (a) clean surface of recycled OCC sample, 40 times magnification, the scale bar is 500 microns, (b) a layer of adhesive contaminant on recycled OCC sample, 40 times magnification, the scale bar is 500 microns, and (c) a layer of adhesive contaminant (enlarged) on recycled OCC sample, 300 times magnification, the scale bar is 50 microns.

SEM images of contaminants on Residential wastepaper are shown in Fig. 3.5. The primary contaminants on residential wastepaper are food residue, e.g., oil and grease. Unlike adhesive contaminants on recycled OCC, these oil contaminants attach to the fibers surface in the form of small particles or wrap fiber wall structure in the form of thin films. The presence of these contaminants significantly reduces inter-fiber contacting areas, occupies hydroxyl groups, and thus leads to reductions in recycled paper strength.

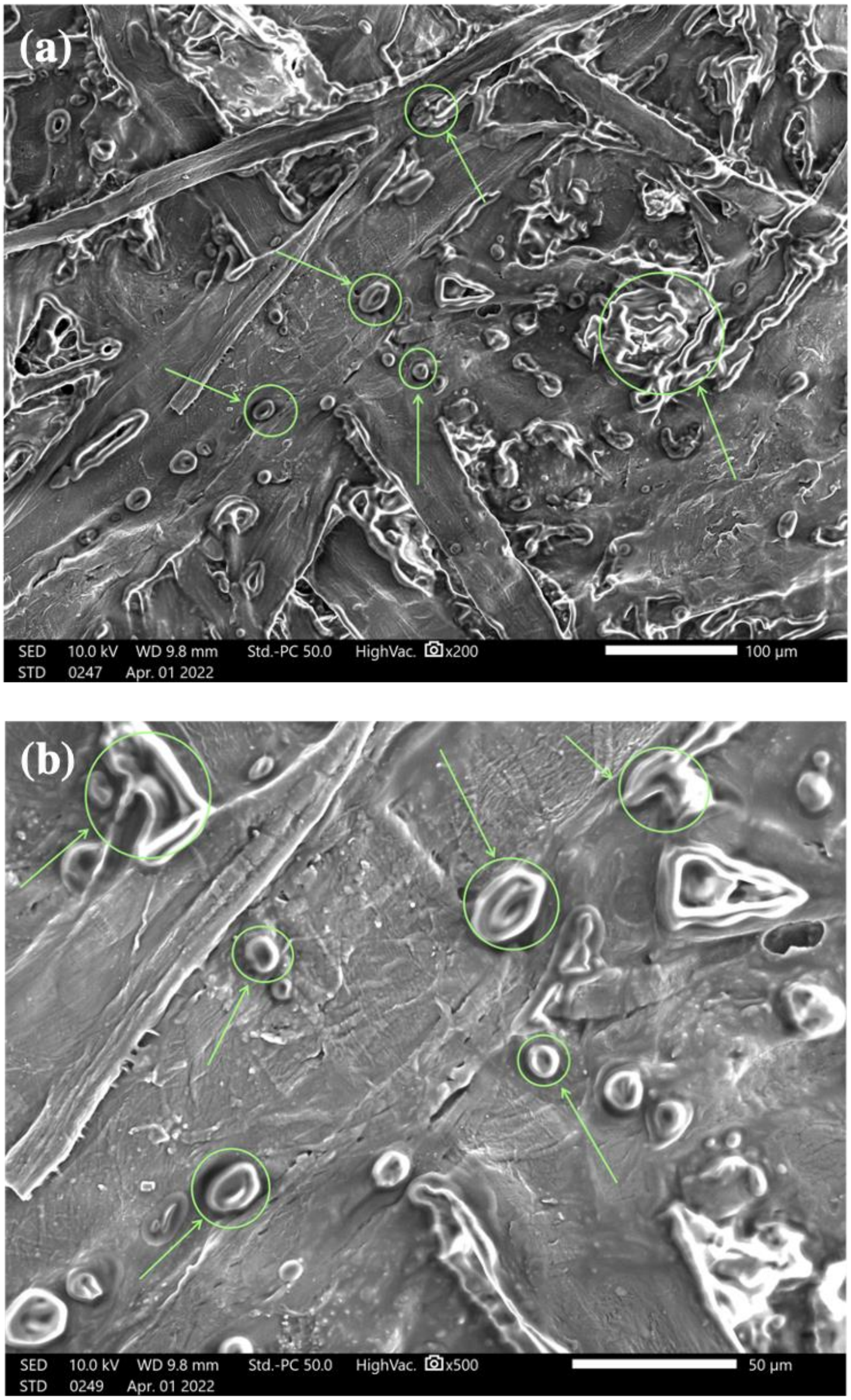


Figure 3.5. SEM images of sticky contaminants on Residential Wastepaper, (a) sticky contaminants in forms of oil droplets and films, 200 times magnification, the scale bar is 100 microns, (b) sticky contaminants in forms of droplets and films attached to recycled fiber surface, 500 times magnification, the scale bar is 50 microns.

3.3.2 Size, Number, and Quantity of Sticky Contaminants in Recycled Papers

Sticky contaminants in multiple recycled paper grades were extracted using water and THF following TAPPI T204, and the weight percentage of stickies in fibers were calculated using Equation (3.1). The results of all recycled paper grades are indicated in Table 3.2.

Table 3.2. Quantity of sticky contaminants in recycled papers.

Recycled paper grades	Stickies content (wt%)			In reference papers
	Water extractives	THF extractives	Total	
Residential	7.7	7.1	14.8	n.a.
OCC	0.9	3.6	4.5	5~6% [202]
Kraft Liner	5.1	<0.1	5.1	
Bleached Kraft	5.3	<0.1	5.3	n.a.
Box	<0.1	<0.1	<0.1	n.a.
ONP	2.9	0.6	3.5	1.1% [200]
Mixed Office	3.6	<0.1	3.6	

Among all seven wastepaper grades, the content of sticky contaminants in Residential reaches up to 14.8%, which is the highest among all grades. This is mainly contributed by the noticeable amount of grease and oil from food residues on residential waste papers. Approximately 50% of the food residue contaminants dissolves in water, and the rest can be extracted using THF. OCC material contains 4.5% stickies in total, with a majority only soluble in organic solvent THF. It is observed from the appearance, OCC stock is contaminated with significant numbers of labels and packaging tapes, both involving the use of pressure sensitive adhesives. These organic polymers have low solubility in water. This explains the relatively high level of THF soluble stickies, 3.6%. Kraft liners, Bleached kraft, ONP and Mixed office contain 5.1%, 5.3%, 3.5%, and

3.6% stickies in total, respectively. Most of these stickies are soluble in water. They are likely contributed by ink substances, or other papermaking additives. ONP and Mixed office paper have the lowest stickies content among all recycled grades besides of Box. From the appearance, both are much cleaner source of fibers with only lightly printed with ink. Box paper barely contains any solvent extractable sticky contaminants.

Table 3.3. Size and number of stickies in wastepaper.

	Specific stickies area (mm^2/kg)	Specific stickies number (kg^{-1})	Average stickies size (mm^2)
Residential	37715	32167	1.17
OCC	12738	13833	0.93
Kraft Liner	9752	7833	1.24
Bleached Kraft	5301	8000	0.66
Box	1767	3000	0.59
ONP	2209	5000	0.44

The physical properties of sticky contaminants presented in recycled paper sheets, including size and number, were determined using a thermal pick-up method, and the resulted are presented in Table 3.3. The specific number of stickies and the specific heat-set area of stickies in paper sheets agree with the content of stickies presented above. As the most contaminated wastepaper, Residential grade contains over 32000 stickies/kg fibers with a total area of 37715 mm^2. In addition, these stickies counts are relatively large having an average size of 1.17 mm^2. OCC grade contains nearly 14000 stickies/kg fibers with a total area of 12738 mm^2, while the average size of the stickies is around 0.93 mm^2. Kraft liner grade contains around 7800 stickies/kg fibers, which is much less than that of Residential and OCC grade, however, the average size of these stickies is about 1.24 mm^2, which is the largest among all wastepaper grades. Bleached kraft grade also contains 8000 stickies/kg fibers with a much smaller size of 0.66 mm^2. The stickies count in Box, ONP, and Mixed office grades are in the lower range between 3000-5000, with an average size between 0.4-0.7mm^2.

3.3.3 Chemical Composition of Sticky Contaminants

The chemical compositions of the extracted sticky contaminants from each recycled paper grade were characterized using FTIR and GC-MS. The FTIR spectra of stickies extracted from each recycled paper grade are presented in Fig. 3.6 and Fig. 3.7.

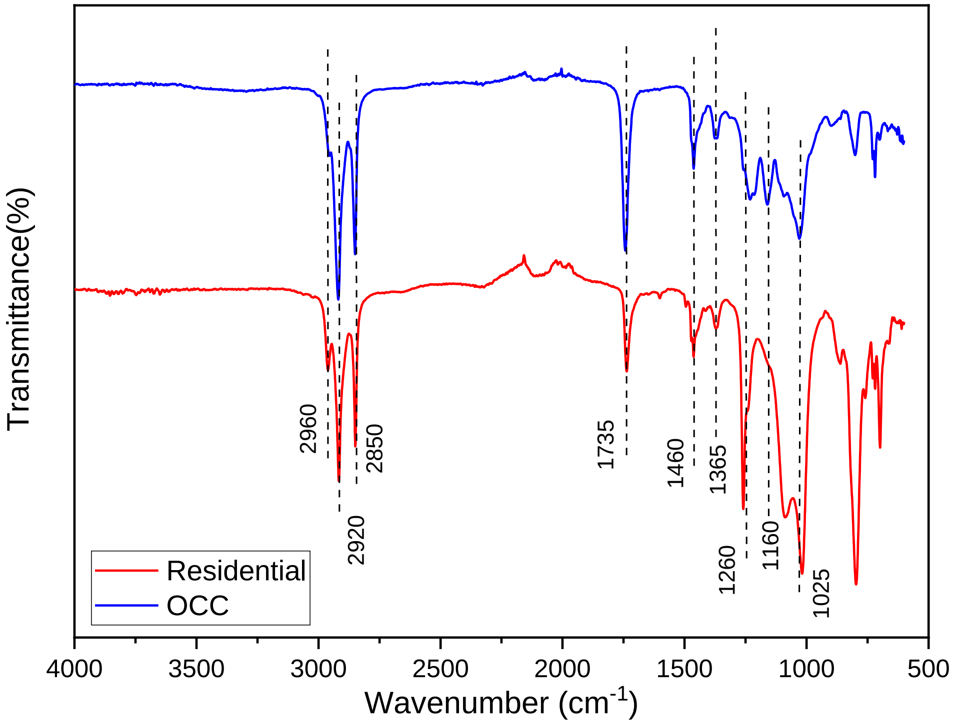


Figure 3.6. FTIR spectrum of THF extracted stickies from OCC and Residential, respectively.

The FTIR spectrum of THF extracted stickies from OCC and Residential are shown in Fig. 3.6, respectively. In the FTIR profile of stickies extracted from OCC, it is first to observe the strong absorption at about 1735 cm^{-1} due to the C=O stretching of the acetate group; and the bands at about 1260 cm^{-1}, 1160 cm^{-1}, and 1025 cm^{-1} due to the C-O stretching of the ester group. Typical C-H stretching absorption bands of alkane are observed at between 2960 cm^{-1}, 2920 cm^{-1} and 2850 cm^{-1}, respectively. C-H bending absorption are observed at 1460 cm^{-1} and 1365 cm^{-1}. These results indicate the presence of polyvinyl acetate (PVAc) polymers, which are generally used as adhesives in packaging [202,203]. As also shown in Fig. 3.6, the extracted stickies from Residential grade presented similar FTIR profile as that of OCC stickies. Regarding the absorption bands, the presence of esters is observed. Evidence of ester groups is identified by the absorption bands at 1735 cm^{-1} due to the C=O stretching and at 1260 cm^{-1}, 1025 cm^{-1} due to the C-O stretching of the ester groups. These components are likely to be introduced by food residue such as residual cooking oils.

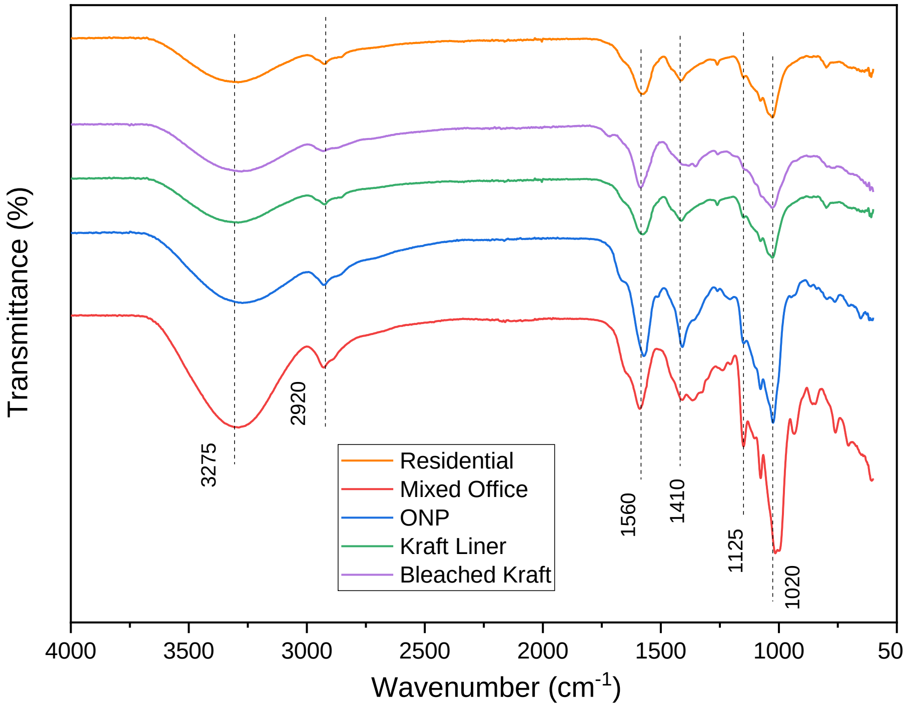


Figure 3.7. FTIR spectrum of water extracted stickies from Residential, Mixed Office, ONP, Kraft Liner, and Bleached Kraft, respectively.

Infrared spectrum of stickies extracted with water from Residential, Mixed Office, ONP, Kraft Liner, and Bleached Kraft grades are presented in Fig. 3.7, respectively. These profiles indicate the presence of ink components with an absorption band at 1560 cm^{-1} which is assigned to the aromatic absorbance of gallate, and an absorption band at 1410 cm^{-1} which is contributed by the symmetric stretch of iron (III)-gallate complex. In addition, the absorption band at 1125 cm^{-1} and 1020 cm^{-1} can be assigned to vibrations of C-O bonds of the ester group. Furthermore, the broad absorption band at 3275 cm^{-1} represents O-H stretching in phenol structure, and the absorption band of C-H stretching is observed at 2920 cm^{-1}. The infrared spectrum analysis indicates the major contribution of water extracted stickies of recycled papers are ink residues.

The GC-MS chromatogram of solvent extracted stickies from OCC is presented in Fig. 3.8, and the major components are presented in Table 3.4. The components in extracted stickies can be divided into five groups. First, dimethylamine and dimethyl propylamine are identified in the GC-MS spectrum at 4.0 min and 6.1 min. They are the monomer units of polyamines, which is a commonly used polymer in papermaking process. The quaternary ammonium group in polyamine structure maintains strong cationic charge in most papermaking conditions, and thus are used extensively for neutralizing excess anionic colloidal charge and establishing anchoring points for anionic retention aids. Second, the two peaks at 7.6 min and 7.8 min represent methyl styrene, which is a monomer compound in styrene acrylates. Styrene acrylates are commonly used as a sizing agent in papermaking process to increase resistance to water penetration. In addition, methyl styrene is also used as the monomer unit for the synthesis of styrene butadiene rubber (SBR), which is a major component in hot melt adhesive as a thermoplastic elastomer. Furthermore, peaks at 10.4 min and 15.0 min indicate the presence of cyclosiloxanes, which is a silicone resin material being widely applied as coating ingredients. Moreover, peaks from 24 min to 35 min are paraffin wax compounds containing carbon atoms ranging from 20 to 33 min. Wax is typically applied on corrugated box to help the board to retain its structural integrity and strength under humid environments. They are typically applied in box plant through curtain coating or cascading. It is also a major component in hot melt adhesives, especially in polyvinyl acetate (PVAc) adhesives. Peak area of each identified peak is calculated to estimate the relative concentration of each component in the extracted stickies, and the estimated percentages are presented in Table 3.5. Paraffin wax is the predominant component in the stickies extracted from OCC, which makes up to 70.1% of total stickies. Considering the average stickies concentration in OCC is 4.5%, the result indicates the concentration of wax in OCC sample in this study is approximately 3.2%. It is common as in a typical curtain coating process, a 600 gsm paper board can pick up 25-35 gsm wax which is about 4.2-5.8%. The percentage of polyamine, styrene, and resins in total stickies are 4.1%, 4.7%, and 6.9%, respectively. Last, 14.7% of total stickies are a mixture of complex compounds which are difficult to identify, including high molecular weight esters and acids. The strong peak at 15.5 min represents butylated hydroxytoluene (BHT), which is an antioxidant agent used in THF.

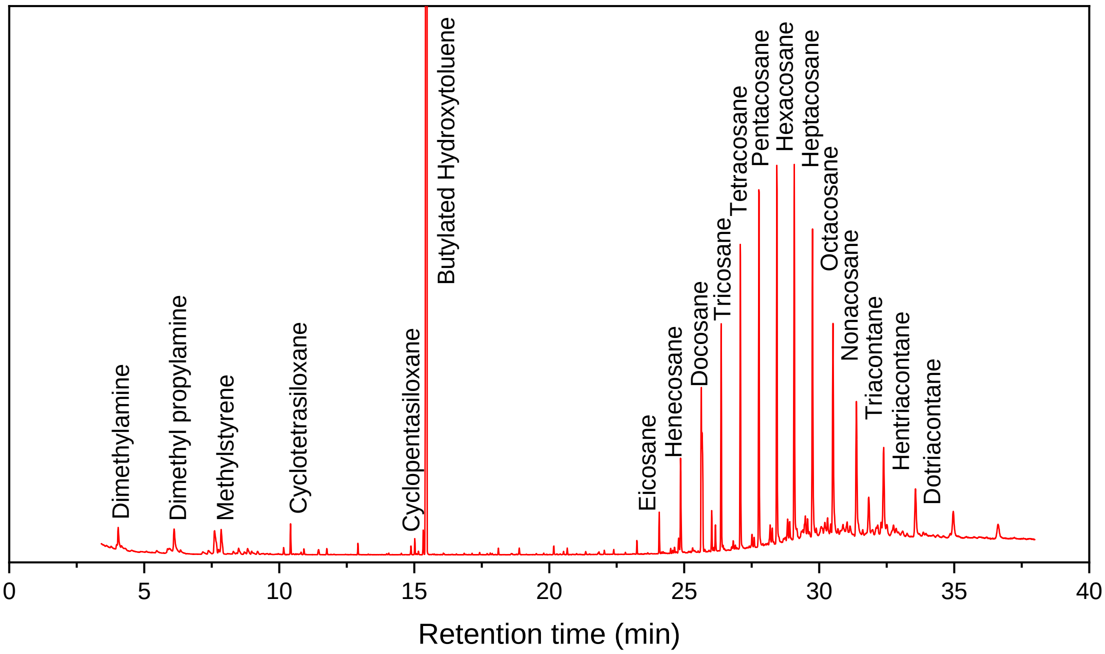


Figure 3.8. GC-MS spectrum of stickies extracted from OCC.

Table 3.4. GC-MS identified chemical compounds in solvent extracted stickies.

Retention time (min)	Compounds	Peak area %
4.0	Dimethylamine	1.8
6.1	Dimethyl propylamine	2.3
7.6	Methylstyrene	4.7
10.4	Cyclotetrasiloxane	3.4
15.0	Cyclopentasiloxane	2.3
15.5	Butylated Hydroxytoluene	n.a.
24.1	Eicosane	0.9
24.9	Henecosane	2.5
25.6	Docosane	3.3
26.4	Tricosane	4.4
27.1	Tetracosane	6.5
27.8	Pentacosane	8.3
28.4	Hexacosane	9.1
29.1	Heptacosane	8.8
29.8	Octacosane	8.6
30.5	Nonacosane	6.8
31.4	Triacontane	5.0
32.4	Hentriacontane	3.6
33.6	Dotriacontane	2.4

Table 3.5. Chemical composition of stickies in OCC based on GC-MS results.

Compounds	Potential origin	Percentage %
Polyamine	Paper additive	4.1
Styrene	Adhesive	4.7
Resin	Coating	6.9
Wax	Surface treatment, adhesive	70.1
Others	Wood extractives, ink residues	14.2

3.3.4 Particle Charge of Dissolved and Colloidal Stickies

The water-soluble stickies typically contain a wide range of anionic dissolved materials, commonly known as anionic trash, or dissolved and colloidal substances (DCS). Some key components may include fatty acid salts, resin acid salts, hemicellulose and its oxidation byproducts, lignin derivatives from pulping, and dispersants or anionic latex and dispersants from coated broke. In addition, various types of bleaching agents tend to oxidize hemicellulose and extractives, further increasing the anionic charge of the dissolved and colloidal fraction of the pulp slurry. DCS not only interfere with the performance of cationic retention aids, cationic dry-strength agents, and wet-strength resins, but also play an important role in deposit problems. In this study, the dissolved charge as well as fiber charge were investigated using colloidal titration. The specific charge quantities of six recycled paper grades are shown in Table 3.6:

Table 3.6. Specific charge quantity of recycled fibers.

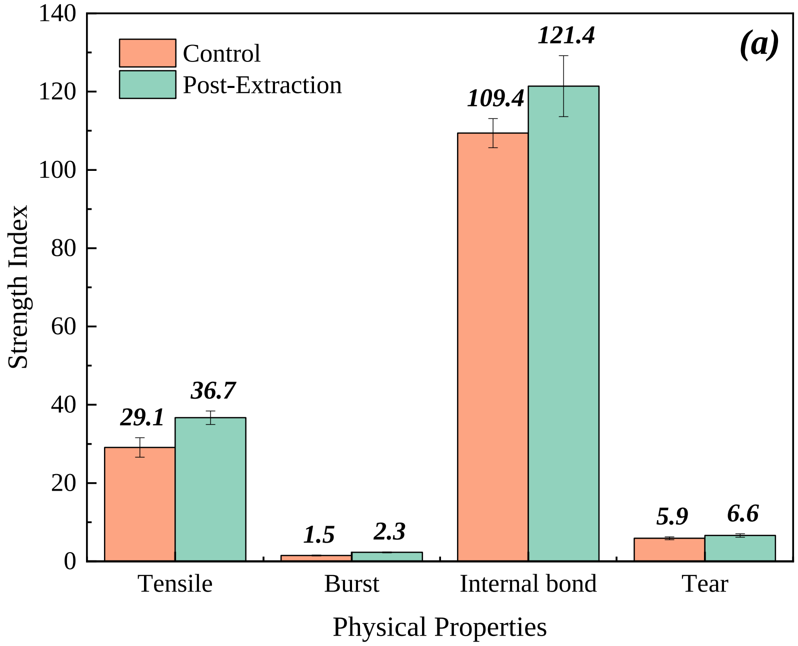
	Recycled paper grades					
	RW	OCC	Kraft	Bleached	ONP	MOW
Total charge of 0.1% fiber suspension (mmol/L)	4.51	4.37	4.19	3.52	2.01	1.86
Dissolved particles charge (mmol/L)	2.37	3.04	3.05	3.42	1.77	1.5
Fiber surface charge (mmol/g)	2.14	1.33	1.14	0.1	0.24	0.36

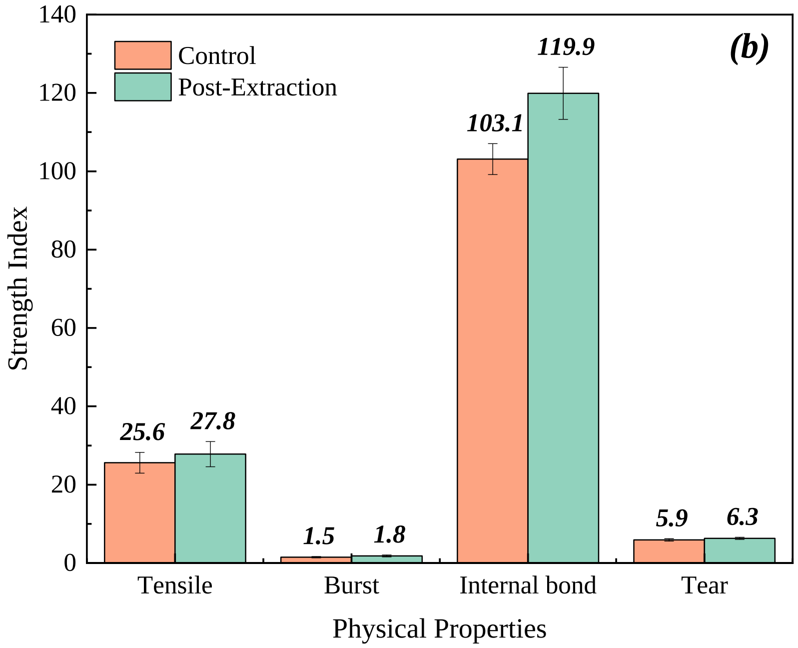
The results indicate that all recycled fibers and dissolved stickies carry negative charge. Among all grades, Residential possess the highest total charge of 4.51 mmol/L, followed by OCC containing 4.37 mmol/L total charge and Kraft liner containing 4.19 mmol/L total charge. Additionally, over 30% of the total charge in these three grades is contributed by fiber surface charge. Fibers derived from Residential contain 2.14 mmol negative charge per gram of dry fiber, which is the highest among all samples, followed by OCC fibers containing 1.33 mmol negative charge per gram of dry pulp, and Kraft liner fibers containing 1.14 mmol negative charge per gram of dry pulp. Studies have reported that surface charge on virgin fibers varies between 0.02-0.3 mmol/g depending on the types of fibers, lignin content, refining level, etc. [205–207]. Although the surface charge of recycled fibers is not clearly determined, some research articles have reported that the ability to absorb cationic polymers on recycled fibers is significantly reduced by 20-50% due to repeated drying and recycling process [208–210]. As a result, the surface charge of secondary fibers in this study is found to be much higher than the surface charge of the fibers themselves. Therefore, the results indicate that sticky contaminants heavily deposit on the fiber surface and result in a high surface charge.

