

Assessment of enzymatic treatment and ultrasonication of wood and old corrugated container pulp as an alternative to refining

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Abstract

The effect of ultrasonication and enzymatic treatment on paper pulp was investigated as an alternative to conventional refining. The present study focused on three specific pulp types: Hardwood (*Eucalyptus globulus*), softwood (*Pinus radiata*) and recycled (old corrugated containers or OCC) pulps. The pilot-scale experiments were done using a single-disk refiner and Hielscher UID1000 ultrasonicator. Within each experiment, enzymatic treatment and ultrasonication amplitudes were varied. Endoglucanase was used for enzymatic treatment, and dosages as well as the sequences of treatments varied. The freeness of the pulp and the strength properties of the paper sheets made from the pulp were tested for each of the treatment combinations.

Ultrasonication was effective in modifying the pulp fibres at low energies (between 0 and 20 kWh/t). The stronger softwood fibres seemed to be effectively modified by ultrasonication. The strength properties of the hardwood and recycled fibres, however, could not be developed using ultrasonication without seriously affecting the freeness of the pulp. It seemed that ultrasonication at low to medium amplitudes (53 μm and 80 μm) was most effective in developing the hardwood and OCC fibres. Ultrasonication at medium to high amplitudes was most effective in developing the softwood fibres.

The combination of low enzymatic dosage and ultrasonication appeared to increase the tensile strength and the tear strength of the fibres more than ultrasonication on its own. The added enzymatic treatment did not, however, counter the decrease in freeness as expected. High enzymatic dosage (200 g/t) seemed to result in higher strength and freeness results at low energies (0 to 10 kWh/t). At higher energies, however, the strength and freeness results were similar when compared to the low enzymatic dosage (50 g/t) treatment. When the pulp was enzymatically treated after ultrasonication, there was no strength benefit, but the pulp freeness seemed to have increased.

Ultrasonication and enzymatic treatment seemed to be the most effective when treating softwood fibres. The reason may be that the softwood fibres were stronger

than the hardwood and OCC fibres and were efficiently modified by the longer treatment times. Ultrasonication did not appear to be a viable alternative to mechanical refining, due to the notably longer treatment times required to modify the fibres and the severe freeness decrease compared to mechanical refining. Ultrasonication may be considered as an effective pre-treatment for mechanical refining to limit the energy used.

Keywords: Endoglucanase, mechanical refining, paper pulp, ultrasonication

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CHAPTER 1: Introduction

1.1 General Introduction: Background and motivation

The growth in electronic technology over the last couple of years has placed the sales of paper and paper-based products at risk (Edmonds *et al.*, 2012; Wolfensberger, 2013). Not only do schools and tertiary institutions support the use of tablets and electronic copies of text books, but people also tend to download books and read them on electronic equipment (Robinson, 2013; Jacobs, 2013). The hotly debated argument over the future of newspapers is still under way. Some believe that newspapers are here to stay, but the majority of people believe that they would 'go the way of the vinyl' (McLeod, 2009). If this trend continues, it will severely affect the sales of paper-based products. In order to remain competitive, it is important to produce paper using energy-efficient processes.

Producing paper from wood is an energy-intensive process. The refining of pulp is one of the steps in the papermaking process that consumes the most energy, and is also the part of the process most in need of optimisation (Josefsson, 2010:1). This statement is based on the fact that mechanical refining is not only energy-intensive, but moreover reduces the strength of individual pulp fibres. Fibres are not only fibrillated, but are also cut and bent, thus increasing the amount of fine fibre material produced. While the production of fine fibre material improves the surface smoothness of the paper, an excess does have a negative effect on the paper properties, especially the freeness. Excess fine fibre material also clogs papermaking machinery, reducing the overall efficiency of the process (Miao *et al.*, 2013:1432).

The problem with mechanical refining is, however, not limited to the damage inflicted on the fibres. The problem is that the paper fibre has to be developed for optimal strength, and that the process used should be cost-effective. The method currently used for developing fibres, namely mechanical refining, is an expensive, energy-intensive process that can by no means be described as environmentally friendly based on the amount of energy used. The growth in technology puts extra strain on the process and forces paper mills to focus on optimisation and introducing new technology to solve and overcome these problems.