In addition, the results of this study showed that bleached kraft also has a significantly high total charge. However, the contribution of fiber surface charge is minimal, which is significantly less than that of Residential, OCC, and Kraft liner fibers. On the other hand, the dissolved charge in Bleached kraft fibers is 3.42 mmol/L, which is the highest among all fibers. ONP and Mixed office, as the least contaminated recycled grades, contain 2.01 mmol/L and 1.86 mmol/L total charge, respectively. Like Bleached kraft, over 80% of the total charge in these two grades was contributed by dissolved particles. This may be due to the high amount of water-soluble ink substances in these cases.

3.3.5 Impact of Sticky Contaminants on Paper Product Strength Properties

Paper sheets were made using recycled fibers prior to solvent extraction (stickies retained) and recycled fibers post-solvent extraction (stickies removed). The physical strength properties of these paper sheets were measured and compared in order to study the impact of the presence of sticky contaminants on paper products strength properties. The results are presented in Fig. 3.9(a)(b)(c). All sheets exhibited slightly increased physical strength as sticky contaminants were removed through solvent extraction. The most significant improvement is observed on OCC sheets, where tensile strength increased by 26% from 29.1 to 36.7, burst strength increased by 53% from 1.5 to 2.3, and tear resistance increased by 12% from 5.9 to 6.6. For Kraft liner sheets, tensile strength increased slightly from 43.1 to 44.5 (3%), tear index increased slightly from 7.4 to 7.9 (7%), and burst strength increased significantly from 2.8 to 3.3 (18%). Meanwhile, the tensile strength of Mixed office sheets increased by 11% from 51.4 to 57.0, the tear resistance increased slightly from 9.0 to 9.3 (3%), and the burst strength increased remarkably from 3.5 to 4.2 (20%). These results indicate that the removal of sticky contaminants can improve paper product physical strength properties, which is in agreement with previous research that the sticky contaminants in recycled fibers occupy accessible hydroxyl groups and reduce contacting areas, thus leads to reduction in paper physical strength [19].

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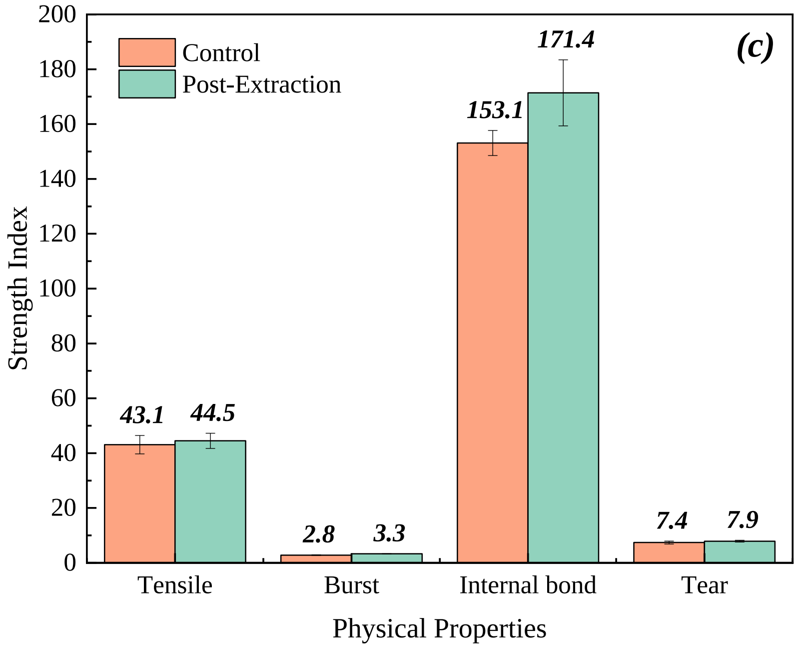
(c)
Control
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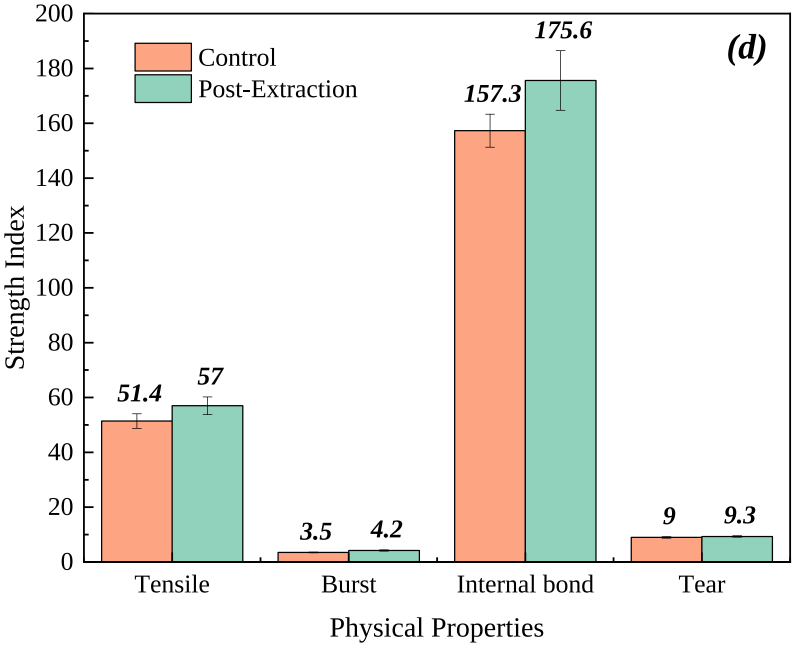


Figure 3.9. Physical strength properties of recycled paper sheets. (a) OCC, (b) RW, (c) DLK, and (d) MOW.

3.4 Conclusions

The identification and characterization of sticky contaminants in recycled fibers indicate that these stickies vary in size, number, and weight by different paper grades and their collection source. In this study, most wastepaper grades collected from a local paper recycling mills contain 3-5 wt% stickies, while a curb side collected grade contains 15 wt% stickies. The average size of these stickies present in recycled paper sheets is in the range between 0.4 to 1.2 mm^2 depending on the wastepaper grade. Additionally, the chemical analysis of THF extracted stickies by FTIR and GC/MS provides evidence that the major components in the contaminants are polyvinyl acetate (PVAc) polymers, styrene-butadiene rubber (SBR), paraffin wax, resin, and polyamines. In addition, these stickies deposit heavily on fiber surface leading to high negative charge in fibers suspension ranging between 2~4.5 mmol/L and a high negative charge on the fiber surface up to

2.1 mmol/g. Furthermore, the removal of stickies by solvent extraction can improve the quality of recycled paper products indicated by comparing the physical strength properties of recycled paper sheets prior to and after stickies extraction. SEM images explain that sticky contaminants cover fiber surface, reduce contacting areas, and occupy accessible hydroxyl groups, thus leads to reductions in paper strength. These findings will assist addressing the knowledge gaps in understanding the nature of stickies and their behaviors, and to eventually develop highly efficient technologies for contamination removal in the paper recycling process.

CHAPTER IV

CONTROL OF STICKIES IN WASTEPAPER RECYCLING THROUGH ENZYMATIC TREATMENT

4.1 Introduction

Wastepaper recycling has great significance in saving resources and reducing greenhouse gas (GHG) emissions. Unfortunately, the presence of sticky contaminants or stickies in wastepaper results in product quality decline during the remanufacturing process and also causes mechanical issues of the paper machine runnability [50,171]. Stickies are complex chemicals that are originated from various sources in wastepaper. The most common sources of stickies are pressure-sensitive adhesives from box labels and hot-melt adhesives applied intensively in paper packaging [211,212]. The major components in the stickies are polyvinyl acetate (PVAc) polymers, acrylic and styrene containing polymers, and paraffin [20,175,212]. Wood extractives, rosins, and wet strength additives are other possible causes of sticky deposits. These sticky contaminants inhibit inter-fiber bonding by reducing fiber-fiber contacting areas, leading to a decline in remanufacturing paper quality [212]. On the other hand, they can be found as spots on forming fabrics, press felts, and dryer fabrics, as well as deposits on press section pickup rolls and on calender stacks. This can sheet picking, web breaks, dirt specks, and holes in the finished product [200,203]. In addition, the electronegative properties of stickies in recycled feedstock will attract various cationic substances, which further reduces product quality and causes paper machine failures [212,213].

Mechanical and chemical methods have been developed to solve sticky problems in the paper remanufacturing process. The most common sticky removal systems are mechanical methods including screening, centrifugal cleaning, flotation, dispersing, and water clarification. However, “microstickies”, having a diameter of less than 100 um, can carry through the typical screening and cleaning process. In addition, the high energy consumption and producing larger amounts of industrial wastewater are the major drawbacks of these strategies [63]. In recent years, innovative technologies such as enzymes have attracted much attention in industrial applications because of their high activity, mild reaction conditions, and broad substrate scope [214]. In the papermaking industry, enzymes can be used for lignin degradation, paper deinking, bleaching, and wastewater treatment [215,216]. For eliminating stickies, enzymes such as amylase, pectinase, xylanase, lipase, and esterase have been used [217,218]. Among these enzymes, lipase and esterase are carboxylic ester hydrolases that are able to hydrolyze ester bonds, resulting in decreasing the adhering object volume and weakening the adhesion properties [219]. The esterase or lipase is an alternative used for stickies removal because most of the stickies contain ester compounds such as polyvinyl acetate (Fig 4.1). The sticky deposits in paper or pulp bearing polyvinyl acetate can be hydrolyzed by thermophilic esterase under elevated temperatures. After ester bond digestion, polyvinyl alcohol and acetic acid were released, resulting in a decreasing sticky deposit volume and weakening its adhesion ability [56]. However, enzymes are sensitive to reaction conditions such as temperature, pH, and organic solvent [220]. Moreover, many paper recycling and remanufacturing processes are conducted under extreme conditions, such as high temperatures with alkaline conditions, which might inactivate the enzymes resulting in significantly decreasing their efficiencies in practical applications [221]. For example, the temperature in paper recycling mills can be as high as 100°C [222]. Thus, enzymes that have the properties of tolerating extreme processing conditions such as strongly acidic or alkaline, and high temperature are highly desired in paper remanufacturing process.

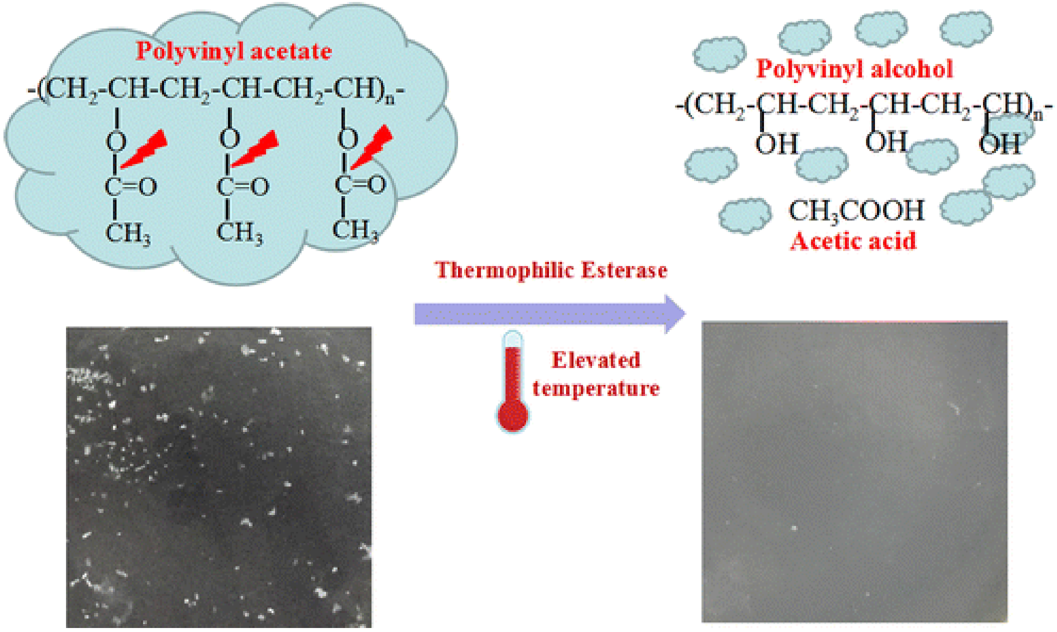


Figure 4.1. Scheme of stickies degradation by thermophilic esterase [56].

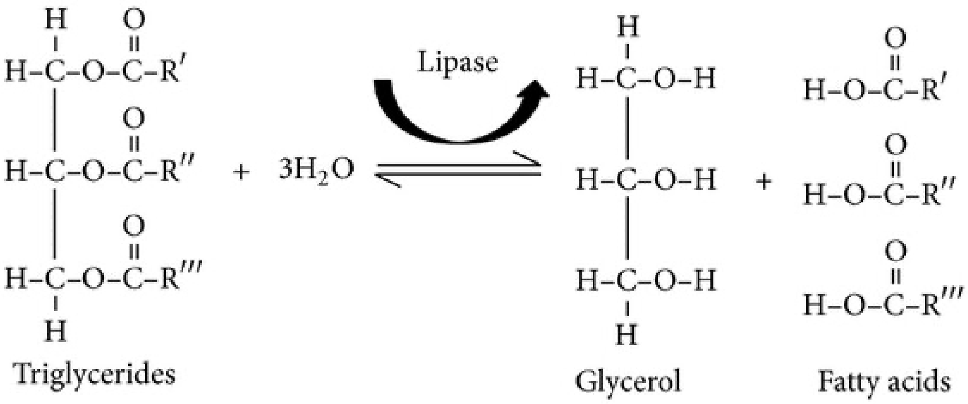


Figure 4.2. Scheme of fatty esters degradation by lipase [223].

In practice, wastepaper recycling involves multiple grades, some with a certain amount of lignin or completely mechanical fibers. In such cases, other enzymes such as lignin-degrading enzymes, cellulases, and hemicellulases can also play significantly important roles in stickies removal. These enzymes can possibly facilitate the release of stickies particles from fiber surfaces and thus providing more accessibility to lipase and esterase. Therefore, based on the results from preliminary studies, three enzymes or enzyme formulations are investigated and compared in this chapter, to explore a potential biotechnology for application in wastepaper recycling process. The two enzyme formulations are mixture of esterase, lipase, cellulase, xylanase, pectinase, and amylase at different ratios. Their efficiencies in sticky deposit control in wastepaper recycling were evaluated. The results showed that these enzyme formulations have great potential in solving stickies problems in the paper recycling and remanufacturing practice.

4.2 Experimental

4.2.1 Materials

Multiple grades of wastepaper feedstock were obtained from local paper recycling mills and from residential curb-side collection. These include residential wastepaper (RW), old corrugated containerboard (OCC), recycled boxboard cuttings (Box), recycled kraft linerboard (DLK), printed bleached kraft paper (Bleached), mixed office wastepaper (MOW), and old newsprint paper (ONP). Residential mainly consists of food containers such as burger boxes, pizza boxes, food wrapping papers, etc. These papers are highly contaminated with oil and grease. OCC includes mostly post-consumer packaging materials, such as containerboards obtained from wholesale stores. Box consists cuttings of multiply paperboards that are used in the production of folding paper cartons such as cereal boxes. Kraft Liner is sorted paperboard with Kraft liners, which are mainly from postal packaging boxes. Bleached Kraft are heavily printed sheet with a high calliper, made of bleached sulfite pulp. They are typically used as feedstock for converting mills to make high-grade packaging boxes. Mixed Office is common printing and writing paper, which can be found in typical workplace. ONP is a mixture of used newspaper and old grocery store flyers. Photos of these wastepaper are shown in Fig. 3.1.

Samples of enzyme formulations are provided by Novozymes (USA) – Enzyme formulation StickAway (Enzyme SA) and Enzyme Formulation Resinase A 2X (Enzyme RES). Both enzymes are thermophilic lipase/esterase-based formulations in combination with multiple activities including but not limit to cellulase, xylanase, amylase, pectinase, etc. Commercial *Candida Rugosa* Lipase (CAS 9001-62-1) was purchased from Millipore Sigma (USA). All other chemicals used in this work such as tetrahydrofuran (THF) were purchased from Millipore Sigma (USA) and used without further purification.

4.2.2 Enzyme Treatment

All enzyme treatments were carried out at 2% of pulp consistency. The temperature and pH were adjusted not only to accommodate most of the enzyme components, but also to accommodate the paper recycling process in mill practice. Enzyme dosage was tested ranging from 0.01 mg/g to 0.5 mg/g for promising results. Constant agitation at 400 rpm provided by electrical stirrer was applied during the enzyme treatment. At the end of the treatment, enzyme reaction was deactivated by maintaining temperature at 100^{o}C for 15 min. Subsequently, the fibers were washed with deionized water through a Buchner funnel. The washed solids were used for making handsheets and subsequent analysis. The control sample was treated in the same manner as the enzyme treated samples except for enzyme addition.

4.2.3 Stickies Measurements and Removal Rates

The quantification of stickies in enzyme-treated fibers were determined using solvent extraction method following TAPPI standard method T204. The fibers were extracted with tetrahydrofuran (THF) to obtain/remove organic stickies. Extraction process was maintained for 4 hours (predetermined), and the heat was controlled to provide a boiling rate which cycles the solvent at least 6 times per hour. Solvent was partially evaporated to 20ml in the extraction flask using rotary evaporator, and then transferred to a weighing dish with a small amount fresh solvent. The weighing dish and content were dried in an oven for 1 hour at 105°C±3°C, cooled in a desiccator, and weighed to the nearest 0.1mg.

The content of sticky contaminants was calculated using equation (4.1):

$$Content\ of\ sticky\ contaminants\ (wt\%) = \frac{W_f - W_e}{W_f} \times 100\% \qquad (4.1)$$

where

W_f = oven-dry weight of recycled fibers prior to extraction, g

W_e = oven-dry weight of recycled fibers post extraction, g

The stickies removal rate is expressed as the percentage of stickies removed after enzyme treatment (4.2):

$$Removal\ rate\ (\%) = \left(1 - \frac{Content\ of\ stickies\ after\ enzyme\ treatment}{Content\ of\ stickies\ prior\ to\ enzyme\ treatment}\right) \times 100\% \quad (4.2)$$

The size and number of sticky contaminants in recycled paper were determined by a modified "pick-up" method following TAPPI T277. Handsheets which were made from enzyme treated fibers or control fibers were placed between two coated filter papers. The three sheets were heated and pressed under controlled conditions (7 tons, 177°C) for 5min. Once the coated papers were removed from the handsheets, the coating were picked up by the stickies and a contrast was created on the handsheet, which readily allowed the measurement of area and number of heat-set stickies.

The specific stickies area, specific stickies number, and average stickies size were calculated using the following equations (4.3), (4.4), and (4.5), respectively:

$$S_a = \frac{A}{M} \qquad (4.3)$$

$$S_n = \frac{N}{M} \qquad (4.4)$$

$$D = \frac{S_a}{S_n} \qquad (4.5)$$

where

Sa = Specific stickies area, mm^2/kg

Sn = Specific stickies number, kg^{-1}

D = Average stickies size, mm^2

A = Total area of stickies, mm^2

M = Total O.D. mass of handsheets, kg

N = Total stickies count.

4.2.4 Imaging Analysis

A JSM-IT200 (Jeol USA Inc.) field emission scanning electron microscope (FE-SEM) was utilized to observe the stickies on fiber surface. Dried paper sheets made of control and enzyme modified secondary fibers were immobilized on conductive tape and coated with thin gold layer. A low acceleration voltage 10 kV was used to prevent degradation of cellulose (Blomstedt et al., 2007). The images were observed with the resolution of 0.1 nm.

An Asylum Research MFP-3D Research Atomic Force Microscopy (AFM) was utilized to investigate the stickies deposit on fiber surface close to the atomic level. The AFM experiments were performed in tapping mode at ambient relative humidity and temperature. The scan was done at a rate of 0.5 Hz, with an image resolution of 256 × 256 pixel, using a standard Cr/Au coated silicon-nitrite cantilever with a nominal spring constant of 0.009~0.1 N/m resonance frequency of

19~73 kHz. The height image and amplitude image were simultaneous recorded and exported using Igor Pro 6.04 software for further analysis.

4.2.5 Quality of Remanufactured Paper

TAPPI standard handsheets were made using the control and enzyme modified secondary fibers following standard T205. The physical properties of remanufactured sheets were investigated following TAPPI standards including T403 burst strength, T494 tensile strength, T414 tear resistance, and T541 internal bond strength.

4.3 Results and Discussion

4.3.1 Stickies Removal by Enzyme Treatment – Enzyme Efficiency and Stability under various conditions

Table 4.1. Changes of stickies quantity and size in paper remanufacturing process.

Stages	Quantify of stickies (wt%)	Number of stickies (counts per kg)	Average size of stickies (mm^2)
Re-pulping	8.27	52,321	7.41
Coarse screening	1.60	32,241	1.21
Fine screening	1.88	47,857	0.78
Cyclone cleaning	1.32	34,655	0.99

As previously discussed in Chapter 3, the sticky contaminants have heterogenous nature which makes them difficult to remove in the conventional paper recycling process. In practice, mechanical screening and cleaning are not effective against these tacky contaminants. Their behavior and pathway during the paper recycling process are revealed by the changes in quantity and size at different recycling stages. As shown in Table 4.1, most sticky contaminants in the system are removed in the coarse screening stage, along with a significant size reduction from 7.4 mm^2 to 1.2 mm^2. The subsequent fine screening stage does not effectively remove stickies, instead, the contaminants are broken down into smaller particles in this stage which is supported by the reduced size and increased number. Cyclone cleaning removed slightly more stickies, but the increased size suggests re-agglomeration of stickies into macrostickies which can cause deposit problems on paper machine. Therefore, more efficient, and economic removal technology is needed to tackle these microstickies.

To develop new biotechnology for stickies removal in paper remanufacturing, three enzymes were studied in this research to evaluate the potential for stickies control. Recycled OCC fibers containing 4.5% stickies were used as base substrate in enzyme treatments, and the removal rate of stickies was measured. The impact of treatment conditions such as temperature, dosage, residence time and pH on stickies control were investigated in this section, and the results are shown in Fig. 4.3-4.6 and Table 4.2-4.5. First, as shown in Fig 4.3 and Table 4.2, enzyme treatment temperature has critical impact on the removal of stickies. All three enzymes showed similar activity at 20^{o}C, 40^{o}C and 50^{o}C, but different performances were observed at elevated temperature. The stickies removal rate by enzyme SA increased significantly from 22.1% to 65.7% with elevated temperature from 20^{o}C to 80^{o}C, presenting the best overall performance against sticky contaminants. Enzyme RES presented higher efficiency on stickies removal at temperature range 20-50^{o}C than that of enzyme SA, but the activity declined drastically to 44.1% at 80^{o}C. Commercial lipase was less effective on stickies removal comparing to enzyme formulations SA and RES. The removal rate provided by lipase peaked at 42.1% at 50^{o}C, and then declined significantly to 6.6% at 80^{o}C. Overall, the two enzyme formulations showed better performance in stickies removal under various reaction temperatures comparing to a commercial lipase. At high temperature, enzyme RES and lipase displayed declined activity against stickies. This is due to the fact that high temperature will denature the lipases, causing them lose their activity [56]. In the contrast, thermophilic esterase can maintain high hydrolysis activity at high reaction temperatures

[56]. The possible reason that enzyme SA presented better performance at 80°C is that the formulation contains a higher percentage of thermophilic esterase.

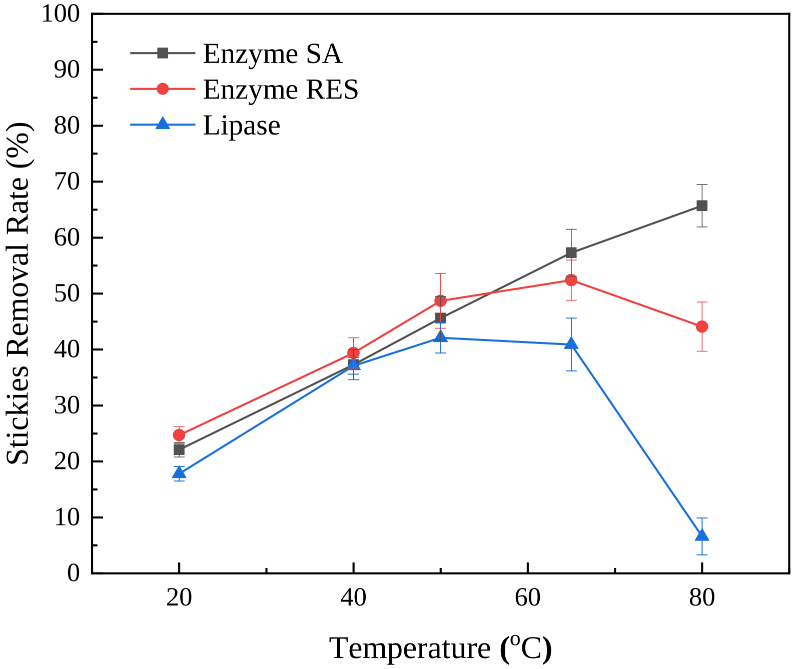


Figure 4.3. The effect of enzyme treatment temperature on stickies removal rate (Enzyme dosage 0.05 mg/g, pH 7, residence time 60 min).

Table 4.2. The effect of enzyme treatment temperature on stickies removal rate (Enzyme dosage 0.05 mg/g, pH 7, residence time 60 min).

Temperature	Stickies removal rate (%)		
(°C)	Enzyme SA	Enzyme RES	Lipase
20	22.1	24.7	17.8
40	37.3	39.4	37.1
50	45.6	48.7	42.1
65	57.3	52.4	40.9
80	65.7	44.1	6.6

Second, enzyme dosage also presented a critical impact on stickies removal. At a lower dosage 0.05 mg/g, about 45% stickies can be removed by either of the three enzymes at 50°C within 1hr treatment. With increasing dosage, the amount of stickies removed by the enzyme treatment can be significantly improved by up to 90% as indicated in Fig 4.4 and Table 4.3. When the dosage increased to 0.2 mg/g, enzyme SA degraded 86.1% of stickies during 1hr treatment, while enzyme RES removed 93.4% of total stickies. Although commercial lipase removed relatively fewer stickies when compared to SA and RES, the amount of stickies removed during enzyme treatment improved significantly to 76.7% when the dosage increased to 0.5 mg/g. In addition, extending the enzyme treatment residence time can contribute to stickies removal but to a certain limit. As indicated in Fig. 4.5 and Table 4.4, the stickies removal rate improved remarkably from the 20% range to the 60-80% range when the treatment was extended from 15 minutes to 2 hours, however, the trend did not continue after that. Enzyme SA removed 31.5% stickies within 30 minutes and removed 69.2% stickies when extended to 2 hours, but barely any improvement was observed when the reaction was extended to 4 hours. Similarly, enzyme RES removed 34.1% of stickies at 30 min, 77.1% of stickies at 2 hours extension, and slightly more stickies, 80.4% at 4 hours reaction time. The activity of commercial lipase against stickies was generally lower than that of enzymes SA and RES. Commercial lipase only removed 22.5% of stickies within 30 minutes and removed 61.6% as the reaction was extended to 2 hours. Similarly, a slight improvement in the removal of 65.2% stickies by commercial lipase at 4 hours of reaction. The possible reason is that enzyme activity might be inhibited by the increased released product, such as acetic acid.

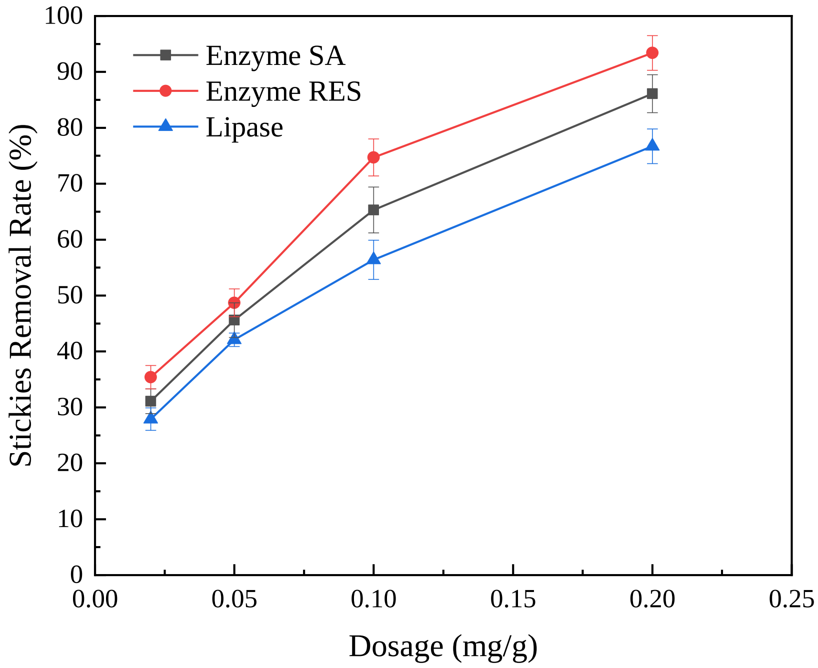


Figure 4.4. The effect of enzyme dosage on stickies removal rate (Temperature 50^{o}C, pH 7, residence time 60 min).

Table 4.3. The effect of enzyme dosage on stickies removal rate (Temperature 50^{o}C, pH 7, residence time 60 min).

Enzyme dosage (mg/g)	Stickies removal rate (%)		
	Enzyme SA	Enzyme RES	Lipase
0.02	31.1	35.4	27.9
0.05	45.6	48.7	42.1
0.1	65.3	74.7	56.4
0.2	86.1	93.4	76.7

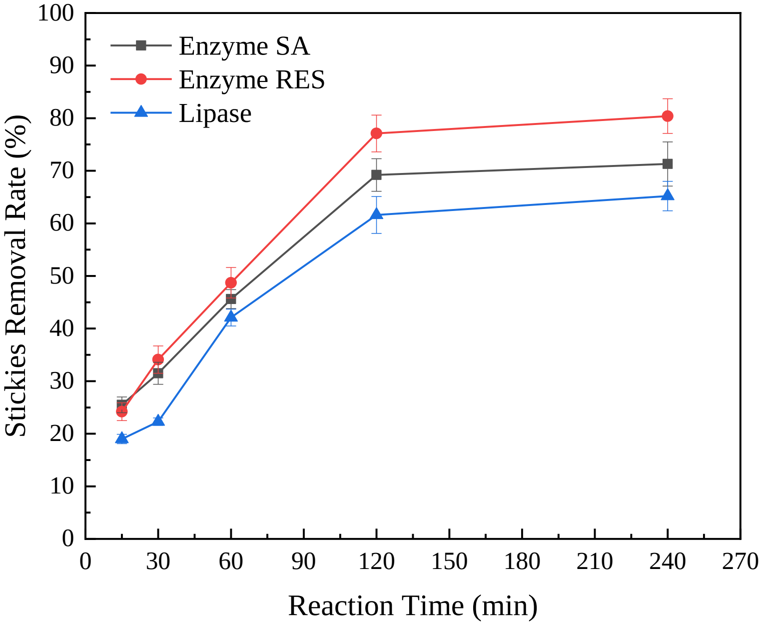


Figure 4.5. The effect of enzyme treatment residence time on stickies removal rate (Temperature 50°C, pH 7, enzyme dosage 0.05 mg/g).

Table 4.4. The effect of enzyme treatment residence time on stickies removal rate (Temperature 50°C, pH 7, enzyme dosage 0.05 mg/g).

Residence time (min)	Stickies removal rate (%)		
	Enzyme SA	Enzyme RES	Lipase
15	25.5	24.2	19.0
30	31.5	34.1	22.3
60	45.6	48.7	42.1
120	69.2	77.1	61.6
240	71.3	80.4	65.2

Furthermore, the impact of pH was investigated as well, and the results are presented in Fig. 4.6 and Table 4.5. In general, the stickies removal rate by all three enzymes peaked at pH 8 indicating that the degradation of sticky contaminants by enzymes favors slightly alkaline environment. At pH 8, enzyme RES presented 55.9% stickies removal rate which is the highest among all three enzymes. Enzyme formulation SA presented slightly lower removal rate of 52.3% at pH 8 and 45.6% in pH neutral environment, however, it exhibited excellent stability under various pH values. Under extreme alkaline condition pH 10, the removal rate by enzyme RES declined to 47.2%, while enzyme SA maintain its efficiency at 49.8%. On the other hand, the stickies removal efficiency of commercial lipase was relatively lower at 33.2% in acidic environment, and reached its maximum when the reaction was taken place in an alkaline condition – 50.4% removal efficiency at pH 8. Similar trend was observed with lipase where the efficiency decreased to 34.7% at pH 10.

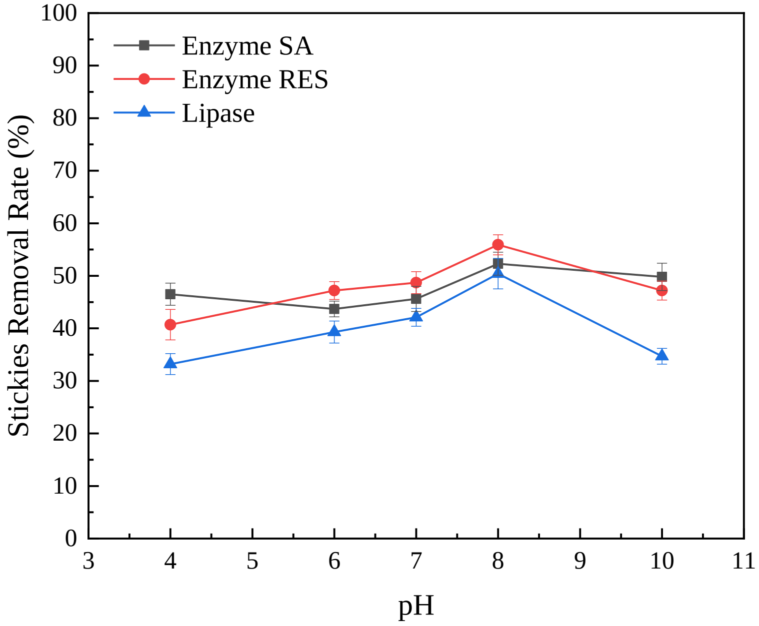


Figure 4.6. The effect of treatment pH on stickies removal rate (Temperature 50°C, residence time 60 min, enzyme dosage 0.05mg/g).

Table 4.5. The effect of treatment pH on stickies removal rate (Temperature 50°C, residence time 60 min, enzyme dosage 0.05mg/g).

pH	Stickies removal rate (%)		
	Enzyme SA	Enzyme RES	Lipase
4.0	46.5	40.7	33.2
6.0	43.7	47.2	39.3
7.0	45.6	48.7	42.1
8.0	52.3	55.9	50.4
10.0	49.8	47.2	34.7

In summary, all three enzymes were effective to remove sticky contaminants in fiber recycling process. The enzyme formulation SA and enzyme formulation RES presented higher overall performance against tacky stickies when comparing to commercial lipase. Enzyme treatment temperature, pH, residence time and enzyme dosage play critical roles in this process. Elevating temperature facilitated the degradation of sticky contaminants from 20°C to 65°C, however, loss of activity was observed on enzyme RES and commercial lipase when temperature was further increased to 80°C. Extending the enzyme treatment from 30 minutes to 2 hours can significantly improve the stickies removal, however, the trend plateaued after 2 hours. In practice, 30 minutes to 60 minutes treatment would be ideal depending on the specific recycling process. Additionally, stickies removal rate was significantly improved with increasing enzyme dosage. In this study, 0.2 mg/g lipase removed 76.7% stickies in OCC fibers within 1hr, while enzyme SA and enzyme RES removed 86.1% and 93.4% stickies under same conditions, respectively. Furthermore, all three enzymes preferred alkaline environment for the degradation of organic stickies. The maximum stickies removal was observed at pH 8 in all cases. It is also worth mentioning that in practice, many paper recycling and remanufacturing processes are conducted under extreme conditions, such as high temperature and acidic/alkaline conditions. To review the stability of enzymes under such conditions, the stickies removal rate of three enzymes were evaluated and the results are summarized in Fig. 4.7. Both enzyme SA and enzyme RES maintained effective for contamination removal under extreme conditions; while the commercial lipase experienced deactivation at high temperature, and acidic/alkaline conditions. It lost 30% activity at pH 4 and pH 10 and lost nearly 85% activity at high temperature. On the other hand, enzyme RES exhibited highest efficiency among all three enzymes for the removal of stickies when applied under optimal conditions, however, the stickies removal rate reduced by over 16% under high temperature and high alkaline conditions. Meanwhile, enzyme SA exhibited excellent stability at high temperature and under high alkalinity even though its stickies removal efficiency under optimal conditions was slightly lower than that of enzyme RES. The efficiency of enzyme SA only declined by 5% at pH 10, and even improved by nearly 15% at high temperature. These results indicated that the combination of lipase and esterase with polymeric carbohydrate hydrolase can improve not only the stickies removal rate, but also the stability under high temperature and acidic/alkaline environments [56,213,224].

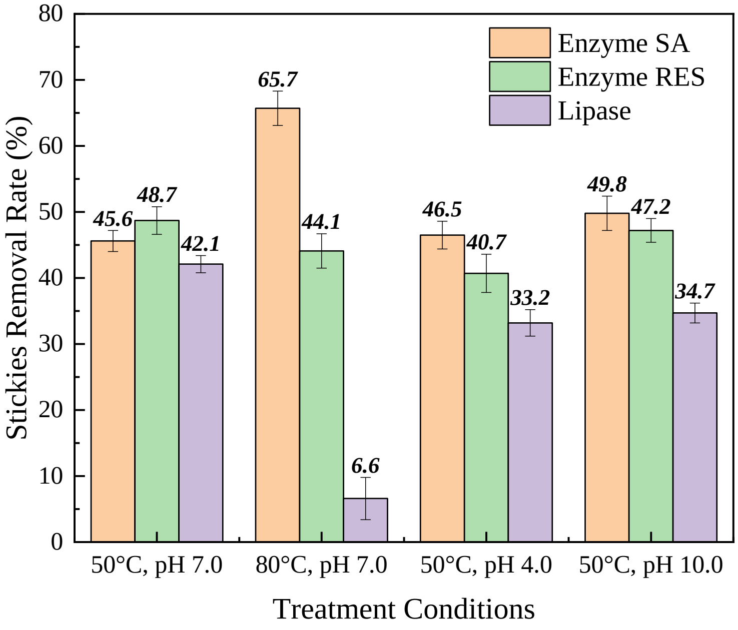


Figure 4.7. The stickies removal rate of enzymes under extreme conditions.

4.3.2 Use Multiple Grades of Wastepaper as Substrate

As discussed in Chapter 3, the quantity and composition of organic sticky contaminants in secondary fibers can vary significantly by the wastepaper grades [212]. In this section, the potential of previously discussed enzyme formulations being utilized for stickies removal in practical paper remanufacturing process is evaluated using multiple wastepaper grades, including residential wastepaper (RW), old corrugated containerboard (OCC), recycled boxboard cuttings (Box), recycled kraft linerboard (DLK), printed bleached kraft paper (Bleached), mixed office wastepaper (MOW), and old newsprint paper (ONP). Enzyme formulation SA was employed to remove stickies in multiple grades of wastepaper since it presented excellent stability under various conditions. In this study, the enzyme treatment was performed at 50^{o}C for 1 hour with the addition of 0.25 mg/g enzyme at neutral pH. This is not only to optimize the performance of enzymes but also to accommodate the industrial fiber recycling process. The quantity of stickies in recycled fibers with and without enzyme treatment was determined using the solvent extraction method, and the results are shown in Fig. 4.8.

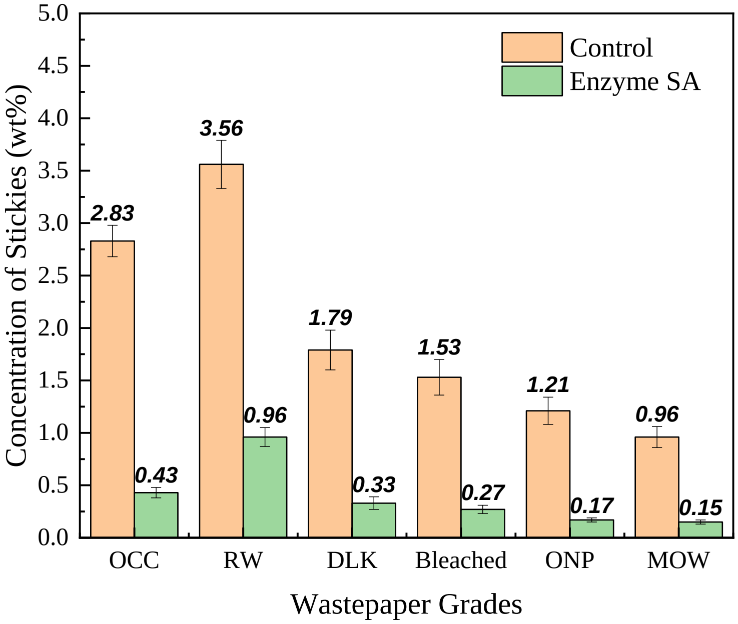


Figure 4.8. The content of stickies in multiple wastepaper grades before and after enzyme treatment.

Under these conditions, after enzymatic treatment, the stickies content in all recycled paper samples decreased significantly. The stickies content was reduced to 0.34% in OCC, 0.33% in DLK, 0.7% in bleached kraft, 0.17% in ONP, and 0.15% in MOW, respectively. When compared to control tests, the stickies removal rate was 88% in OCC, 81.6% in DLK, 82.4% in bleached kraft, 86% in ONP, and 84.4% in MOW, respectively. These results indicated that the designed enzyme formulation is highly effective for stickies removal. However, for residential wastepaper, the content of sticky contaminants was reduced to 0.96%, with a relatively lower stickies removal rate at 73%. This is mainly due to the significantly high amount of contaminants present in residential wastepaper. As previously determined, residential wastepaper contains up to 14.8% sticky contaminants, while the other grades contain 3.5% to 5.3% sticky contaminants. It is critical that the developed technology can eliminate sticky contaminants in the most problematic wastepaper grade. In order to achieve that, treatment of residential wastepaper with enzyme formulation SA was modified with either increased dosage or extended time. As shown in Fig 4.9., by increasing the dosage of enzyme SA from 0.25 mg/g to 0.5 mg/g, the contamination level in residential wastepaper can be further reduced to 0.31%. On the other hand, by extending the treatment with enzyme SA to 2 hours at 50°C with the dosage of 0.25 mg/g, nearly 98% of contamination was removed with only 0.06% remaining stickies. Furthermore, enzyme RES was found more effective when tackling the high contamination level in residential wastepaper grade. At 50°C, 0.25 mg/g enzyme RES removed 87% stickies within 1 hour of treatment, which was slightly higher than that of enzyme SA. This agrees with previous results that enzyme RES exhibited higher contamination removal efficiency than that of enzyme SA under optimal conditions. As a result, both enzyme formulations have presented great potential in removing stickies in the practical paper recycling process.

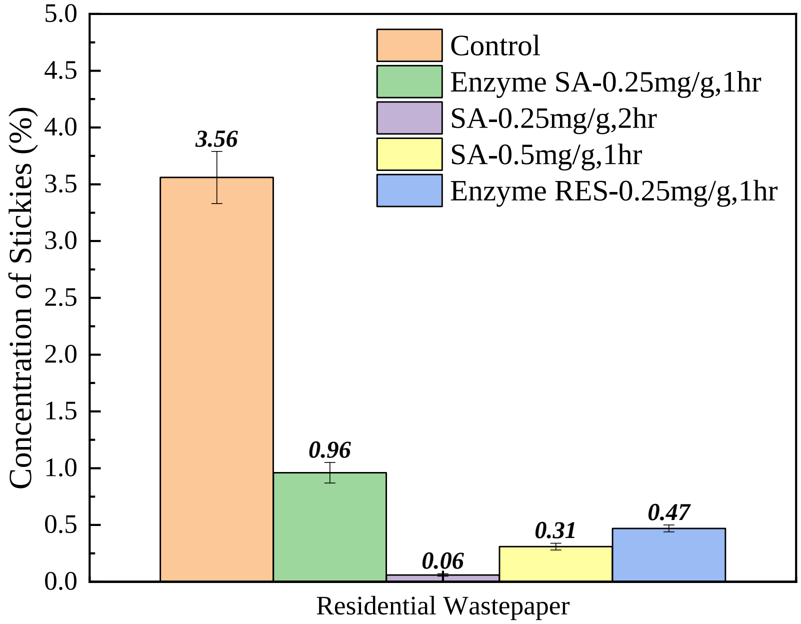


Figure 4.9. Contamination removal in Residential Wastepaper by enzyme treatments.

4.3.3 Surface Characterization

Surface analysis techniques such as Field Emission Scanning Electron Microscopy (FE-SEM) and Atomic Force Microscopy (AFM) were utilized to analyze fiber surface structure and the removal of stickies contaminants on fiber surface. The images were taken on remanufactured paper sheet made of recycled fibers with and without enzyme treatment. Each sample was observed with 20-30 images and the most representative images are presented and discussed in this section. The SEM images of recycled fibers with and without enzyme treatment are shown in Fig 4.10. Fig. 4.10 (a) and (b) presented sticky deposits on fiber surface. It is noted that a tar-like material attached to fiber surface which can be identified as stickies [212]. The presence of stickies covered the fiber wall structure and microfibrils. In contrast, as shown in Fig. 4.10 (c) and (d), most of the sticky deposits were removed from the fiber surface after being treated with enzymes. And the microfibrils and secondary cell wall structure were exposed.