In view of this, alternative methods that use less energy and have a smaller impact on the fibre strength have been investigated, but have shown limited success. These alternative methods range from enzyme treatment of fibres prior to mechanical refining to combining ultrasonication and mechanical refining (Loosvelt, 2009:22; Yachmenev *et al.*, 2008:111).

1.2 Aims and objectives

The aim of this study was to test alternatives for the energy-intensive mechanical refining process by investigating ultrasonication and enzymatic treatment separately as well as in combination. The variables investigated during the ultrasonication experiments included the treatment energy applied and the amplitude, as well as the treatment time. In the case of the enzymatic treatment experiments, the enzyme dosage and treatment times were varied. For the combined experiments, ultrasonication and the enzymatic treatment sequence were also investigated.

All of the experiments were conducted utilising three of the most commonly used pulps and exposing them to a series of mechanical refining, ultrasonication and enzymatic treatments. Following the treatments, a series of tests were done to determine the freeness and strength properties of these modified pulps.

1.3 Scope

In order to achieve the aims and objectives outlined in Section 1.2, the study was divided into the following chapters:

- Chapter 2: Literature reivew
 - Previous studies on mechanical refining, ultrasonication and enzymatic treatment, or the combination of these, were researched.
 - Different enzymes, wood types and the paper production process were also researched.
- Chapter 3: Materials and methods
 - The experiment was designed to ensure that all treatment and testing procedures were consistent through all experiments.

- A testing procedure was set up to ensure accurate testing and information gathering.
- Chapter 4: Hardwood experiment results and discussion
 - Using previous studies and the experimental design and testing procedures set up as described in the preceding chapters, the hardwood pulp results were reported and discussed.
- Chapter 5: Softwood experiment results and discussion
 - Using previous studies and the experimental design and testing procedures as described in the preceding chapters, the softwood pulp results were reported and discussed.
- Chapter 6: Old corrugated containers results and discussion
 - Using previous studies and the experimental design and testing procedures as described in the preceding chapters, the OCC pulp results were reported and discussed.
- Chapter 7: Conclusions and recommendations
 - All the experiments are reviewed to compare the findings and consider the positive and negative results.
 - Based on the results, the exact process could be identified as an alternative to mechanical refining.

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CHAPTER 2: Literature review

2.1 Introduction

Paper is a product used in many different applications worldwide. The majority of paper products are used for wrapping, packaging, hygiene and information handling (Smook, 1997:1). Paper is made by converting raw plant material including wood to a low-consistency pulp. The consistency of the pulp refers to the quantity of solids per unit volume of pulp (Bierman, 1996:18). The pulp is then bleached using selective bleaching agents, such as chlorine, chlorine dioxide and oxygen (Sjöström, 1993:194). Bleaching agents decolour and degrade the lignin, whereafter the bleached pulp is refined (Bierman, 1996:123, 128). The modified pulp is fed to a paper machine, which converts it to paper (Bierman, 1996:123; Smook, 1997:36). This review will focus on the refining section of the papermaking process.

The refining phase determines the quality of the end product; it is therefore crucial that the refining phase is effective (Lumiainen, 2000:1). During the refining phase the pulp fibres are collapsed and the primary fibre walls are loosened to promote fibre to fibre bonding (Ek *et al.*, 2009:440; Lumiainen, 2000:2; Smook, 1997:197). Mechanical refining is one of the most expensive processes in paper production due to the large amounts of energy needed to refine the pulp to the desired level (Josefsson, 2010:1), hence any alternatives to the mechanical refining process are of interest.

The use of fibre-modification enzymes in the mechanical refining process has been investigated as an alternative, due to the enhanced fibre processing capabilities of this application (Yachmenev *et al.*, 2002:559). Fibre-modifying enzymes do not only save energy, they can also improve and change the fibre properties of pulp (Blomstedt *et al.*, 2010:1164). The fibre-modifying enzymes on their own do not produce the desired modification effect, hence a form of mechanical refining is needed (Loosvelt, 2009:2).

Ultrasonication has the capability to induce effects similar to that of mechanical refining on the fibre properties (Josefsson, 2010:33). Based on the energy consumption and duration of ultrasonication, the refining results in terms of fibre development were promising, though the financial implications were not resolved (Josefsson, 2010:33; Shi *et al.*, 2013:897; Thompson & Doraiswamy, 1999:1216).