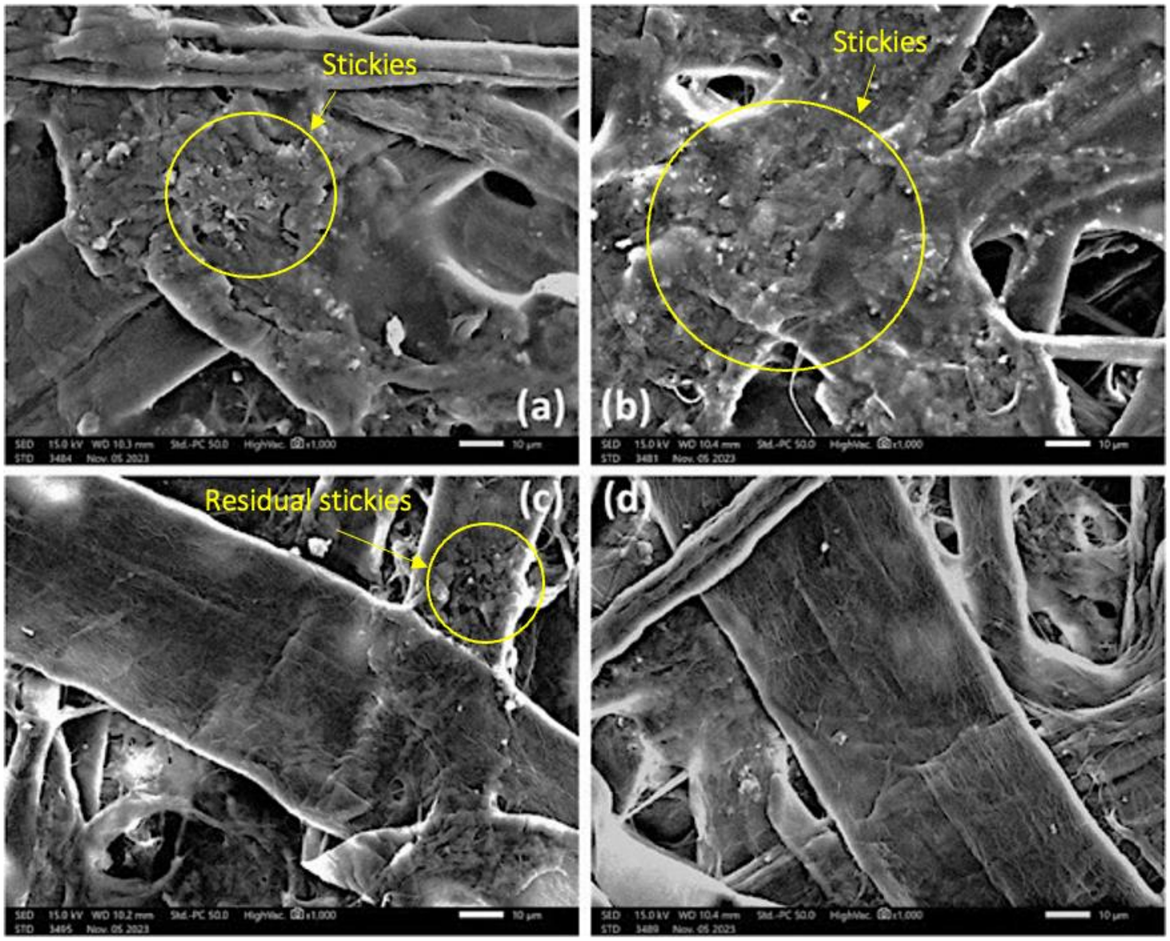


Figure 4.10. SEM images of the presence of stickies on recycled fiber surface (a) (b) and SEM images of recycled fiber surface after stickies are removed by enzymes (c) (d). (Magnification 1000x, scale bar is 10 μm)

AFM provides a much better resolution, allowing the fine structure of the cellulose micro-fibrils to be observed on a nanoscale. After reviewing multiple areas on recycled fibers, the representative AFM images of recycled fibers before and after enzyme are presented in Fig. 4.11, and the results agree with SEM images. Fig. 4.11(a) presented a 20 μm x 20 μm non-fibrillar area on recycled fiber surface, where the fiber is covered by a tar-like material. Based on the observations under SEM, the tar-like material can be identified as the sticky contaminants. As shown Fig. 4.11(b), after enzyme treatment, the recycled fiber exhibits a fibrillar structure, where microfibrils of the secondary cell wall were exposed. These results agree with the findings in Chapter 3, indicating that the presence of stickies deposits on remanufactured paper sheets can reduce paper quality due to the reduced fiber contacting areas. Additionally, these images provided evidence that enzyme formulations removed stickies deposits on remanufacture paper sheets.

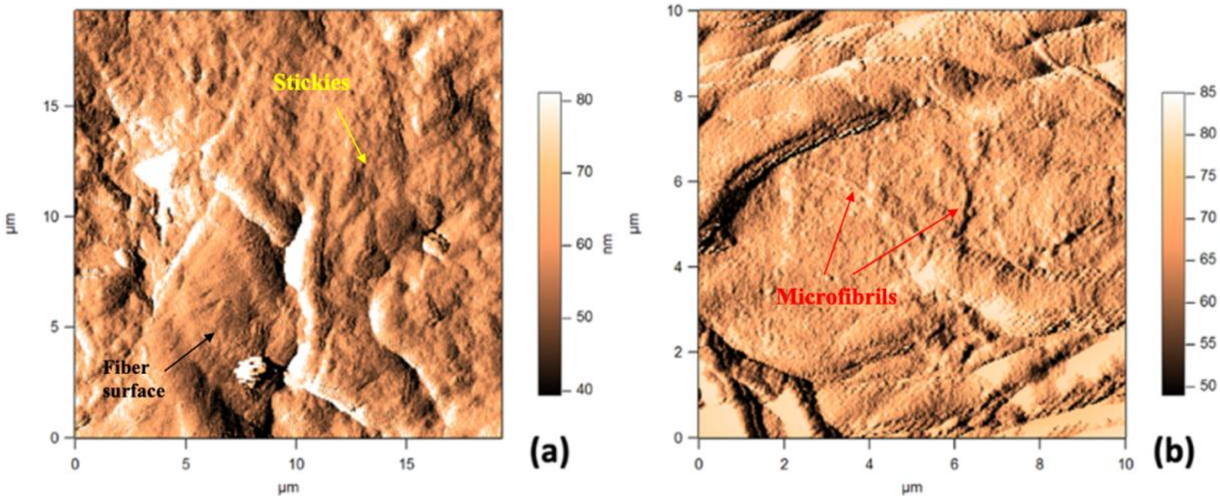
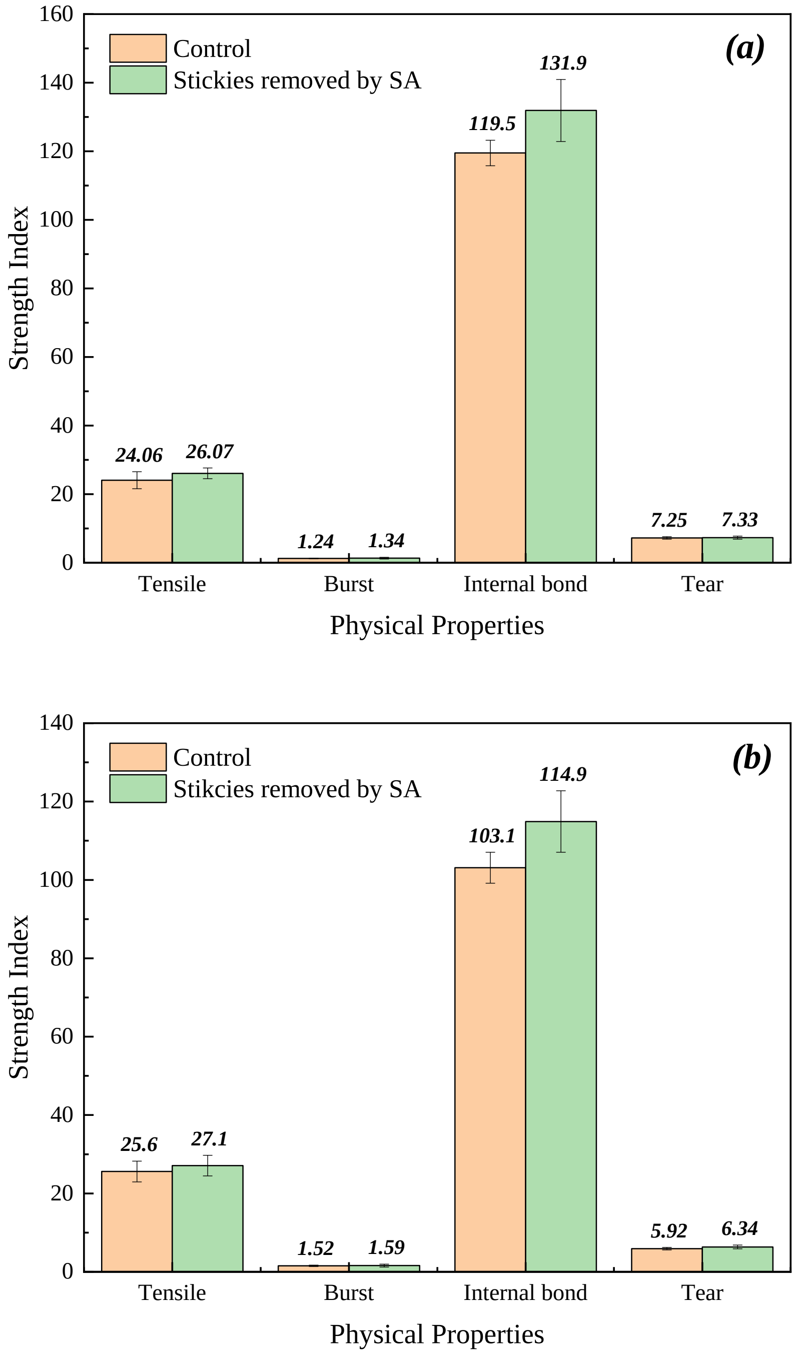


Figure 4.11. AFM image of the presence of stickies on recycled fiber surface before enzyme treatment (a) and the exposure of fibrillar area after the stickies are removed by enzyme (b).

4.3.4 The Impact of Stickies Removal on Paper Strength



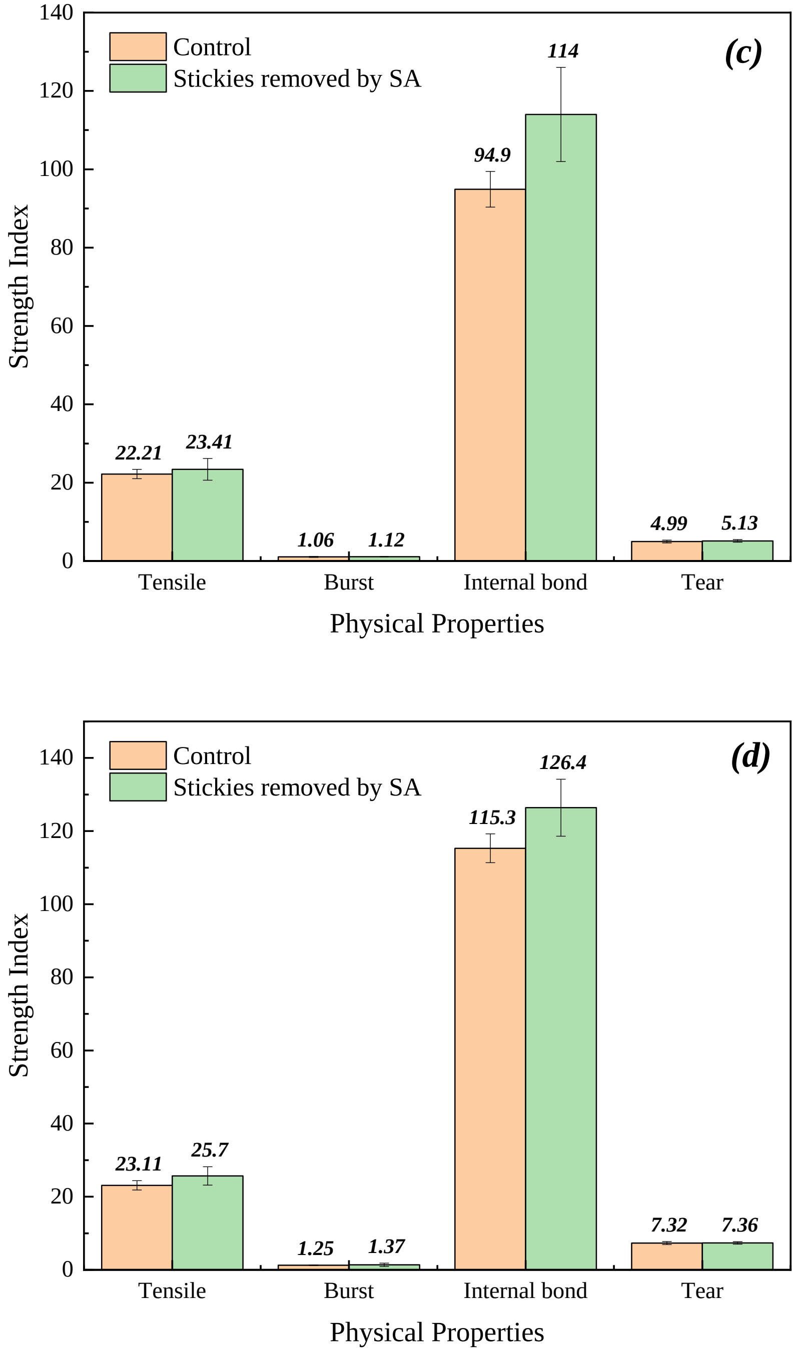


Figure 4.12. Impact on the strength properties of remanufactured paper by enzyme-assisted stickies removal. (a)OCC, (b)RW, (c)ONP, (d) MOW.

Previously in Chapter 3, the SEM results indicated that the presence of sticky contaminants can inhibit inter-fiber bonding and reduce remanufactured paper strength. This conclusion was verified by the physical strength properties of remanufacturing paper sheets with stickies completely removed by organic solvents in section 3.3.5. In Chapter 4, although enzymes formulations can remove 80-90% sticky contaminations, the impact on strength improvement is not significant. As shown in Fig 4.12(a), as 88% contaminations are removed by enzyme SA in OCC grade, most significant improvement was observed on internal bond about 11% from 119.5 J/m^2 to 131.9 J/m^2. Other strength properties only improved by less than 10% - burst strength increased by 8% from 1.24 $kPa\cdot m^2/g$ to 1.34 $kPa\cdot m^2/g$, tensile strength increased by 8.4% from 24.06 N·m/g to 26.07 N·m/g, while no improvement was observed on tear strength. Similarly, as shown in Fig 4.12(b), no significant improvement on physical strength was observed on residential wastepaper grade, even though 73% of sticky contaminants were removed. The enzymatic removal of organic contaminants can improve remanufactured paper properties; however, the improvement is very limited. To further improve physical properties and solve the downgrading issue related with using secondary fibers, we will develop and investigate enzyme-assisted mechanical refining.

4.4 Conclusions

This work aimed to develop an enzymatic strategy to solve the problem of sticky deposits in wastepaper recycling. The stickies removal efficiency of three enzymes were investigated, and the two enzyme formulations presented higher overall performance when comparing to a commercial lipase. Enzymatic treatment temperature, pH, residence time and enzyme dosage play critical role in the process, and the results indicated the optimal conditions for enzymatic stickies removal is 65^{o}C, 30-60min, in slightly alkaline (pH 8.0) environment. At optimal condition, 86.1% stickies were removed by enzyme formulation SA and 93.4% stickies were removed by enzyme formulation RES. Under extreme conditions, enzyme SA exhibited excellent stability while commercial lipase experienced significant deactivation. In practice, over 80% stickies can be removed by enzyme SA when applied on multiple grades of wastepaper, including OCC, ONP, DLK, and MOW. Fiber surface structure was revealed using SEM and AFM. At micro-scale level, stickies deposits were observed as patch-like material that attached to fiber and covered microfibrils on fiber surface. After enzyme treatment, the stickies deposits were removed, and microfibrils were exposed on fiber surface. Furthermore, the removal of stickies can slightly improve the strength properties of remanufactured paper. In OCC grade, strength properties including internal bond, burst strength and tensile strength increased by 8-11% when 88% of stickies are removed by enzyme formulation SA. These results indicated that the enzyme mixture harbouring thermophilic lipase and esterase has great potential for stickies control in wastepaper recycling.

CHAPTER V

ENZYME-AIDED MODIFICATION OF CELLULOSIC FIBERS FOR RESTORING FIBER QUALITY IN PAPER RECYCLING

5.1 Introduction

The production and consumption of paper and paperboard products have increased considerably in the past five years, while the secondary fibers have become increasingly critical as a raw material in the pulp and paper industry. Wastepaper recycling and remanufacturing ensure sustainability as they can preserve wood resources and reduce greenhouse gas emissions. In addition, comparing to the virgin papermaking process, 30-60% energy can be saved as the embodied energy in secondary fibers are recovered in paper remanufacturing process [12]. Recycling also saves landfill space and reduces water usage. Paper recycling rate in US has increased significantly over the past three decades, however, it plateaued and held approximately steady in the range of 65-68% since 2010 and yet to exceed 70% [225]. The utilization of secondary fibers is limited by its low quality due to loss of strength during recycling and the presence of various contaminations [60].

Detrimental changes in the structure and surface properties of fibers are unavoidable during conventional paper recycling practices leading to reductions in fiber strength such as tensile, burst, fold, and stretch, and also in density and drainage [61–63]. It is commonly accepted that the loss of strength during recycling is caused by repeated wetting and drying, leading to hornification, surface deactivation, and reductions in the wet flexibility and bonding properties of the fibers [64] . Many attempts have been made to explain the exact causes and mechanisms involved in hornification, and the most prevalent hypothesis is the formation of intra-fiber hydrogen bonds among the cellulose microfibrils, which restrict cellulose swelling and decrease its absorption capacity. In addition to drying, fiber morphology is also changed by other mechanical and chemical treatments such as pulping, refining and bleaching. Efforts have been made to upgrade the properties of recycled fibers through mechanical refining, chemical additives, fractionation or blending of virgin pulp. However, most of these strategies mentioned above make fibers more deteriorated in the next recycling process; not even mention the high energy consumption and complex process [226–228]. Therefore, the development of cost effective and sustainable technology to restore recycled fiber quality has become increasingly critical to paper industry.

In recent years, modifications of secondary fibers by using enzymes have been investigated. Cellulases hydrolyze cellulosic fibers causing layers or fibrils on fiber surface to peel off, which makes fiber surface becomes wrinkled and rough [134,229,230]. These modifications can result in substantial increase in fiber strength or fiber drainage which would greatly benefit any subsequent process [231–235]. Studies pointed out that pretreatment of recycled fibers with cellulase enzymes having cellobiohydrolase as a major activity, can improve fibrillation and facilitate subsequent refining process, or reduce energy requirement for the subsequent refining process without any significant loss of fiber strength [236–239]. Valchev et al. improved the refining degree of recycled fibers up to 25% and improved fiber drainage up to 45% by treating fibers with cellulosic enzymes [240]. The effect of enzyme treatment showed that breaking length slowly increased with enzyme dosage, while tear index and burst index decreased. The obtained results can be interpreted to be due to the partial degradation of colloidal substances of secondary fibers, which retain water causing slower dewatering of the fibers [240]. Huang et al. reported 44% improvement in refining degree, 19% improvement in ring crush resistance, and 25% improvement in tensile strength when recycled fibers were pretreated with cellulase prior to mechanical refining [241]. In the recent research performed by Verma et al., cellulase treatment of recycled fiber for quality improvements as a result of selective and controlled hydrolysis was investigated [235]. Significant improvements in tensile index and smoothness were observed. SEM analysis indicated a high degree of fiber collapse on enzyme treated fiber, along with extensive fiber wall peeling. These changes generally contribute to an increase in relative bonded area which is the reason for increased fiber-fiber bonding and improved fiber strength [235].

Wastepaper recycling involves multiple grades, some with a certain amount of lignin or completely mechanical fibers. The stock may also contain a significant amount of impurities such as ink particles, stickies, pitch, surfactants, etc. [212]. In such cases, other enzymes such as lignin-modifying enzymes and hemicellulases can also play significantly important roles in the enzymatic modification of recycled fibers [242]. Oksanen et al. treated recycled fibers with purified cellulases and hemicellulases and investigated the changes in fiber properties caused by enzymatic modification [227]. It is reported that the endoglucanases significantly improved pulp drainage even at low dosage levels, and combining hemicellulases with the endoglucanase treatments increased the positive effects of the endoglucanases on pulp drainage [227]. Huang et al. also found that the refining of secondary fibers from old corrugated container (OCC) with commercial amylase can increase their mechanical strength [241]. The addition of 1 % of amylase in the refining process increased the ring crush index and tensile index of the secondary fibers by 18.3 % and 15.6 %, respectively. Olsen et al discovered a method using a mixture of cellulase and pectinase enzymes to accomplish the goal of simultaneously restore fiber drainage and maintain physical properties [243]. The improvement on secondary fiber properties through enzymatic pretreatment have been demonstrated by many studies. However, the detailed mechanism of the enzyme actions is still not sufficiently understood. Without fully understanding the fundamentals of enzyme mechanisms on recycled fiber ultrastructure and chemistry, a wider range application of this green technology is limited.

This study explores the modifications of recycled cellulosic fibers when treated with enzyme formulation containing multiple enzyme species in combination with mechanical refining. The fundamental changes in fiber physical and chemical characteristics (e.g., fiber length, swelling capacity, surface morphology, chemistry) are investigated using techniques such as FQA, WRV, SEM and FTIR. The results reveal the mechanism of enzyme actions on secondary fibers. In addition, recycled fiber quality, in terms of handsheet physical properties, are determined following TAPPI standard methods. Furthermore, the developed enzyme-aided mechanical modification technology for restoring fiber quality is investigated on multiple wastepaper grades.

5.2 Experimental

5.2.1 Materials

Secondary fibers were obtained from local paper recycling mill. Multiple grades of wastepaper were collected, including old corrugated containerboard (OCC), residential wastepaper (RW), mixed office wastepaper (MOW,) and old newsprint (ONP). OCC includes mostly post-consumer packaging materials, such as containerboards obtain from wholesale stores. Residential wastepaper mainly consists of food containers such as burger boxes, pizza boxes, food wrapping papers, etc. ONP is a mixture of used newspaper and old grocery store flyers. Photos of these wastepaper are shown in Fig. 5.1.

Commercial enzyme FiberCare (Enzyme FC) samples including cellulase, xylanase, amylase, oxidoreductase, lipase, etc. were provided by Novozyme, USA. Through preliminary study and optimization, a few enzymes were mixed in certain ratio to create multi-component enzyme formulation. The optimum pH and temperature range for the enzyme formulation is pH 6-8 and 40-60°C.

Figure 5.1. Recycled OCC and ONP collected from local paper recycling mill, residential wastepaper RW collected from curb side, and MOW collected from office.

5.2.2 Enzyme Modification

The secondary fibers were treated with enzyme mixture at 3% pulp consistency for 15 min to 4 hr. The temperature and pH were adjusted not only to accommodate most of the enzyme components, but also to accommodate the fiber recycling process in industrial practice: temperature 40-70^{o}C, and pH 5.5-8.0 (adjusted with phosphate buffer). Enzyme dosage was tested ranging from 0.01 mg/g o.d. fibers to 0.5 mg/g o.d. fibers for promising results. Constant agitation at 400 rpm provided by electrical mixer was applied during the enzyme treatment. At end of the treatment, enzyme reaction was deactivated by increasing temperature to 100°C and maintaining it for 15 min. Subsequently, the fibers were washed with deionized water through a Buchner funnel. The washed solids were used for analysis and subsequent mechanical refining. The control sample was treated in the same manner as the enzyme treated samples except for enzyme addition.

5.2.3 Mechanical Refining

Following enzyme modification, the secondary fibers were refined using a PFI mill according to TAPPI test method T248. The pulp was pre-soaked and disintegrated prior to refining. Following the disintegration, the pulp was adjusted to 10% consistency and transferred to the beater house for refining. PFI mill refining took place at up to 10000 refining revolutions with 0.2mm bar clearance to comply with Canadian Standard Freeness (CSF) in the range of 500-300 ml. Canadian standard freeness, which is commonly used to evaluate refining degrees and correlate to fiber drainage and properties, was measured following TAPPI test method T227.

5.2.4 Fiber Morphology, Quality, and Swelling Capacity

The swelling capacity of secondary fibers was evaluated by determining the water retention value (WRV). Following TAPPI method UM256, approximately 1.0 g o.d. fibers with a starting consistency of 10%, was centrifuged at 900 G force for 130 min at 21°C and then weighed before and after drying. WRV is calculated as follows:

$$WRV = \frac{m_1 - m_2}{m_2} \times 100\% \qquad (5.1)$$

where m_1 is the weight of wet pulp after centrifugation, and m_2 is the weight of dry pulp.

A LDA02 HiRes Fiber Quality Analyzer (FQA) (OpTest Equipment Inc) was used to determine the fiber length and fines content of pulp samples subjected to enzyme pretreatment following TAPPI method T232. The pulp samples were diluted with deionized water to 0.1% consistency and then tested using a projection method. In the test, over 20000 fibers were counted, the length weight average length and length weighted fiber percentage were calculated by the automated FQA analyzer.

A JSM-IT200 (Jeol USA Inc.) field emission scanning electron microscope (FE-SEM) was utilized to investigate the fiber surface morphology. Dried paper sheets made of control and enzyme modified secondary fibers were immobilized on conductive tape and coated with thin gold layer. A low acceleration voltage 10 kV was used to prevent degradation of cellulose [204]. The images were observed with the resolution of 0.1 nm.

5.2.5 Reducing Sugars

The content of reducing sugars released from enzyme modification of cellulose was measured using dinitrosalicylic acid (DNS) method. The colorimetric reaction was carried out in 15 mL Falcon type tubes using 2 ml sample liquid and 2 mL DNS reagent. Reference solutions between 0.1 g/L to 0.3 g/L of glucose were prepared. The tubes were manually vortexed, boiled in water bather for 5 min, and cooled to room temperature in an ice bath. Then the solution was diluted by adding deionized water up to 15 mL. The absorption of 540 nm wavelength was measured using spectrophotometer, and the glucose concentration was calculated using a standard calibration curve of reference solutions.

5.2.6 X-Ray Diffraction (XRD) of Fibers

X-ray diffraction patterns of the fiber samples were collected on Rigaku SmartLab diffractometer using a Ni-filtered Cu-Kα radiation with wavelength of 0.1542 nm. The X-ray unit operated at 40 kV and 300 mA. Angular scanning was conducted from (2θ) 5-40°C at 1°C/min. The wide-angle X-ray scattering patternes of the samples were obtained using xxxx software. The crystallinity index of cellulose in fiber samples was calculated from diffraction intensity data using the following equation based on the method described by Segal et al. [244]:

$$Crystallinity\ index\ (\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \qquad (5.2)$$

Where I_{200} is the maximum intensity of the (200) lattice diffraction (at 2θ=22.6°C), and I_{am} is the peak intensity of amorphous phase diffraction (at 2θ=18.6°C).

5.2.7 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR characterization was performed using a Perkin Elmer Spectrum 100 instrument with attenuated total reflection accessory. The paper handsheets made of control and enzyme modified secondary fibers were placed in close contact with the internal reflection element to perform the characterization. The acquisition of each spectrum has provided 20 scans in the range of 500-4000 cm-1, with a resolution of 4 cm^{-1}. FTIR spectra were compared with those of the electronic library of the instrument and with ones reported in the literatures.

5.2.8 Characterization of Physical Properties

TAPPI standard handsheets were made using the control and enzyme modified secondary fibers following standard T205. The physical properties of remanufactured sheets were investigated following TAPPI standards including T403 burst strength, T494 tensile strength, T414 tear resistance, and T541 internal bond strength.

5.3 Results and Discussion

5.3.1 Improvement on Internal and External Fibrillation Through Enzyme Pretreatment

The strength deficit in recycled paper is due to a loss of flexibility caused by hornification, which is a consequence of the irreversible change of cell wall structure through the repeated drying and rewetting process [245]. Cellulose fibrils are tightly packed through hydrogen bonding upon drying. The hydrogen bonding causes the shrinkage and loss of pores in the cell wall. When rewetting, this packed cell wall structure swells and some of the hydrogen bonds are broken, which leads to a pattern of internal fibrillation (also known as swelling). This provides fiber flexibility as well as more contacting areas for inter-fiber bonding, thus develops remanufactured paper strength. However, the swelling capacity of secondary fibers is significantly reduced as hornification occurs, in which case rewetting can only partially reopen the tightly packed cell wall structure, leading to significantly reduced contacting area for inter-fiber bonding [246,247]. Mechanical refining is commonly required to improve the re-swelling capacity of secondary fibers. In this study, enzyme pretreatment of recycled fibers followed by mechanical refining was performed to investigate the effect of enzyme modification on fiber swelling capacity. Recycled old corrugated container (OCC) fibers collected from local paper recycling mill were modified using multi-component enzyme formulation at pre-determined conditions. The enzymatic modified fibers were then refined with PFI refiner at various refining levels to yield pulp samples with freeness range from 500-300ml. The water retention value (WRV) and Canadian standard freeness (CSF) of pulp samples were determined to evaluate the swelling capacity, and the results are presented in Fig. 5.2, Fig. 5.3, and Table 5.1.

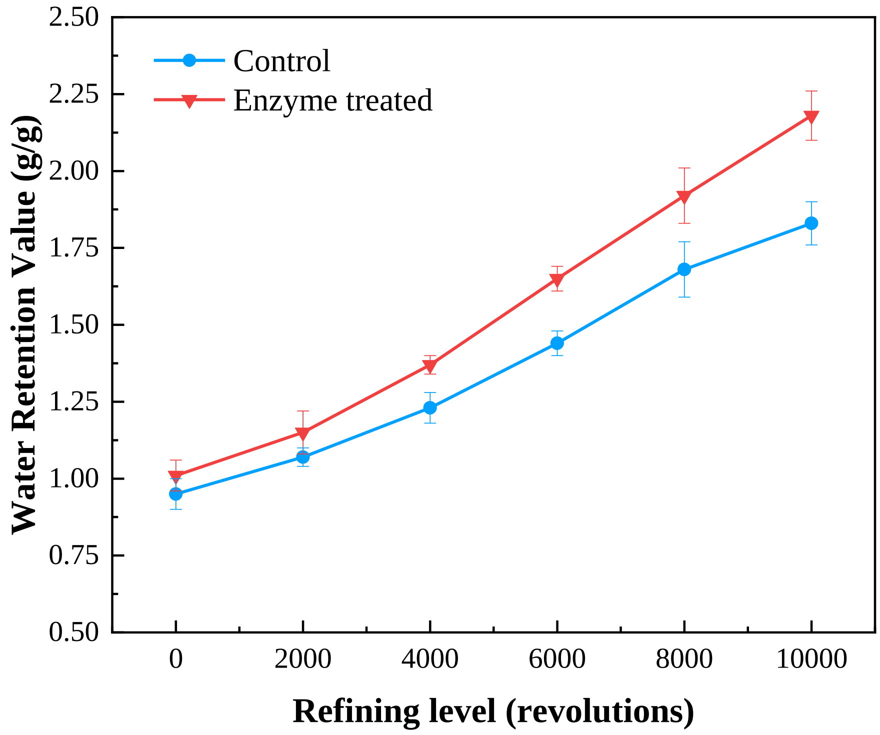


Figure 5.2. WRV of secondary fibers with and without enzyme treatment.

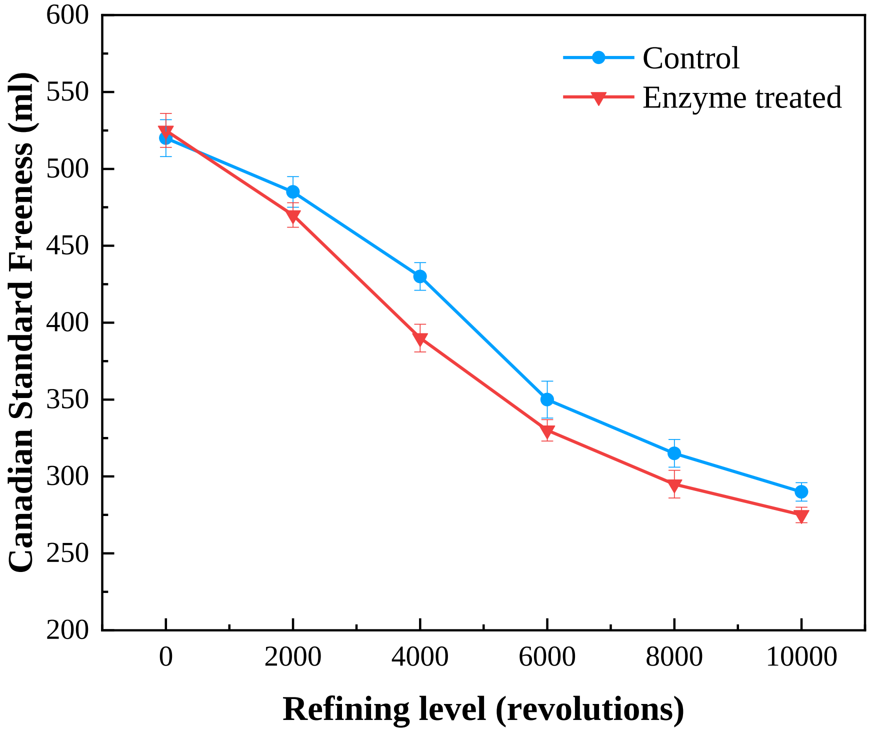


Figure 5.3. Freeness of secondary fibers with and without enzyme treatment.

Table 5.1. Water retention value (WRV) and CSF of secondary fibers.

Refining levels (revolutions)	Water retention value (g/g)		Freeness (ml)	
	Control	Enzyme treated	Control	Enzyme treated
0	0.95	1.01	520	525
2000	1.07	1.15	485	470
4000	1.23	1.37	430	390
6000	1.44	1.65	350	330
8000	1.68	1.92	315	295
10000	1.83	2.18	290	275

It is first noted that as refining energy increases, the swelling capacity of secondary fibers increased significantly in both cases. The water retention value of control fibers increased from 0.95 g/g to 1.83 g/g, while the WRV of enzyme treated fibers increased from 1.01 g/g to 2.18 g/g. This is due to the delamination of the primary layer (P layer) and secondary layer (S1) of fiber cell walls, caused by the cyclic compression action of forces during the refining [66,248]. This results in the breakage of inner bonds and causes the pore structure inside the cell wall to expand and swell, which is indicated by the increased WRV. On the other hand, as the secondary layer (S2 layer) of the fiber cell wall is exposed, fibrils are peeled off from the fiber surface, leading to significantly increased specific surface areas on the fiber surface [66]. As a result, fiber-fiber bonding is improved, as well as fiber-water bonding. This is supported by the reduced freeness in both cases. The CSF of control fibers decreased from 520 ml to 290 ml during the refining process, while the CSF of enzyme treated fibers decreased from 525 ml to 275 ml. Additionally, when comparing the properties of enzyme treated fibers to that of control fibers, the improvement in swelling capacity and reduction in freeness were much more significant. Prior to mechanical refining, enzyme treated fibers presented 1.01 g/g WRV and 525 ml CSF, which is similar to control fibers having 0.95 g/g WRV and 520 ml CSF. However, as the refining level increased from 2000 revolutions to 10000 revolutions, WRV and CSF of enzyme treated fibers improved from 1.15 g/g to 2.18 g/g and from 470 ml to 275 ml, respectively; while the WRV and CSF of control fibers ended up to 1.83 g/g and 290 ml at 10000 refining revolutions. These results indicate that enzymes' actions on the fiber surface and inner layers weakened the fiber cell wall structure, which facilitated the subsequent mechanical refining process. With the same amount of energy input, significant improvements in both internal and external fibrillation were achieved through enzyme-assisted mechanical refining. From another perspective, refining energy can be reduced by 20-30% with enzyme pretreatment without any impact on fiber swelling capacity and freeness. For example, to improve the swelling capacity of secondary fibers to 1.44 g/g, 6000 refining revolutions were required, which resulted in 350 ml CSF. In the case that secondary fibers were pretreated with enzyme formulation, the above target was achieved with only 4000 refining revolutions, which was more than 30% than that without enzyme.

5.3.2 Fiber Length and Fines Content

As previously discussed, mechanical refining of recycled fibers creates both internal fibrillation and external fibrillation which develop swelled, flexible fibers with improved surface areas for inter-fiber bonding. However, fines formation and fiber shortening are inevitable during this process. Secondary fines consist of fragments of fiber cell walls produced during the refining because of external fibrillation. They are undesirable in most cases as the presence of excessive fines does not contribute to paper strength but reduces pulp drainage significantly. Reduction in fiber length is also undesirable as many of the paper physical properties are highly dependent on fiber length. To study the impact of enzyme treatment on fiber length and fines formation, fiber quality analysis (FQA) was carried out in this study, and the average fiber length (length-weighted), fines percentage (length-weighted) are presented in Fig. 5.4, Fig. 5.5, and Table 5.2.

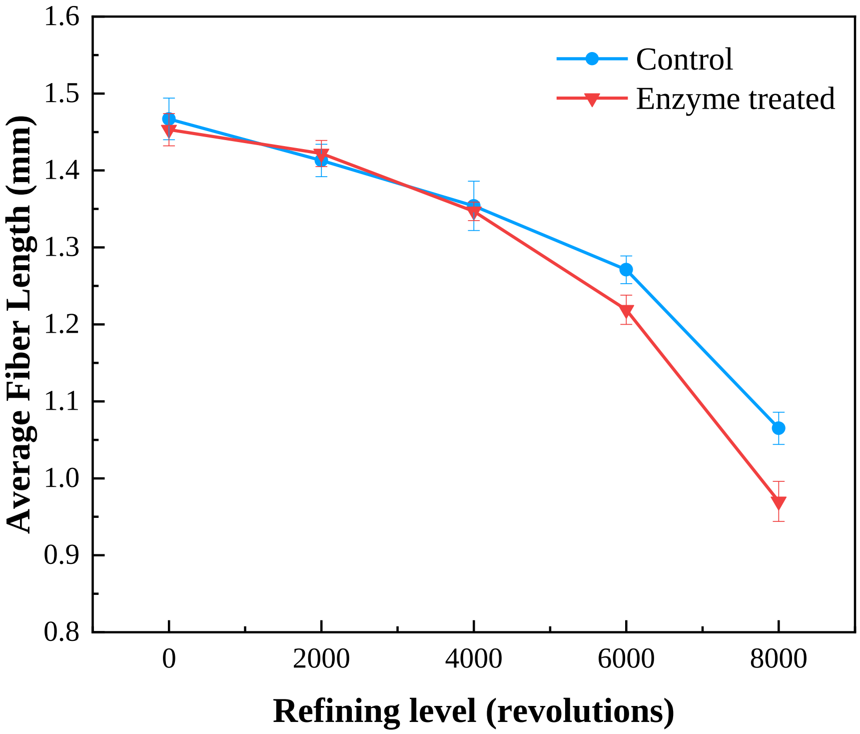


Figure 5.4. Length weighted average fiber length of secondary fibers as refining level increases.

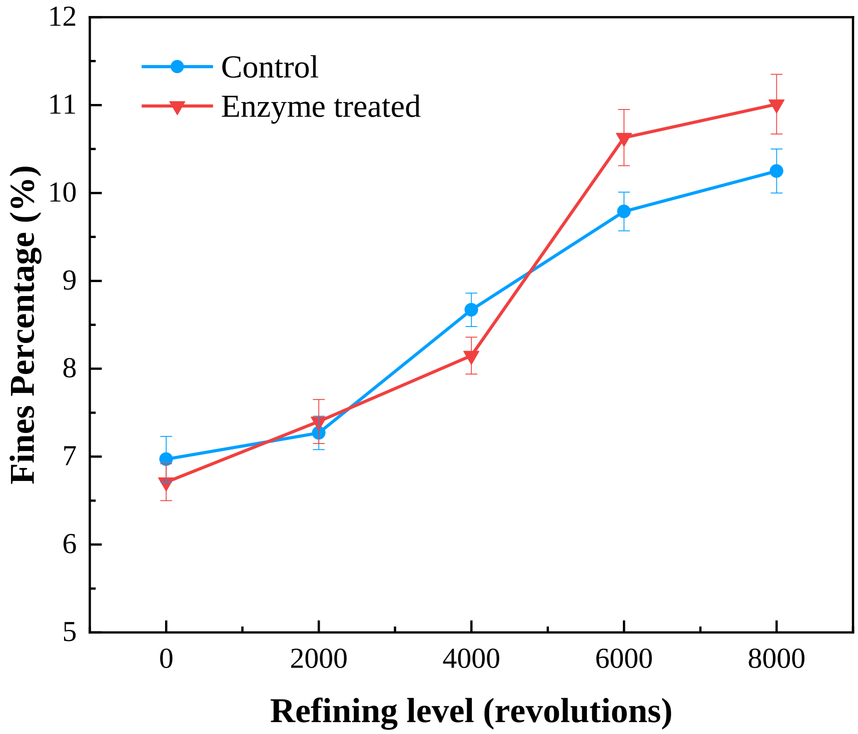


Figure 5.5. Length weighted fines percentage of secondary fibers with increasing refining.

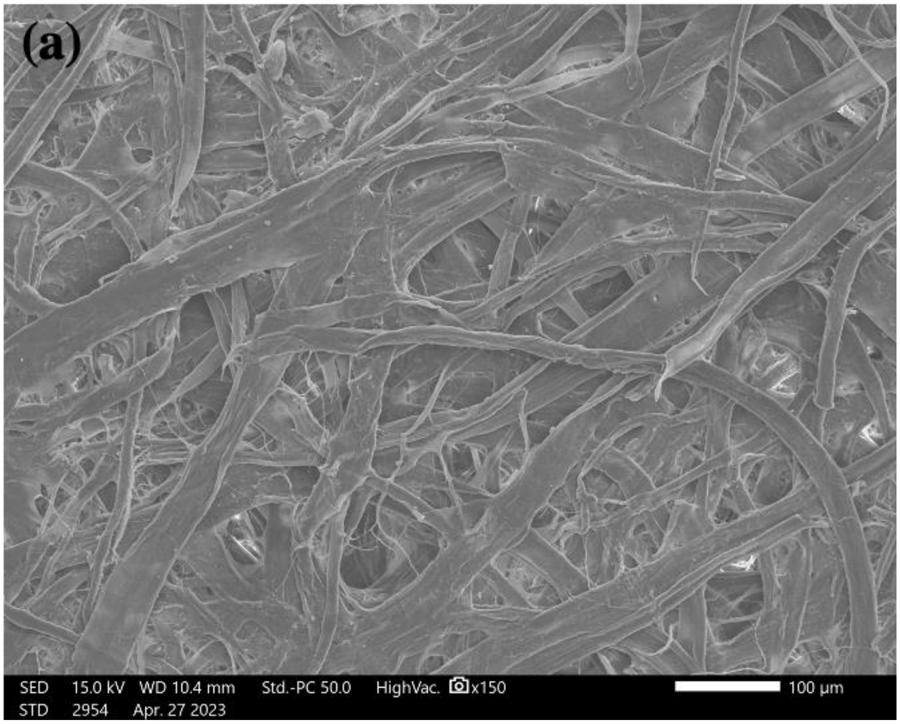
Table 5.2. Fiber length and fines percentage of recycled fibers treated with and without enzymes.

Refining levels (revolutions)	Average fiber length (length weighted, mm)		Fines percentage (length weighted, %)	
	Control	Enzyme treated	Control	Enzyme treated
0	1.467	1.453	6.97	6.71
2000	1.413	1.422	7.27	7.40
4000	1.354	1.347	8.67	8.15
6000	1.271	1.219	9.79	10.63
8000	1.065	0.970	10.25	11.01

As expected, the average fiber length of untreated OCC fibers decreased from 1.467 mm to 1.065 mm with increasing refining revolutions, while the fines percentage increased from 6.97%

to 10.25%. Although enzyme pretreatment facilitated external fibrillation during refining process, it did not lead to significant reduction in fiber length and increase in fines percentage. At moderate refining levels (2000 revolutions and 4000 revolutions), the fiber length and fines percentage of enzyme treated fibers were at the same level when comparing to untreated fibers. When the intensity of refining increased, fines formation and fiber shortening were emphasized by enzyme pretreatment. At 6000 revolutions, enzyme treated fibers had an average length of 1.219 mm, and contained 10.63% fines, while the untreated fibers had an average length of 1.271 mm and contained 9.79% fines. Similarly, at 8000 revolutions, enzyme treated fibers had an average length of 0.97 mm and contained 11.01% fines, while the control fibers had an average length of 1.065 mm and contained 10.25% fines. The difference on fiber length and fines percentage between control and enzyme treated fibers were much more significant when intense refining was applied.

5.3.3 Effect of Enzyme on Fiber Structure



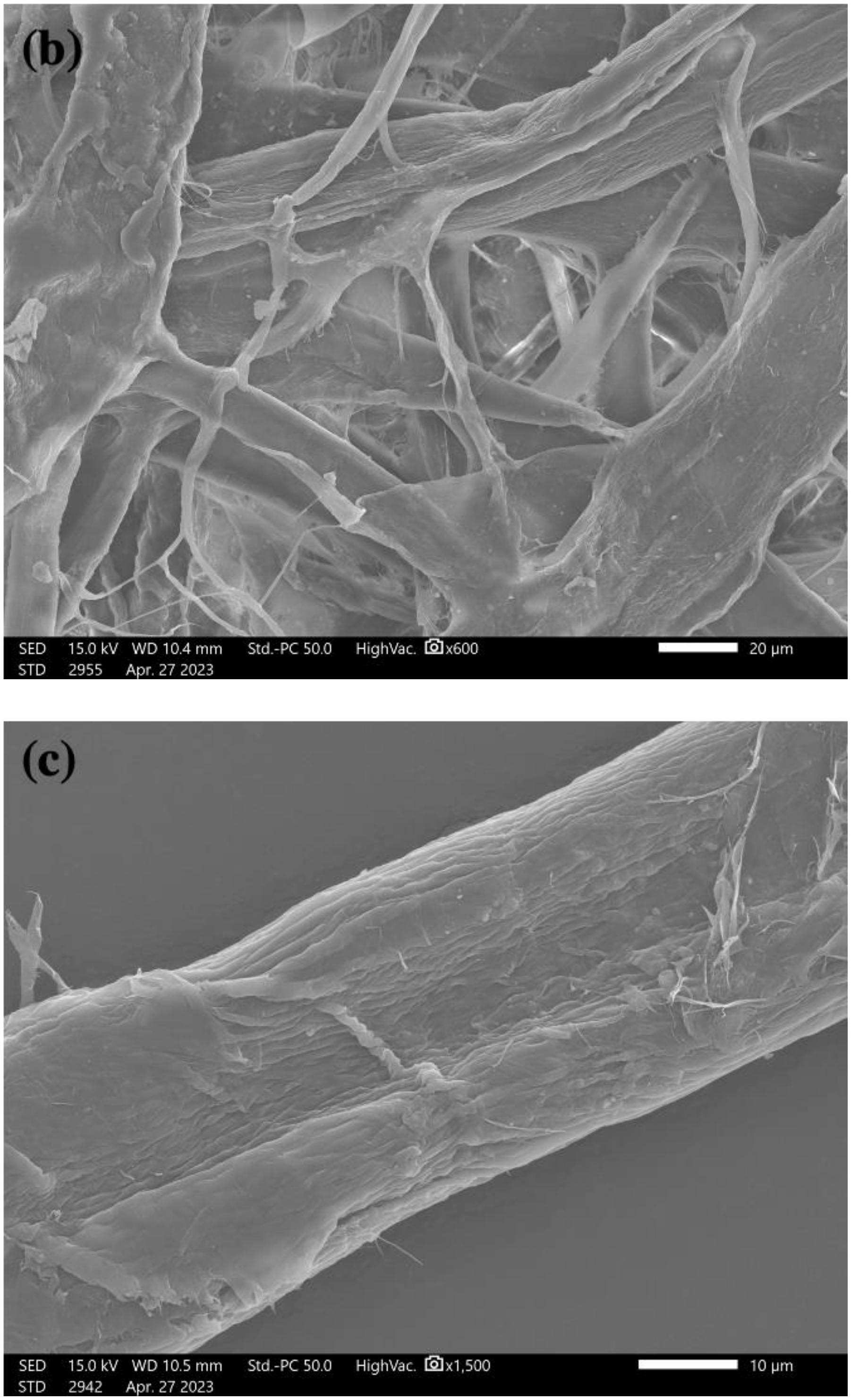
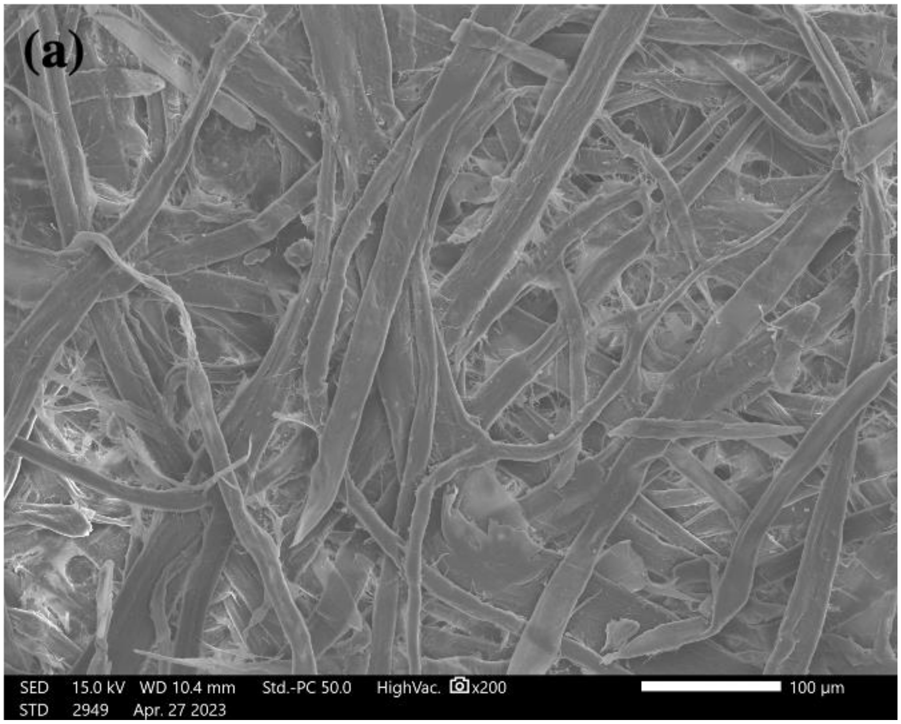


Figure 5.6. SEM images of untreated and unrefined secondary fibers, (a) paper surface, scale bar is 100 microns, (b) fiber-fiber contact, scale bar is 20 microns, and (c) fiber surface, scale bar is 10 microns.