Combining ultrasonication with enzymes has proven effective in enhancing the properties of recycled paper, but regarding inter-fibre bonding properties it is considered a mild treatment compared to mechanical refining (Da Silva *et al.*, 2013:659).

2.2 Pulp types used in experiments

Softwood species include conifers, or needle-leaved trees (Bierman, 1996:16). The softwood species also do not have vessels like the hardwood, because the wood cells (tracheids and ray cells) are open, enabling them to act as conduits and transport nutrients and water throughout the tree (Bierman, 1996:16; Sjöström, 1993:7). Softwood is used to increase the tear strength in paper due to the longer fibre length of the tracheids (Bierman, 1996:16). An example of softwood and hardwood at 144x magnification can be seen in Figure 2.1.

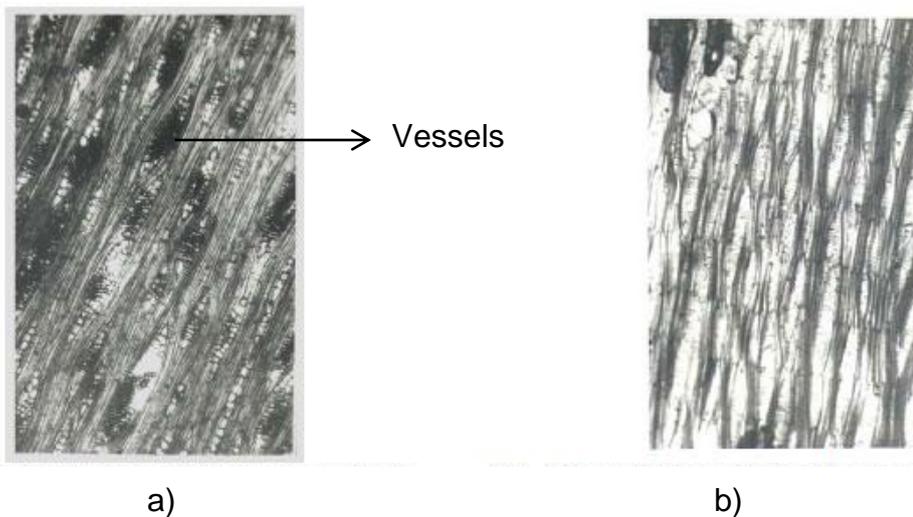


Figure 2.1: a) *Khaya senegalensis* (Hardwood) b) *Triplochiton scleroxylon* (Softwood), both at 144x magnification, showing vessels in hardwood and lack of vessels in softwood (Boeing Consult, 2014).

Environmental sustainability has caused an increase in the demand for recycled fibres, where old corrugated containers (OCC) are one of the primary fibre resources used in papermaking (Chen *et al.*, 2011: 298; Guo *et al.*, 2011:5). It is difficult to identify the mixture of fibres found in OCC pulp, because the pulp has been recycled multiple times. It is speculated that OCC consists of a mixture of unbleached softwood and

recycled OCC for the lining and OCC for the corrugating flute. The structure can be seen in Figure 2.2.

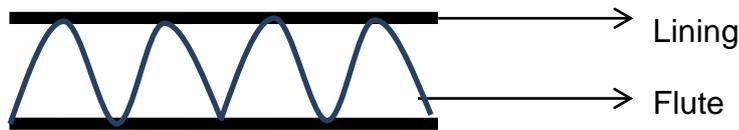


Figure 2.2: OCC structure showing the flute (corrugating medium) and lining. (Redrawn from Tiêng Anh Ky Thuât, 2014).

2.3 Mechanical refining

In the papermaking process the refining phase is defined as the modification of the fibres so that they can be used to produce paper or board with the desired properties. (Bierman, 1996:137; Josefsson, 2010:2). The main purpose of refining is to improve the bonding ability of the fibres so they can form smooth and strong paper sheets with good printing qualities (Ek *et al.*, 2009:440; Smook, 1997:197). The refining effects might be better understood if the physical properties of a fibre is investigated.