(a)
SED 15.0 kV WD 10.4 mm Std.-PC 50.0 HighVac. x200
100 µm
STD 2949 Apr. 27 2023

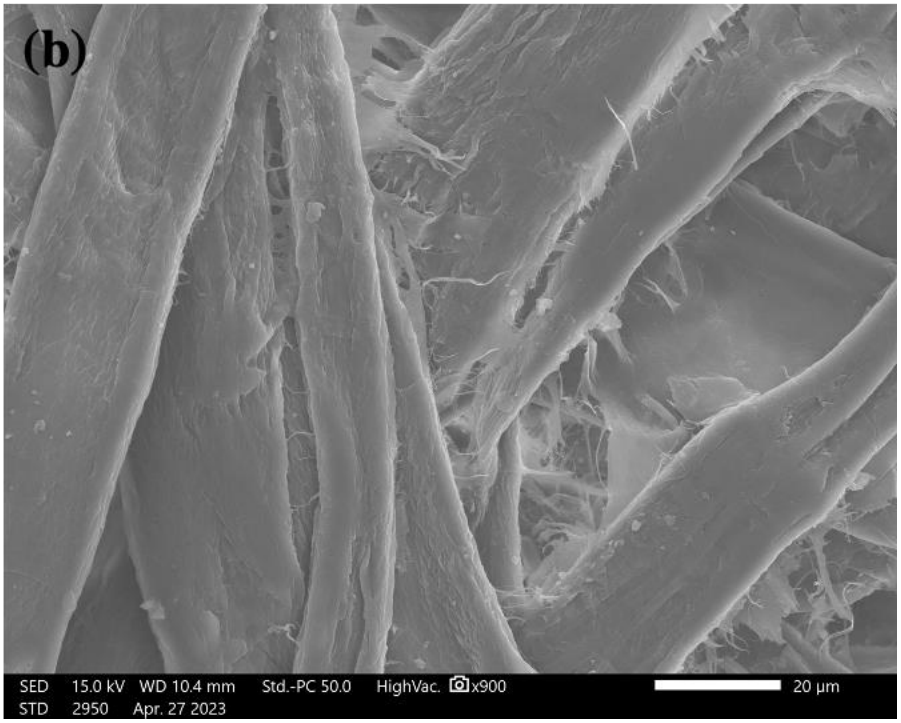
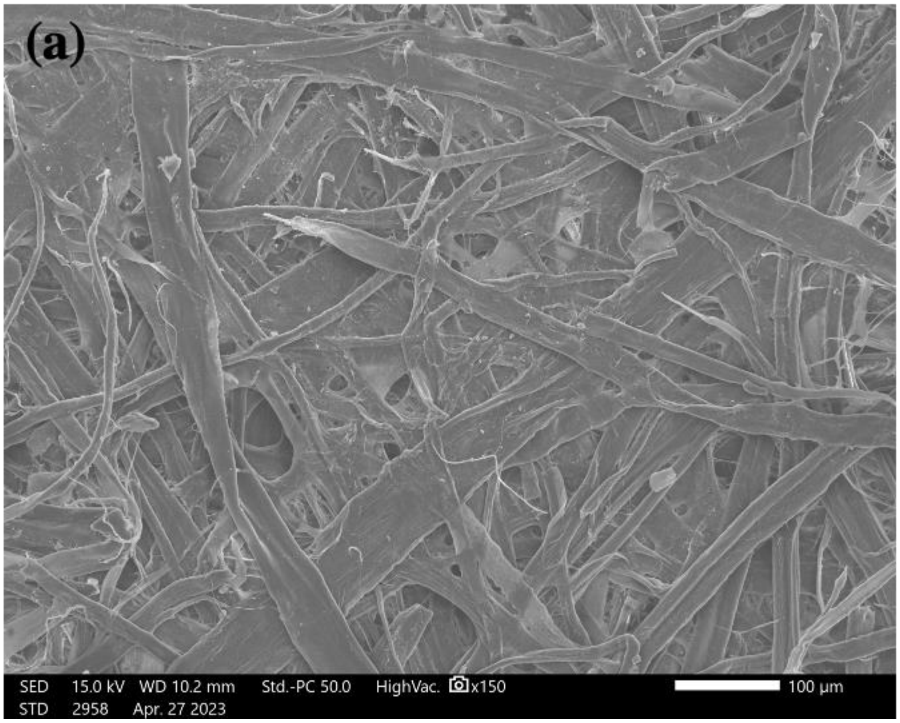

(b)
SED 15.0 kV WD 10.4 mm Std.-PC 50.0 HighVac. x900
20 µm
STD 2950 Apr. 27 2023

Figure 5.7. SEM images of untreated secondary fibers refined at 6000 revolutions, (a) paper surface network, scale bar is 100 microns, (b) fiber-fiber contact, scale bar is 20 microns, and (c) fiber surface, scale bar is 10 microns.



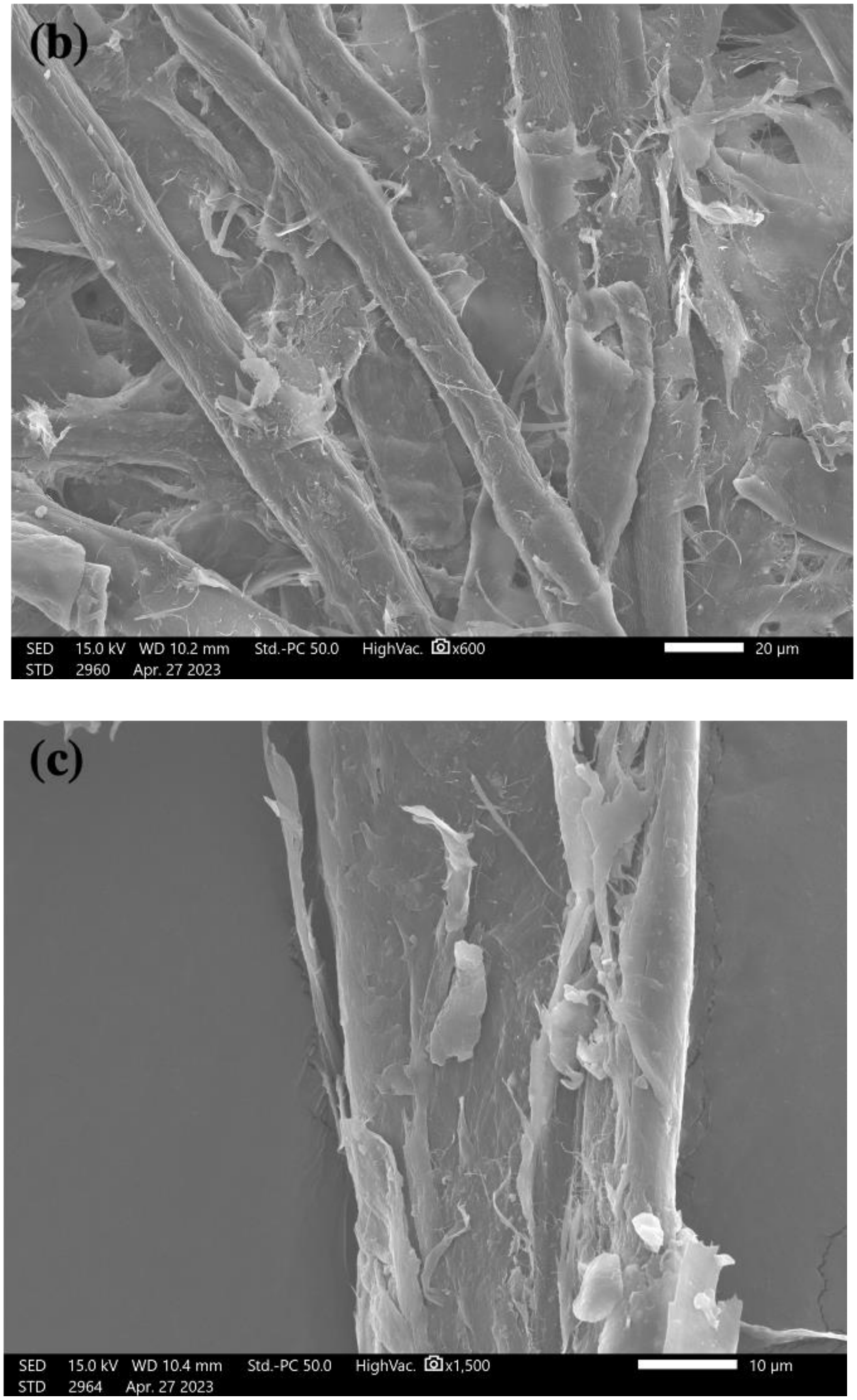


Figure 5.8. SEM images of enzyme treated secondary fibers refined at 6000 revolutions, (a) paper surface, scale bar is 100 microns, (b) fiber-fiber contact, scale bar is 20 microns, and (c) fiber surface, scale bar is 10 microns.

The fiber morphology was investigated using scanning electron microscope with 20-30 images on each specimen and the most representative SEM images of blank OCC fibers (untreated and unrefined), control OCC fibers (untreated but refined at 6000 revolutions), and enzyme treated OCC fibers (refined at 6000 revolutions) are presented in Fig. 5.6, 5.7 and 5.8, respectively. As shown in Fig. 5.6(c), the unrefined OCC fibers were relatively intact, and the fiber surface was smooth with minimal external fibrillation. In Fig. 5.6(a) and 5.6(b), the pore size of the fiber network was relatively large, and the fibers were not conformable. Meanwhile, because of refining, delaminating of wall layers reduced the stiffness of fibers and thus the fibers became more flexible or collapsible. The collapsed fibers were observed in Fig. 5.7(a), giving more intimate contact and leading to a denser fiber network in Fig. 5.7(b). Additionally, fragments were peeled off fiber surface, and some fiber splitting and cutting were observed in Fig. 5.7(c). It’s noted from Fig. 5.8, when the secondary fibers were treated enzymes, the fibers became much more flexible, and the fiber structure are completely collapsed when the paper sheet is formed (Fig. 5.8(a)). Significant amount of fragments peeled off, exposing S1 and S2 layers. The surface fibrillation made the fibrils loose, contributing to the increased number of fines (Fig. 5.8(b) and 5.8(c)). Additionally, fiber splitting was observed as well, leading to reduced fiber length. The visual observations from SEM analysis of fiber surface structure agree with FQA results, indicating that enzymes loosened fiber cell wall structure, facilitated the subsequent refining process, and yielded more fibrillation on fiber surface.

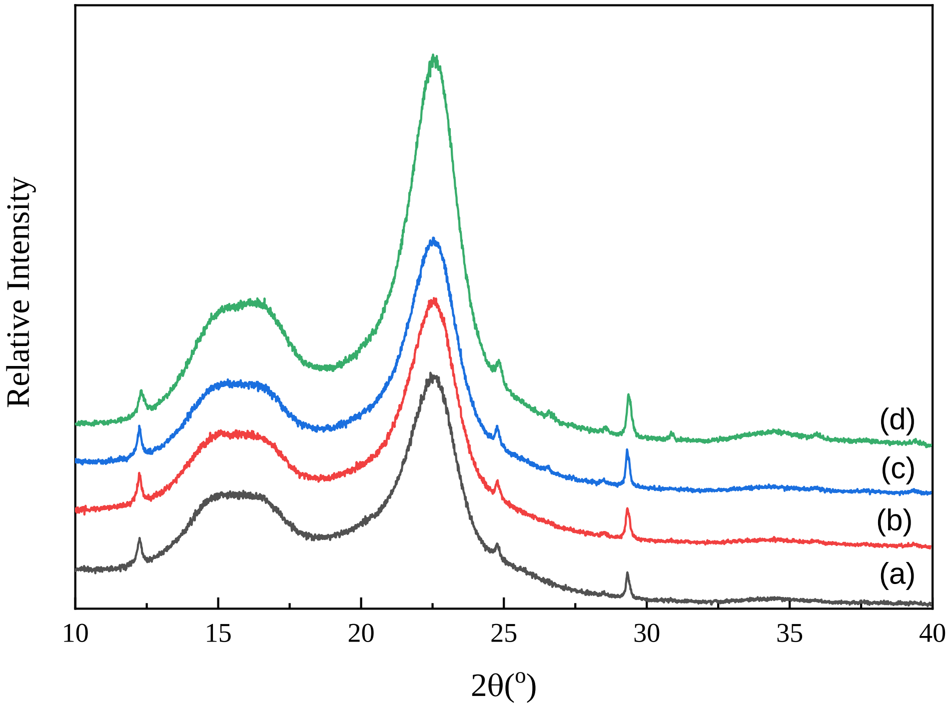


Figure 5.9. XRD spectra of control and enzyme-treated OCC fibers, (a) untreated OCC fibers, (b) OCC fibers treated with 0.1mg/g enzyme for 1hr, (c) OCC fibers treated with 0.5 mg/g enzyme for 1hr, and (d) OCC fibers treated with 0.5 mg/g enzyme for 4hr.

The X-ray diffraction intensity profiles of the untreated and enzyme-treated fiber samples are shown in Figure 5.9. Three main peaks are observed at 15.2°, 16.5° and 22.7°, corresponding to $(1\bar{1}0)$, (110), and (200), respectively. However, the $(1\bar{1}0)$ and (110) peaks overlapped in the recycled fiber samples. The main peak with Miller index (200) at 22.7° was slightly increased after enzyme treatment, while the overlapped peak $(1\bar{1}0)$ and (110) remain the same. The crystallinity index of OCC fibers before and after enzyme treatment were assessed from XRD spectra based on the Segal peak height method. The crystallinity indexes of the untreated and treated OCC fibers are 65.4% (a), 67.9% (b), 69.2% (c) and 74.7% (d), respectively. With the addition of 0.5 mg/g enzyme, the crystallinity index of OCC fibers increased to 69.2% at 1hr treatment, and significantly to 74.7% at 4hr treatment, comparing to the original untreated fibers with a crystallinity index of 65.4%. This result indicates that enzymes preferentially attack the amorphous regions, leading to an increase in the concentration of crystalline domains. The tightly packed chains in the crystalline regions limit access and penetration to enzymes. Similar findings have been reported previously [235,249,250]. Studies have also shown that the rate of enzyme treatment is typically faster for amorphous cellulose when comparing to crystalline cellulose [251–253].

On the other hand, some conflicting results are also reported in the literature. Few groups on investigators have reported an increase in crystallinity as enzyme treatment proceeds [254,255]. Several other studies did not find any appreciable increase in crystallinity during the course of enzyme hydrolysis [256]. Sinisyn et al. found that crystallinity initially increases with time, then decreases, and finally levels off [257].

5.3.4 Impact of Enzyme Treatment on Chemical Property – FTIR

Fig. 5.10 presents FTIR profiles of secondary fibers treated with or without enzyme. The broad absorption peak between 3600-3000cm^{-1} was assigned to O-H vibrations. The peak at 2900 cm^{-1} was related to the aliphatic saturated CH_2 and CH_2OH stretching vibration of cellulose. The absorption peak in the 1590 cm^{-1} region was due the bound water and carboxylate. The characteristic peaks from 1400 to 1300 cm^{-1} were attributed to the stretching vibration from acetyl groups in hemicellulose. The absorption peak at 1030 cm^{-1} was assigned as the CO stretching at the C3 position. The absorption peak at 670-550 cm^{-1} was related to CH deformation and OH out-of-plane bending. It can be seen that enzyme pretreatment has no significant impact on the functional groups of the recycled fibers during refining process.

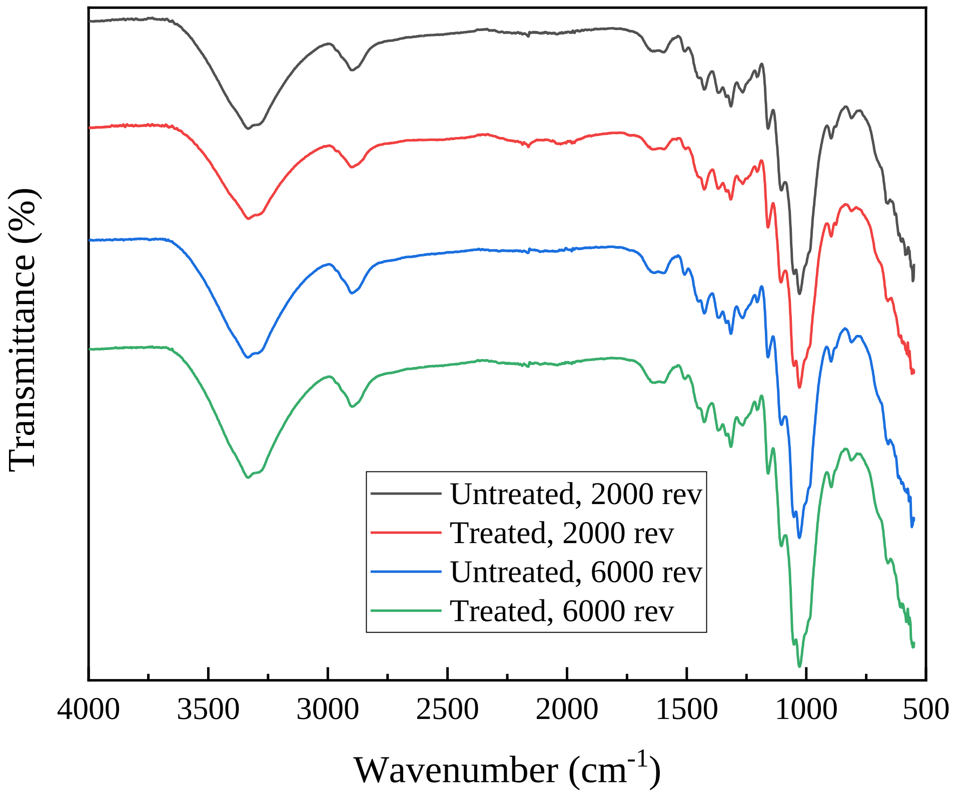


Figure 5.10. FTIR profiles of refined secondary fibers with and without enzyme pretreatment.

5.3.5 Reducing Sugars

The release of reducing sugars from recycled fibers by enzyme hydrolysis was investigated to gain understanding of the enzyme reaction mechanism. After enzyme treatment, the fiber suspension was filtered through Buchner funnel and washed with deionized water. The filtrate liquid was collected and the quantity of reducing sugars was measured using DNS method. The quantities of reducing sugar from different enzyme modifications are presented in Table 5.3.

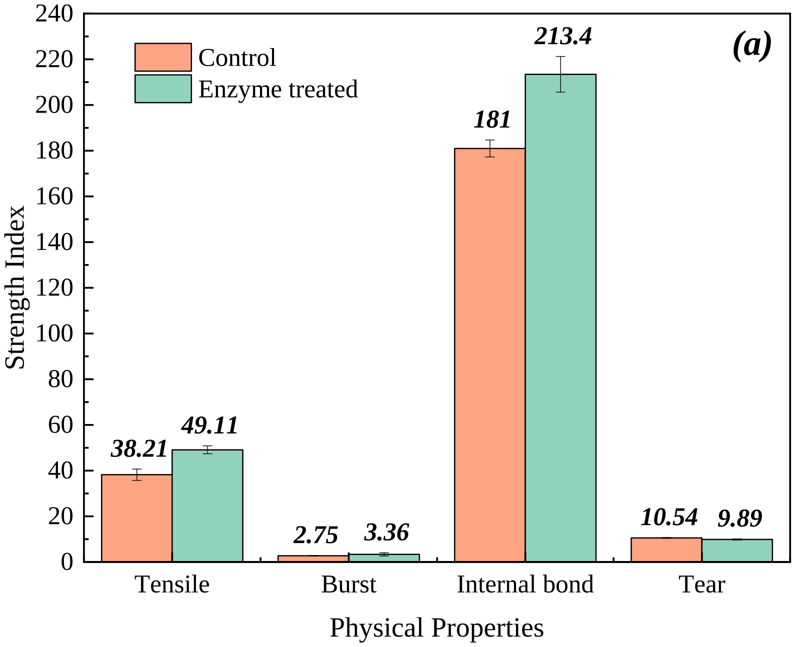
In the filtrate liquid from enzyme treated pulp suspension, the presence of glucose was observed. With 0.1 mg/g enzyme, 10.6 mg glucose was released from 1 g dry fibers during 1 hour of treatment. The amount of glucose increased significantly to 14.7 mg/g and 17.9 mg/g with increasing enzyme dosage of 0.5 mg/g and 2.0 mg/g, respectively. When the treatment was extended to 4 hours, 26.1 mg glucose was released from the treatment with 2 mg/g enzyme. This is due to the hydrolysis of cellulose into glucose by cellulases. In cellulase enzyme system, endoglucanase randomly hydrolyzes that β-1,4-glycosidic bonds, reducing the polymerization of cellulose molecules; and exoglucanase removes glucose units from the nonreducing end of the chain and hydrolyzes cellulose and cellooligosaccharides to produce cellobiose; meanwhile, β-glucosidase degrades cellobiose to yield glucose.

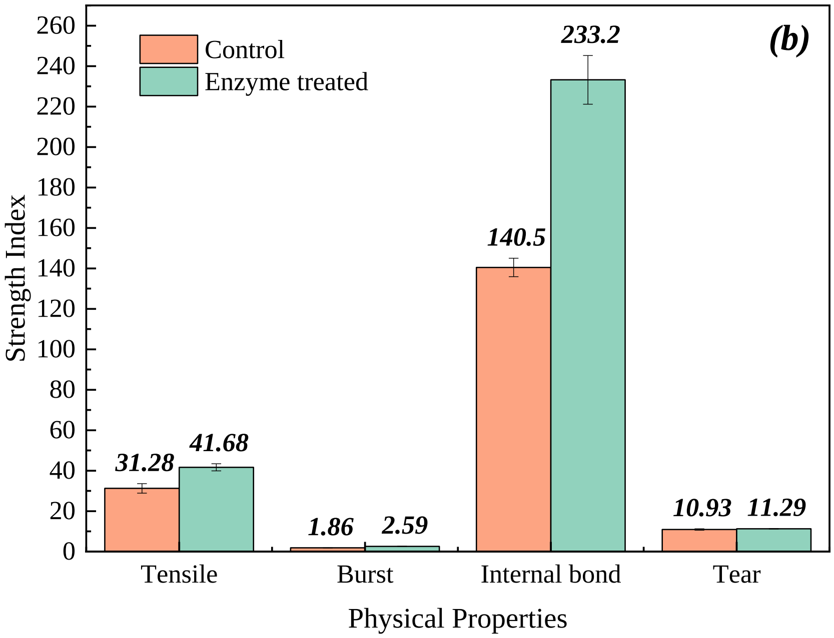
Table 5.3. Release of reducing sugars by enzyme modification.

Treatment conditions	Reducing sugars (mg /g o.d. fiber)	
	AVG	STD
Control	0	-
0.1 mg/g, 1hr	10.6	0.54
0.5 mg/g, 1hr	14.7	0.84
2.0 mg/g, 1hr	17.9	1.01
2.0 mg/g, 4hr	26.1	0.67

5.3.6 Strength Improvement on Multiple Wastepaper Grades

The enzyme pretreatment assisted mechanical refining of secondary fibers to create more surface fibrillation and made fibers more flexible for closer inter-fiber contact. The impact of enzyme pretreatment on the physical properties of remanufactured paper sheets was investigated. Secondary fibers from multiple wastepaper grades including old corrugated container (OCC), old newsprint (ONP), mixed office wastepaper, and Residential wastepaper (RW) were treated with 0.1 mg/g multi-component enzyme formulation at 50°C for 1hr, followed by PFI refining at 4000 revolutions to yield approximately 400ml CSF. TAPPI standard 60 g/m^2 handsheets were made using enzyme treated fibers, and the physical properties including tensile strength, tear resistance, burst strength, and internal fiber bonding were determined and compared to that of sheets made from control fibers. The physical properties of OCC sheets, RW sheets, ONP sheets, and MOW sheets are presented in Fig. 5.11(a)-(d), respectively.


(a)
Control
Enzyme treated
Strength Index
240
220
200
180
160
140
120
100
80
60
40
20
0
38.21
49.11
2.75
3.36
181
213.4
10.54
9.89
Tensile
Burst
Internal bond
Tear
Physical Properties


(b)
Control
Enzyme treated
Strength Index
260
240
220
200
180
160
140
120
100
80
60
40
20
0
31.28
41.68
1.86
2.59
140.5
233.2
10.93
11.29
Tensile
Burst
Internal bond
Tear
Physical Properties

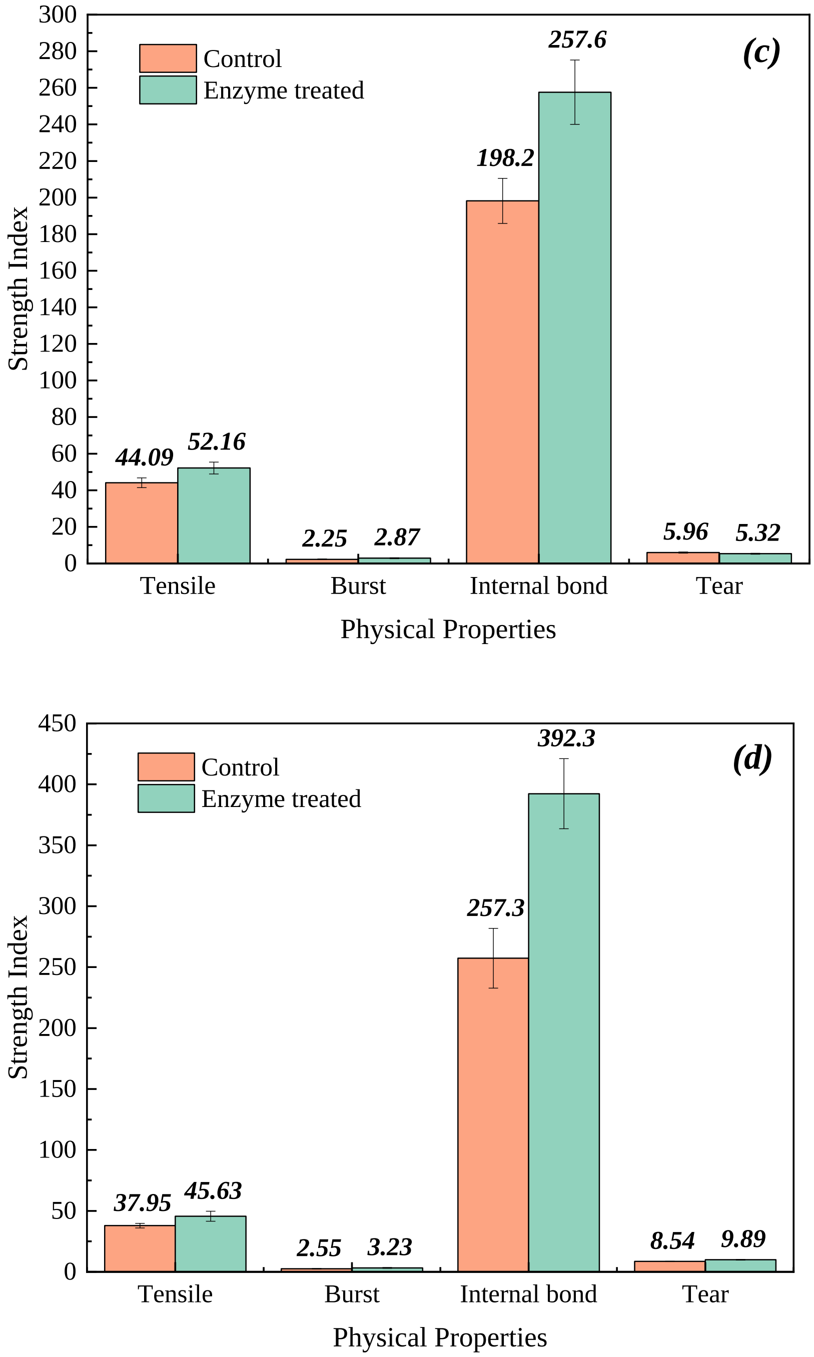


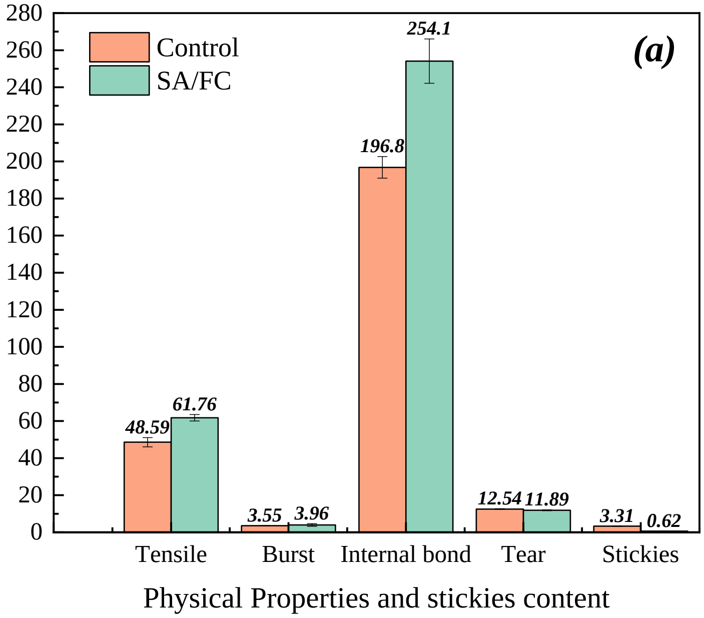
Figure 5.11. Improvements in physical properties of remanufactured paper made of (a) OCC fibers, (b) residential wastepaper fibers, (c) ONP fibers, (d) MOW fibers.

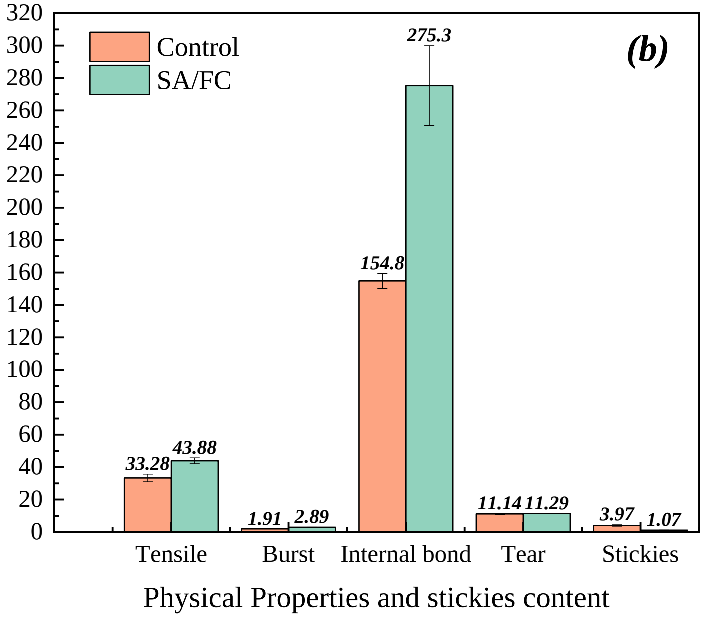
The combination of enzyme treatment and mechanical refining yielded significant improvement on physical properties of remanufactured paper sheets. For example, the tensile strength of OCC grade was improved by 28.5% from 38.21 N•m/g to 49.11 N•m/g, burst strength was improved by 22% from 2.75 kPa•m^2/g to 3.36 kPa•m^2/g, internal bonding strength improved by 17.9% from 181 J/m^2 to 213.4 J/m^2, and tear resistance strength slightly decreased by 6.2% from 10.5 mN•m^2/g to 9.9 mN•m^2/g, due to inevitable fiber shortening caused by enzymatic treatment. The improvement is even more significant on Residential Wastepaper grade, the tensile strength was improved by 33.2% from 31.28 N•m/g to 41.68 N•m/g, burst strength was improved by 39.2% from 1.86 kPa•m^2/g to 2.59 kPa•m^2/g, and internal bonding strength improved by 66% from 140.5 J/m^2 to 233.2 J/m^2. On ONP grade, the tensile strength was improved by 18.3% from 44.09 N•m/g to 52.16 N•m/g, burst strength was improved by 27.6% from 2.25 kPa•m^2/g to 2.87 kPa•m^2/g, internal bonding strength improved by 30% from 198.2 J/m^2 to 257.6 J/m^2, and tear resistance strength decreased by 11% from 5.96 mN•m^2/g to 5.32 mN•m^2/g.

5.3.7 Development of Enzyme-Aided Technology for Overall Quality Improvement

In the previous chapter, the efficiency of enzyme formulation SA and enzyme formulation RES on the removal of stickies in wastepaper has been investigated. Through optimization, both formulations can reduce sticky contaminants to below 0.5% in wastepaper grades. In this chapter, enzyme-aided mechanical refining with the addition of enzyme formulation FC had been identified to improve the physical properties of remanufactured paper sheets by 20%. In this section, the combination of these enzyme formulations was investigated to develop a single stage enzymatic treatment to achieve contamination removal and quality improvement at the same time. In the work, multiple grades of wastepaper were treated at 50^{o}C for 1hr with the addition of 0.25mg/g formulation SA or RES (stickies removal enzymes) in combination with 0.2 mg/g formulation FC (strength improvement enzyme). The contamination levels and strength properties were determined and presented in Fig 5.12, and Fig. 5.13.

The combination of formulation SA and FC yielded significant improvement on the physical properties of remanufactured paper sheets. For example, in OCC grade, the tensile strength was improved by 27.1% from 48.59 N·m/g to 61.76 N·m/g, burst strength was improved by 11.5% from 3.55 kPa·m^2/g to 3.96 kPa·m^2/g, internal bonding strength improved by 29% from 196.8 J/m^2 to 254.1 J/m^2, and tear resistance strength slightly decreased by 5.2% from 12.54 mN·m^2/g to 11.89 mN·m^2/g, due to inevitable fiber shortening caused by enzymatic treatment. The improvement is even more significant on Residential Wastepaper grade, the tensile strength was improved by 31.9% from 33.28 N·m/g to 43.88 N·m/g, burst strength was improved by 51.3% from 1.91 kPa·m^2/g to 2.89 kPa·m^2/g, and internal bonding strength improved by 77.9% from 154.8 J/m^2 to 275.3 J/m^2. On MOW grade, the tensile strength was improved by 17.8% from 44.95 N·m/g to 52.94 N·m/g, burst strength was improved by 19.6% from 2.91 kPa·m^2/g to 3.48 kPa·m^2/g, internal bonding strength improved by 34.5% from 313.7 J/m^2 to 422.1 J/m^2, and tear resistance strength slightly increased by 11.9% from 9.22 mN·m^2/g to 10.32 mN·m^2/g. On ONP grade, the tensile strength was improved by 21.4% from 47.09 N·m/g to 57.16 N·m/g, burst strength was improved by 24.3% from 2.47 kPa·m^2/g to 3.07 kPa·m^2/g, internal bonding strength improved by 33.5% from 240.2 J/m^2 to 320.6 J/m^2, and tear resistance strength slightly increased by 16.3% from 6.29 mN·m^2/g to 7.32 mN·m^2/g.


(a)
Control
SA/FC
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
48.59
61.76
3.55
3.96
196.8
254.1
12.54
11.89
3.31
0.62
Tensile
Burst
Internal bond
Tear
Stickies
Physical Properties and stickies content


(b)
Control
SA/FC
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
33.28
43.88
1.91
2.89
154.8
275.3
11.14
11.29
3.97
1.07
Tensile
Burst
Internal bond
Tear
Stickies
Physical Properties and stickies content

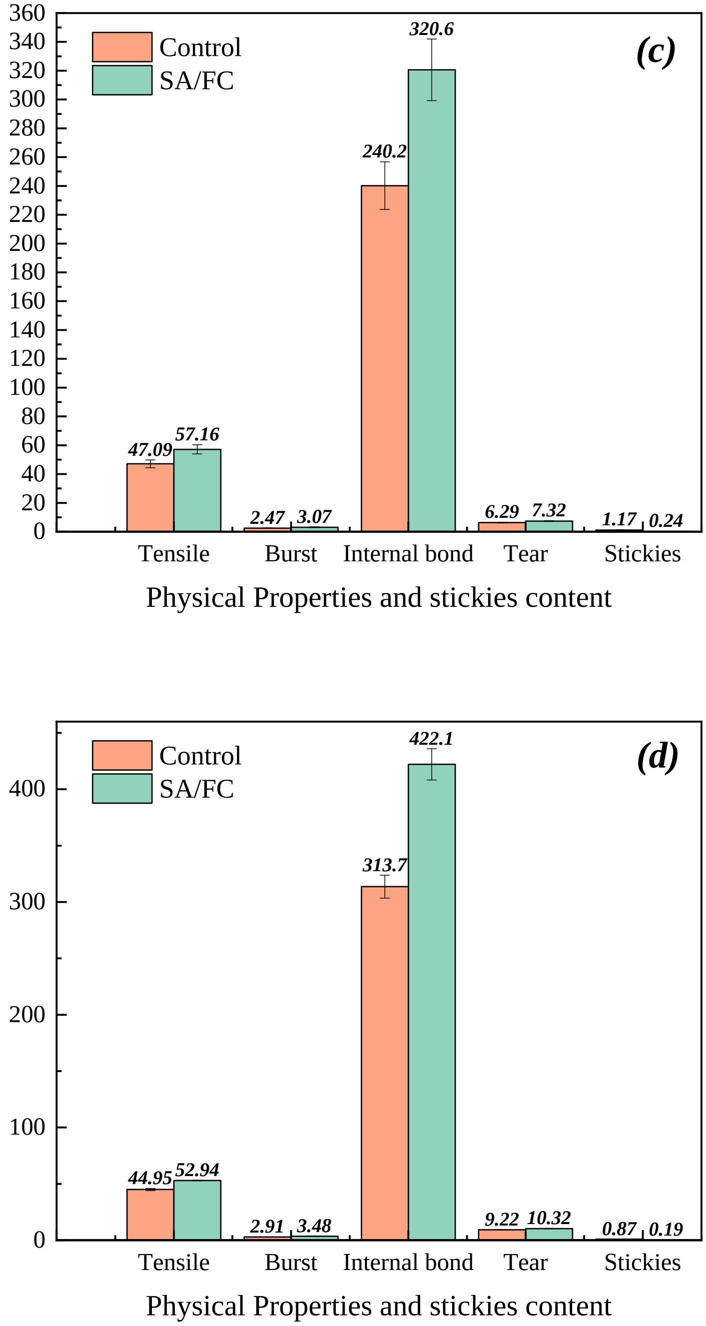


Figure 5.12. Properties of remanufactured paper made of recycled fibers treated by Enzyme SA/FC (a)OCC, (b) RW, (c) ONP, and (d) MOW.

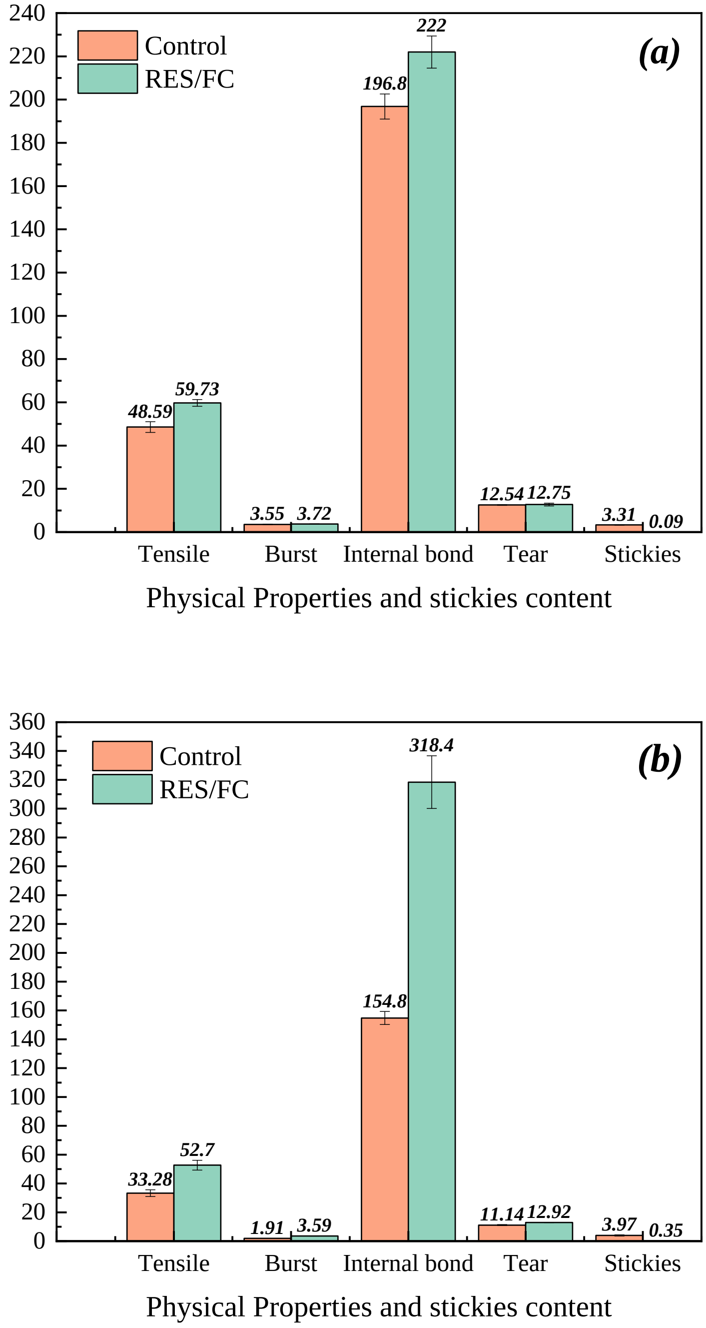


Figure 5.13. Properties of remanufactured paper made of recycled fibers treated by Enzyme RES/FC (a)OCC, (b)RW.

In Chapter 4, enzyme formulation RES exhibited higher efficiency than that of formulation SA under optimal reaction conditions. The combination of formulation RES and FC was also investigated for quality improvement, and the results are presented in Fig 5.13. On OCC grade, the tensile strength was improved by 22.8% from 48.6 N·m/g to 59.7 N·m/g, burst strength was improved slightly by 4.8% from 3.55 kPa·m^2/g to 3.72 kPa·m^2/g, and internal bonding strength improved by 12.8% from 196.8 J/m^2 to 222 J/m^2. On Residential wastepaper, the tensile strength was improved by 58.3% from 33.3 N·m/g to 52.7 N·m/g, burst strength was improved by 88% from 1.91 kPa·m^2/g to 3.59 kPa·m^2/g, internal bonding strength doubled from 154.8 J/m^2 to318.4 J/m^2, and tear resistance strength increased by 16% from 11.14 mN·m^2/g to 12.92 mN·m^2/g.

5.3.8 Pilot Trials of Developed Enzyme-Based Technology

The performance of enzyme formulations was further verified in pilot scale trials using industrial level facility at WMU Paper Pilot Plant. The pilot recycling process starts with repulping in a 1.83 m (6 ft) high-consistency Hydrapulper which breaks down wastepaper into fiber suspension at a consistency between 5-15 wt%. The extraction plate which is installed at the bottom of Hydrapulp has 15.88 mm (5/8 inch) openings. As fiber suspension passes through the extraction plate, oversize contaminations such as plastic bags, metal, glass, Styrofoam, wet-strength flakes, etc., are removed. The pulp slurry passes through two Pressure Screens – one coarse screen equipped with 1.52 mm (0.06 inch) slots and one fine screen equipped with 0.254mm (0.01 inch) slots. When compared to the extraction plate in Hydrapulper, smaller contaminants are removed through Pressure Screens including plastic particles, bark, grits, fiber bundles, etc. Beyond this point, contaminants that have similar sizes of fibers will be removed through Centrifugal Cleaners or Hydrocyclone Cleaners. The hydrocyclone cleaner employs centrifugal forces generated by swirling fluid motion to separate solid particles from the pulp suspension by density. Two types of hydrocyclone cleaners are utilized at WMU Paper Pilot Plant: Forward

Cleaners and Reverse Cleaners. Forward Cleaners remove contaminants with a specific gravity greater than 1.0. In a forward cleaner the centrifugal force on the high specific gravity particles reaches the wall and becomes entrained in a flow that is moving along the wall towards the exit at the bottom of the cone. Most of the desired fibers are dragged inward and upward to leave the hydrocyclone via the top. Such heavy contaminants include metal, glass, sand, grits, stones, etc. Reverse Cleaners are used to remove contaminants from pulp suspension which have densities less than water. For such particles drag and buoyancy forces are greater than the centrifugal forces, so they tend to move towards the core of the hydrocyclone. Such low-density contaminants include plastics, polystyrene foam, adhesives, macro-stickies, and waxes. Beyond this, cleaned pulp suspension is then stored in stock chests for remanufacturing.

In this trial, old corrugated containers (OCC) were recycled and remanufactured into linerboard grade paper sheets. The recycling process started with repulping OCC in a high consistency hydrapulper to break down wastepaper into fiber suspension at 8% consistency and neutral pH for 30 min. Subsequently, the pulp slurry passed through a pressurized screen with 0.254 mm (0.01 inch) slots to remove oversize contaminants including plastic, wet-strength flakes, Styrofoam, tapes, and macro-stickies. Clean pulp slurry was then stored in a stock chest. The combination of stickies removal enzyme formulation SA and refining enzyme formulation FC was employed in this trial with 3 different dosages from low to high. As shown in Table 5.4, each dosage was added into an independent stock chest at 2% pulp consistency, 37.8°C (100°F), pH 7.4, and for the duration time of 1hr. Control pulp was treated the same except without the addition of enzyme. All pulp slurry was then refined using a double disk refiner with the same energy input, followed by remanufacturing into 0.5 m (20 inch) wide linerboard paper on a fourdrinier paper machine. The pilot trial ran continuously for 8 hrs and produced 635 kg (1400 lb) remanufactured linerboard paper.

Table 5.4. Pilot trial conditions.