In single-disk mechanical refining there is only one rotor and one stator. The extent of refining depends on the gap between the bar and grooves on the stator and the rotor disks. Water is forced out of the fibre flocs when the edge of the rotor meets the edge of the stator. As the water is forced out, the fibre flocs are compressed (Josefsson, 2010:2; Lumiainen, 2000:1). Following the compression of the fibre flocs, the rotor and stator edges slide along the fibre flocs and press them against the flat surface of the bar. The movement of the flocs induces vortex flows and promotes fibre stapling on the bar edges. There are two types of consistency refining: low and high (Bierman, 1996:140). In low consistency refining the gap between the rotor and stator is approximately 100 μm , which promotes more fibrillation and fibre cutting (Bierman, 1996:140). This gap size corresponds to an average thickness of two to five swollen fibres or ten to twenty collapsed fibres (Lumiainen, 2000:1-2). The typical structure of a single disk mechanical refiner can be seen in Figure 2.3.

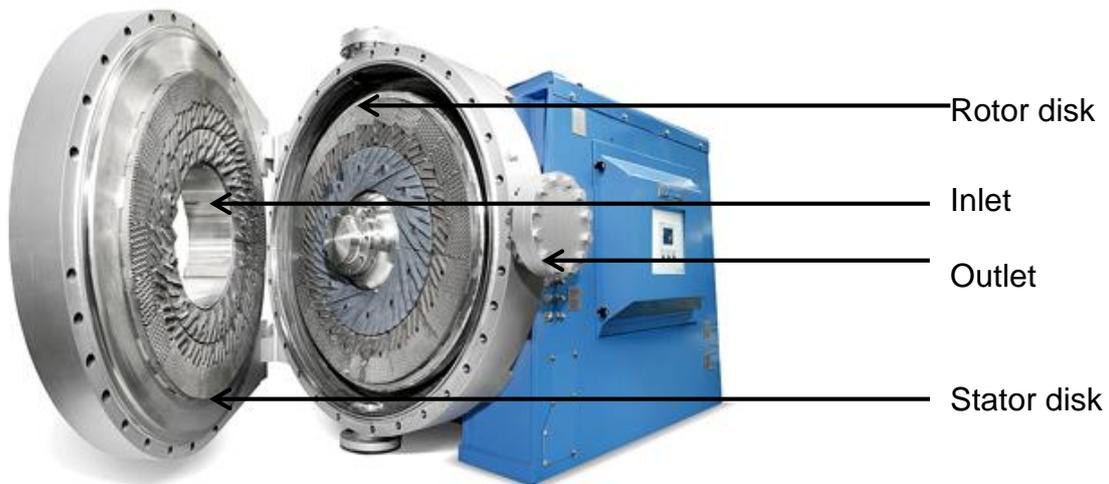


Figure 2.3: Typical structure of a single disk mechanical refiner (Andritz, 2014).

The amount of refining can be evaluated by investigating the specific refining energy (SRE) in kWh/t, and the refining intensity, SEL (specific edge load), in J/m. The definitions can be noted in equations 1 and 2 respectively (Lumiainen, 2000: 4).

$$SRE = \frac{Pt - Pn - Pe}{F * C} \quad (1)$$

$$SEL = \frac{Pt - Pn - Pe}{Zr * Zst * l * n - L * n - Ls} \quad (2)$$

- Where:
- Pt is the total absorbed power [kW]
 - Pn is the no load power/ idling power [kW]
 - Pe is the effective running power (net power) [kW]
 - F is the flow of the pulp [L/min]
 - C is the consistency [%]
 - Zr, Zst refers to the number of rotor/ stator bars
 - l is the common contact length of opposite bars [km]
 - L is the cutting edge length [km/rev]
 - n is the rotation speed [1/s]
 - Ls is the cutting speed of the bars [km/s]

As per equation 1 above, the SRE can be explained as the net amount of energy imparted on the fibres after allowing for the no-load energy needed to run the refiner. The SEL was introduced by Wultsch & Flucher (1958: 334-342) and developed by Brecht and Siewert (1966:4-14), where the SRE was applied to the number of bar crossings within the refiner, as can be seen in the similarity of equation 2 and equation 1.

The most important effects of refining as listed in Chapter 4 of *Refining of Chemical Pulp* (Lumiainen, 2000) are cutting and shortening of fibres, external and internal fibrillation, removal of colloidal material and redistribution of hemicellulose.

During the refining process wood fibres are cut and shortened, producing fines. This fibre alteration results in a decrease in pulp drainage and a drop in the tear strength, but improves the surface properties of the paper, making it smoother (Chen *et al.*, 2010:7041). The shape of the wood fibres is also altered by curling, straightening and the formation of nodes (Ek *et al.*, 2009:440).

External fibrillation occurs when the fibrils on the fibre surface are loosened while remaining attached to the fibre (Bierman, 1996:137; Kang, 2007:4). The surface area of the fibre is enlarged, which results in an increase of binding sites on the fibre (Smook, 1997:197). Internal fibrillation is achieved when the primary wall of the fibre is separated. Swelling takes place because water is allowed to be absorbed between the fibrils and the fibre, causing the dissociation of hydrogen bonds, which increases fibre flexibility (Ek *et al.*, 2009:440). Both effects contribute to fibre swelling and formation of inter-fibre bonds, which in turn will decrease the drainability (freeness) of the pulp. The promotion of binding sites, fibre swelling and formation of inter-fibre bonds contribute to the increase in paper-tear, tensile and bonding strength (Lumiainen, 2000:5).

Colloidal material consists of finely divided solids which do not settle from the pulp suspension. Refining plays a role in removing the colloidal material produced during the pulping and bleaching process. Colloidal material has a negative impact on papermaking machinery and product quality through increasing the pulp's resistance to drainage (Miao *et al.*, 2013:1432).

The redistribution of hemicellulose has also been noted during refining (Lumiainen, 2000:2). Hemicellulose is a group of polysaccharides in the matrix of plant cell walls. It can have linear regions, but predominantly contains branched chains and mainly consists of xylose, glucose, mannose and other sugars (Bierman, 1996:34; Scheller & Ulvskov, 2010:287). Hemicellulose plays an important role in the breaking strength, modulus of elasticity, work-to-rupture and yield stress of the fibres (Spiegelberg, 1966:92).

Lumiainen (2000) noted the effect of mechanical refining as a slight decrease in brightness together with decreased air permeability. Furthermore, an increase in tear strength for softwood and hardwood fibres, followed by a decrease in tear strength, was observed (Chen *et al.*, 2010:7041). Bierman (1996:137) observed an increase in drainage resistance, fracture toughness, tensile strength, tensile stiffness and bonding strength.

The surface conditions and swelling of the pulp fibres influence the drainage resistance, but other factors, like fines and cellulose colloidal material, also contribute. Fibre swelling contributes to the increase in the contact area between adjacent fibres, which in turn increases the paper strength, and increases fibre drainage (Manfredi *et al.*, 2013:297). A refined pulp will have a lower freeness than an unrefined pulp, but a very low freeness means that the paper machine will have to operate at a lower speed than with a higher pulp freeness, which is not ideal. The increase paper strength can be explained by the increased tensile strength. In refining the fibres are ordered, and the curl index is decreased. The combination of the smaller curl index and the higher density network of fibres, due to fibre collapse, will lead to higher tensile strength. (Johansson, 2011:7-9) The tear strength of the paper will be high at lower refining energies, due to a higher content uncollapsed fibres. As refining progresses and more fibres are collapsed, the more the tear strength decreases, this is because tear strength relies more on the individual strength of the fibres (Johansson, 2011,9-14).

2.4 Ultrasonication

Ultrasound has a frequency above 20 kHz, which is beyond the spectrum of human hearing. (Josefsson, 2010:3; Rehman *et al.*, 2013:1392). Ultrasound applications can be divided into two categories: diagnostic ultrasound and power ultrasound.

Diagnostic ultrasound transmits less power and has a frequency in the range of 2 to 10 Mhz. Power ultrasound transmits higher power and has a frequency in the range of 20 to 100 kHz (Mason & Lorimer, 2002:4, 20). Only power ultrasound is sufficiently energetic to be used for biomass treatment (Mason *et al.*, 2002:25; Rehman *et al.*, 2013:1392).