	Control	Dosage A (0.2 mg/g)	Dosage B (0.5 mg/g)	Dosage C (1.0 mg/g)
Consistency (wt%)	2.1	1.9	2.0	1.8
Temperature (ºC)	40	38.9	36.7	37.8
pH	7.4	7.5	7.6	7.4
Duration time (min)	60	60	60	60

Paper sheets were sampled during the trial period from each condition. The sheets were conditioned in standard TAPPI testing lab for 24 hrs. prior to testing. The contamination concentrations were determined using solvent extraction method following TAPPI standard T204, and the results are shown in Fig. 5.14. All three dosages are found effective in reducing contamination concentrations in OCC grade wastepaper to below 0.5% in the pilot scale remanufacturing process.

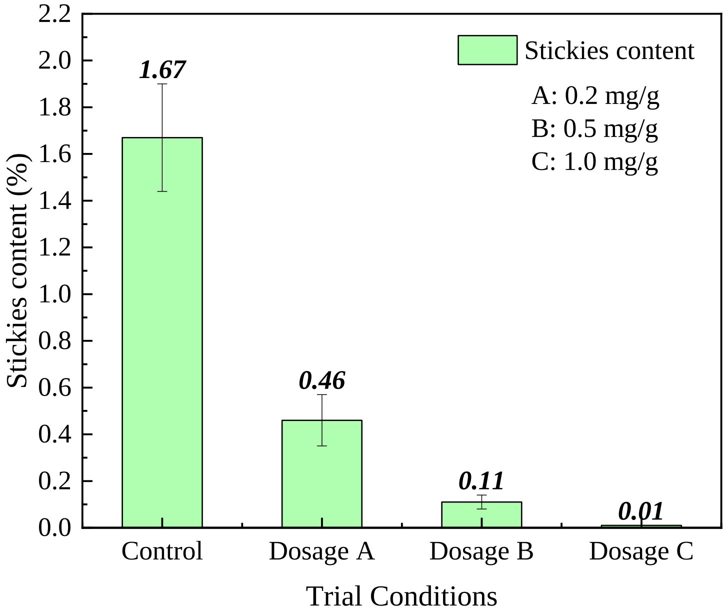


Figure 5.14. Concentration of stickies in remanufactured paper sheet from pilot trial.

Table 5.5. Fundamental properties of remanufactured paper sheets from pilot trial.

	Control	Dosage A (0.2 mg/g)	Dosage B (0.5 mg/g)	Dosage C (1.0 mg/g)
Basis weight (g/m^2)	137.6	143.0	145.9	133.4
Thickness (um)	213	241	242	260
Density (g/cm^3)	0.66	0.60	0.61	0.52
Moisture (wt%)	6.7	6.8	6.3	6.0
Freeness (ml)	495	461	456	430

Table 5.6. Physical properties and improvement % of remanufactured paper sheets.

	Control	Dosage A (0.2 mg/g)	Dosage B (0.5 mg/g)	Dosage C (1.0 mg/g)
Burst strength index (kPa·m^2/g)	2.19	2.25 *(+2.7%)*	2.46 *(+12.3%)*	2.72 *(+24.2%)*
Internal bond strength (J/m^2)	222	233 *(+5.2%)*	281 *(+26.8%)*	308 *(+38.8%)*
Tensile strength – MD (N·m/g)	33.94	34.88 *(+2.8%)*	38.27 *(+12.8%)*	42.00 *(+23.7%)*
Tensile strength – CD (N·m/g)	15.12	17.74 *(+17.3%)*	20.79 *(+37.5%)*	21.80 *(+44.2%)*
Tear resistance – MD (mN·m^2/g)	9.9	11.5 *(+16.2%)*	12.0 *(+21.2%)*	9.3 *(-6.1%)*
Tear resistance – CD (mN·m^2/g)	12.3	13.5 *(+9.8%)*	11.7 *(-4.9%)*	10.3 *(-16.3%)*

Trial sheets were made to be used as linerboard with basis weight in the range of 130-150 g/m^2. As shown in Table 5.5, all trial conditions meet this target, and the trial enzyme formulation did not have any negative impact on pulp drainage and machine runnability. As shown in Table 5.6, the physical strength properties of trial sheets are found enhanced remarkably by the treatment with all three dosages. The burst strength of trial sheets treated at lower dosage (0.2mg/g) improved slightly by 2.7% from 2.19 kPa·m^2/g to 2.25 kPa·m^2/g, while the internal bond strength improved by 5.2% from 222 J/m^2 to 233 J/m^2. Cross direction tensile strength improved significantly by 17% from 15.1 N·m/g to 17.7 N·m/g, and the machine direction tear resistance also increased significantly by 16% from 9.9 mN·m^2/g to 11.5 mN·m^2/g. As enzyme dosage increased to 0.5 mg/g, further improvement on the physical strength properties was observed. The burst strength increased by 12.3% to 2.46 kPa·m^2/g, internal bond strength improved by 26.8% to 281 J/m^2, tensile strength increased to 38.27 N·m/g (MD, by 12.8%) and 20.79 N·m/g (CD, by 37.5%), and the tear resistance enhanced to 12.0 mN·m^2/g (MD, by 21.2%). The high dosage 1.0 mg/g enzyme delivered even more remarkable improvement on fiber quality: all properties improved significantly by up to 40%, except tear resistance. The burst strength of remanufactured paper sheet improved significantly by 24% from 2.19 kPa·m^2/g to 2.72 kPa·m^2/g, while the internal bond increased by 39% from 222 J/m^2 to 308 J/m^2. In addition, MD tensile strength increased by 24% from 33.9 N·m/g to 42.0 N·m/g and CD tensile strength improved by 44% from 15.1 N·m/g to 21.8 N·m/g. Tear resistance decreased slightly on MD by 6.1% from 9.9 mN·m^2/g to 9.3 mN·m^2/g and significantly on CD by 16% from 12.3 mN·m^2/g to 10.3 mN·m^2/g. This is caused by the inevitable fiber shortening in the refining process. A similar effect was observed in medium dosage of 0.5 mg/g, where CD tear resistance was slightly reduced by 4.9%. Detailed physical strength properties of trial sheets are presented in Fig. 5.15-5.18.

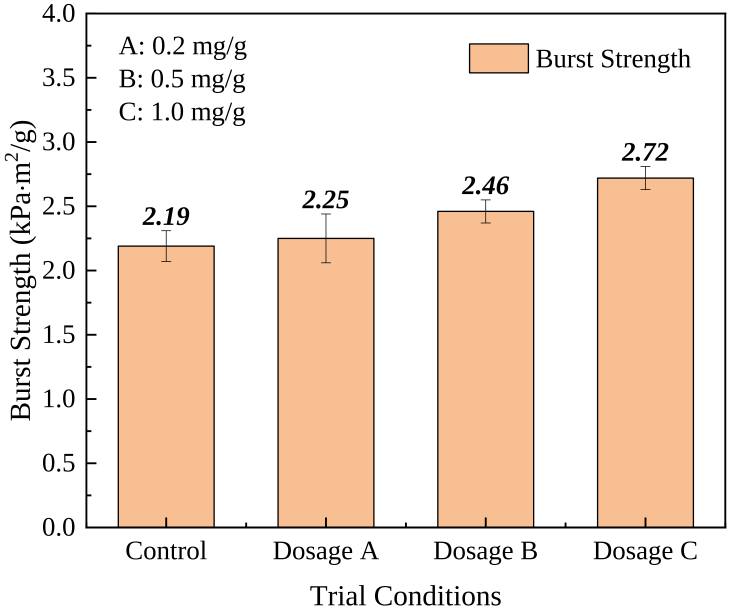


Figure 5.15. Burst strength of remanufactured paper sheet from pilot trial.

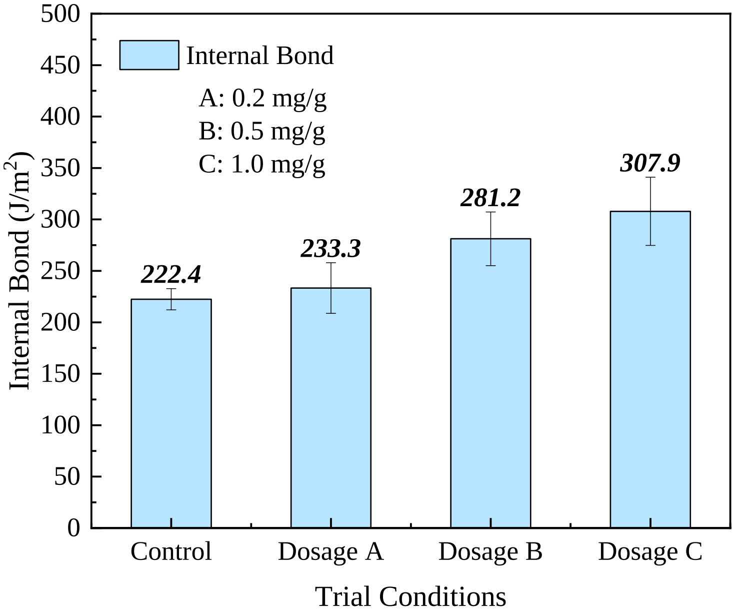


Figure 5.16. Internal bond strength of remanufactured paper sheet from pilot trial.

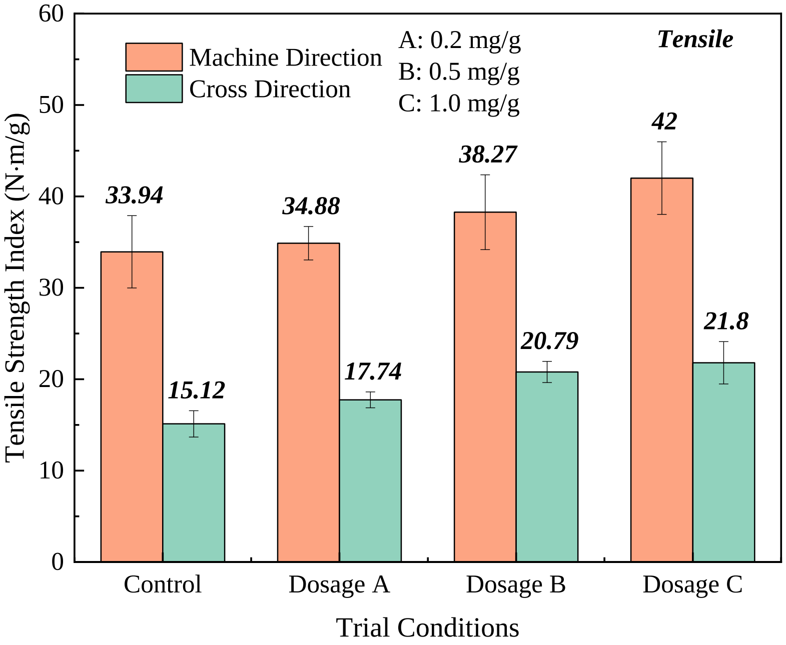


Figure 5.17. Tensile strength of remanufactured paper sheet from pilot trial.

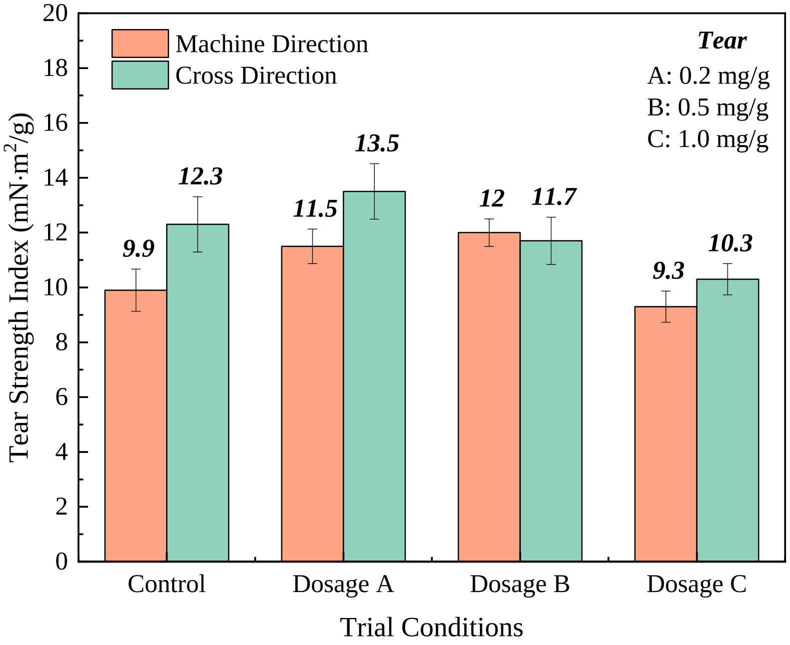


Figure 5.18. Tear strength of remanufactured paper sheet from pilot trial.

5.4 Conclusions

In this work, the effects of enzyme modification of secondary fibers on the subsequent mechanical refining process on the fiber properties were investigated and discussed. The results indicated that enzyme pretreatment can emphasize the subsequent refining effects and significantly affect the fiber surface structure, leading to improvements in recycled fiber quality. The release of reducing sugars and the increase of crystallinity index before and after enzyme modification explain that enzymes, especially cellulases, preferentially attack the amorphous regions of cellulose, and hydrolyze cellulose into glucose. Additionally, SEM revealed that the fiber cell wall structure and inner layers were loosened after enzyme modification, making the fibers much more flexible and collapsible. As a result, with the same amount of energy input, significant improvements on both internal and external fibrillation were achieved through enzyme pretreatment. The swelling capacity of secondary fibers was improved by up to 20%. From another perspective, refining energy can be reduced by 20-30% with enzyme pretreatment without any impact on fiber properties. Inevitable fiber shortening and fines formation were observed from FQA analysis, however, no significant deterioration was observed with enzyme pretreatment at moderate refining levels.

By combining stickies removal enzymes and strength improvement enzymes, the enzyme-assisted mechanical refining process can achieve contamination removal and quality improvement in one-step treatment. When applied together, significant improvements in remanufactured paper quality were observed on multiple wastepaper fibers. On OCC grade and ONP grade, 18-30% improvements were achieved on multiple physical properties including tensile strength, burst strength, and internal fiber bonding strength. When the enzyme was applied to residential wastepaper, 33-66% improvements were achieved.

A pilot trial was carried out to validate the lab results with industrial protocols. In the trial, OCC was recycled and remanufactured into linerboard grade paper sheets. The recycling process started with repulping in a high consistency hydrapulper followed by screening with 0.25 mm (0.01 inch) slots. Formulation SA/FC dosage ranging from low to high (0.2 mg/g to 1.0 mg/g) was applied. All three dosages are found effective in reducing contamination concentrations to an acceptable level (<0.5%). Remarkable improvements in paper quality were achieved as well. Maximum improvements in burst strength and internal bond strength were 24% and 39%, respectively. Tensile strength improved by 24% on MD and 44% on CD. Tear resistance increased with low and medium dosage, then declined in the case of high dosage. This was due to the fiber shortening effect of refining.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The use of recycled fibers continues to grow as the demand and requirement for carbon footprint reduction surges. However, the growth trend discontinued in the past decade due to the difficulties when manufacturing paper from recycled fibers, mainly due to the presence of sticky contaminants and the loss of strength in repeated recycling processes. The application of enzymes in the pulp and paper industry has tremendously improved the green and sustainable development of this industry, not only by increasing the pulp yield and physical properties of paper, but also simultaneously reducing energy consumption in a more environmentally friendly way. In this dissertation, the author investigated enzyme-based technologies for the removal of stickies contaminations and to improve remanufactured paper quality in combination with mechanical refining approach.

First, an integrated methodology utilizing solvent extraction and multiple analytical techniques was developed to identify the organic sticky contaminants presented in multiple wastepaper grades and to reveal the fundamental properties of these sticky contaminants. The quantity of stickies, number, size, and chemical composition vary by different grade. Most wastepaper grades collected from local paper recycling mills contains 3-5 wt.% stickies, while a curb side collected grade contains 15 wt.% stickies. Microscope analysis revealed that the average size of these stickies presented in recycled paper sheets is in the range between 0.4 to 1.2 mm^2 depending on the wastepaper grade. Additionally, the chemical analysis of THF extracted stickies by FTIR and GC/MS provided evidence that the major components in the contaminants are polyvinyl acetate (PVAc) polymers, styrene butadiene rubber (SBR), paraffin wax, resin, and polyamines. In addition, these stickies deposit heavily on fiber surface leading to high negative charge in fibers suspension ranging between 2~4.5 mmol/L and high negative charge on fiber surface up to 2.1 mmol/g. Furthermore, the removal of stickies by solvent extraction can improve the quality of recycled paper products indicated by comparing the physical strength properties of recycled paper sheets prior and after stickies extraction. The findings on fiber-stickies interaction provided fundamental understanding of stickies behaviors on fiber surface. SEM images reveal that sticky contaminants cover fiber surface, reduce contacting areas, and occupy accessible hydroxyl groups, thus leads to reductions in paper strength.

Secondly, the research aimed to develop an enzymatic strategy to solve the problem of sticky deposits in wastepaper recycling. The stickies removal efficiency of three enzymes were investigated, and the two enzyme formulations presented higher overall performance when comparing to a commercial lipase. Enzymatic treatment temperature, pH, residence time and enzyme dosage play critical role in the process, and the results indicated the optimal conditions for enzymatic stickies removal is 65^{o}C, 30-60min, in slightly alkaline (pH 8.0) environment. At optimal condition, 86.1% stickies were removed by enzyme formulation SA and 93.4% stickies were removed by enzyme formulation RES. Under extreme conditions, enzyme SA exhibited excellent stability while commercial lipase experienced significant deactivation. In practice, over 80% stickies can be removed by enzyme SA when applied on multiple grades of wastepaper, including OCC, ONP, DLK, and MOW. The findings provided evidence that multi-component enzyme formulations are effective against stickies and have great stability under extreme conditions. Additionally, fiber surface structure was characterized using SEM and AFM. The findings revealed enzyme actions on stickies at micro-scale level. At micro-scale level, stickies deposits were observed as tar-like material that attached to fiber and covered microfibrils on fiber surface. After enzyme treatment, the stickies deposits were removed, and microfibrils were exposed on fiber surface. Furthermore, the removal of stickies can slightly improve the strength properties of remanufactured paper. In OCC grade, strength properties increased by 8-11% when 88% of stickies are removed by enzyme formulation SA.

Additionally, the modification of secondary fibers by enzymes in combination with subsequent mechanical refining to restore recycled fiber quality was developed. Significant improvement on both internal and external fibrillation were achieved through enzyme pretreatment. The swelling capacity of secondary fibers was improved by up to 20%. From another perspective, refining energy can be reduced by 20-30% with enzyme pretreatment without any impact on fiber properties. Inevitable fiber shortening and fines formation were observed from FQA analysis, however, no significant deterioration was observed with enzyme pretreatment at moderate refining levels. This work also revealed the fundamental mechanisms behind enzyme modification of wood fiber ultrastructure. The releasing of reducing sugars and XRD results indicated that enzymes preferentially attack the amorphous regions of cellulose, and hydrolyze cellulose into glucose. In which case, fiber cell wall structure and inner layers were loosened after enzyme modification, making the fibers much more flexible and collapsible which was revealed by SEM images.

Furthermore, by combining stickies-removal enzymes and strength improvement enzymes, the enzyme-assisted mechanical refining process can achieve contamination removal and quality improvement in one step treatment. When applied together, significant improvements on remanufactured paper quality were observed on multiple wastepaper fibers. On OCC grade and ONP grade, 18-30% improvements were achieved on multiple physical properties including tensile strength, burst strength, and internal fiber bonding strength. When enzyme was applied on residential wastepaper, 33-66% improvements were achieved. Furthermore, the lab results were validated in a pilot trial following industrial protocols. Lab developed enzyme formulations were found effective to reduce contamination concentrations to an acceptable level (<0.5%), and deliver remarkable improvements on paper quality.

6.2 Future Work

Based on the results obtained and the experience gained during this research, the author believes that this work still has the scope to be expanded to understand the actions of enzymes under complex conditions in fiber recycling process, and the synergy between multiple enzymes applied on recycled furnish. There are a few suggestions that can be addressed in the future:

(1) To further enable adaption to the complex environment in paper recycling, it is necessary to develop innovative enzymes formulations with enhanced physical and chemical features such as their thermal stability, resistance to severe pH values and organic solvents.

(2) Further investigation in simulating natural multi-enzyme complexes can improve efficiency and reduce cost.

(3) It is also worth investigating the recycling of enzymes and end-of-life cycles. The enzymes used in the papermaking process are not consumed, and some of them remain in the system. Enzyme recovery can be considered to reduce the cost and improve efficiency.

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APPENDIX A

List of Author's Publications and Awards

A1. Journal Papers

1. **Wang, Y.**, Wang, H., Lin, H., Zheng, Y., Zhao, J., Pelletier, A., & Li, K. (2013). Effects of solvents and catalysts in liquefaction of pinewood sawdust for the production of bio-oils. *Biomass and bioenergy*, *59*, 158-167.
2. **Wang, Y.**, Lin, H., & Zheng, Y. (2014). Hydrotreatment of lignocellulosic biomass derived oil using a sulfided NiMo/γ-Al2O3 catalyst. *Catalysis Science & Technology*, *4*(1), 109-119.
3. **Wang, Y.**, Wang, H., Lin, H., Pelletier, A., Zheng, Y., & Li, K. (2013). Liquefaction of Pinewood in Supercritical Carbon Dioxide (SCCO2). *Current Organic Chemistry*, *17*(15), 1596-1603.
4. Zhou, B., **Wang, Y.**, Jiang, Z., Salam, A., & Li, K. (2021). How do xylanase and hot acid stages differ at enhancing elemental chlorine-free bleaching of hardwood kraft pulp? *Journal of Wood Chemistry and Technology*, *41*(4), 150-159.
5. **Wang, Y.**, Marcello, C., Sawant, N., Salam, A., Abubakr, S., Qi, D., & Li, K. (2023). Identification and characterization of sticky contaminants in multiple recycled paper grades. *Cellulose*, *30*(3), 1957-1970.
6. Li, P., Liu, H., Zhou, M., Lei, H., Jian, B., Liu, R., **Wang, Y.**, & Zhou, B. (2022). Preparation of green magnetic hydrogel from cellulose nanofibril (CNF) originated from soybean residue for effective and rapid removal of copper ions from waste water. *Industrial Crops and Products*, *186*, 115257.

7. Li, P., Zhou, M., Liu, H., Lei, H., Jian, B., Liu, R., **Wang, Y.**, & Zhou, B. (2022). Preparation of green magnetic hydrogel from soybean residue cellulose for effective and rapid removal of copper ions from wastewater. *Journal of Environmental Chemical Engineering*, *10*(5), 108213.

A2. Conference Papers and Presentations

1. **Wang, Y.**, Zheng, Y., Lin, H.F., Wang, H. (2011). Study of Bio-oil from Liquefaction of Pinewood Sawdust. *Canadian 61st Chemical Engineering Conference, London, ON, Canada, October 26, 2011.*
2. **Wang, Y.**, Li, P.Y., Zhou, B.Y., Li, K. (2018). Enzymatic Treatment of Recycled Pulp for Improved Inter-Fiber Bonding and Pulp Drainage. *PaperCon 2018, Charlotte, NC, April 16, 2018.* https://imisrise.tappi.org/TAPPI/Products/18/PAP/18PAP172.aspx
3. **Wang, Y.**, Marcello, C., Sawant, N., Salam, A., Abubakr, S., Qi, D., & Li, K. (2022). Identification and Characterization of Sticky Contaminants in Multiple Recycled Paper Grades. *TAPPICon 2022, Charlotte, NC, May 2, 2022.* https://www.playbacktappi.com/tappi2201-rpta1
4. **Wang, Y.**, Marcello, C., Sawant, N., Sood, S., Haider, Q., Salam, A., & Li, K. (2023). Enzyme-Based Biotechnologies for Removing Stickies and Regaining Fiber Quality in Paper Recycling. *REMADE Circular Economy Tech Summit & Conference, Washington, DC, March 20, 2023.*

A3. Honors and Awards

1. “Compostability Testing of Paper and Plastic Materials to Divert from Landfill”, Recycling Market Development Grant 2022, Michigan Department of Environment, Great Lakes, and

Energy (EGLE)

2. GSA Student Conference Grant 2023, WMU
3. Graduate Student Travel Grant 2022 Spring, WMU
4. Graduate Student Travel Grant 2022 Fall, WMU
5. CEAS Graduate Student Travel Grant 2022, WMU
6. Graduate Student Travel Grant 2018, WMU
7. CEAS Graduate Student Travel Grant 2018, WMU