A solid cylinder, known as a sonotrode, is used to transfer ultrasonic energy to a fluid by means of vibration along its length (Yachmenev *et al.*, 2008:99). There are two different ultrasonication methods: direct ultrasonication and indirect ultrasonication. Direct ultrasonication is when the medium treated is in direct contact with the sonotrode. Indirect ultrasonication is when the ultrasonic energy is transmitted by immersing the medium in a liquid and transmitting the energy through the liquid (Rehman *et al.*, 2013:1393).

Ultrasound can be transmitted through any material possessing elastic properties by supplying kinetic energy to the molecules, causing the molecules to vibrate around their original position (Rehman *et al.*, 2013:1393). The sound wave moves through the material due to kinetic energy being transmitted between the molecules. Once a molecule has transferred its kinetic energy to its neighbour, it returns to its original position (Mason *et al.*, 2002:25). The transfer of kinetic energy causes substantial temperature increases in the medium (McCarthy *et al.*, 2014:147).

Oscillation is induced when more than one sound wave is transmitted through the material. In liquids and gases sound waves are propagated in the longitudinal direction, resulting in the molecules moving forwards and backwards around their original position. The movement of the molecules causes alternating regions of compression and rarefaction, which means that there is an excess of particles in a specific region, resulting in fewer particles in other regions. These effects cause the pressure to vary with time in the specific area through which the sound waves propagate (Josefsson, 2010:3; Rehman *et al.*, 2013:1393). During the rarefaction phase of the ultrasonication, the low pressure causes the formation and growth of gas-filled micro-bubbles in the mixture (Rehman *et al.*, 2013:1393). This phenomenon is known as cavitation.

The formation of the gas-filled micro-bubbles absorbs energy from the oscillating cycles, causing the bubbles to expand (Suslick, 1989:81). During the subsequent compression phase, the micro-bubbles implode, releasing the stored energy in the form of shock waves that propagate through the medium. A schematic representation of cavitation can be seen in Figure 2.4.

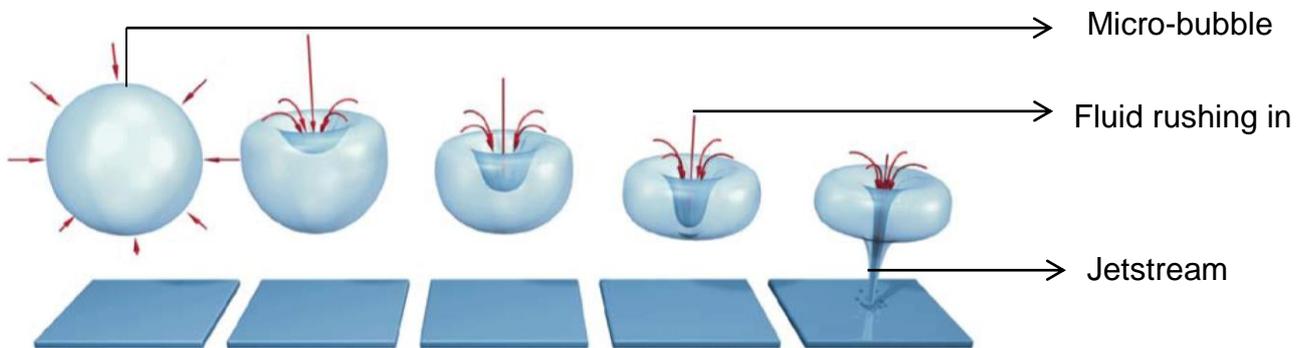


Figure 2.4: Step-by-step representation of cavitation (adapted from Focus-IT, 2014).

The implosion of the bubbles causes an increase in local temperature (by up to 10 000 K) and a pressure increase (of up to 5 000 bar) (Gogate & Pandit, 2008:1093; Rehman *et al.*, 2013:1393; Suslick, 1989:83). The propagated shock waves cause the mixture to move in its direction, resulting in a phenomenon known as acoustic streaming. This streaming occurs in the form of a jet stream that moves at high velocities which, in turn, causes severe micro-scale turbulence (Josefsson, 2010:4). The turbulence enhances the mixing and mass transfer where the solids and liquids interface and also plays a role in the erosion of the solid material in the mixture. This erosion and the turbulence contribute to the fibrillation and collapse of the wood fibres, which is the same effect that is achieved through mechanical refining. Furthermore, the pressure and heat-effects produced by the ultrasonication may lead to the generation of free radicals, facilitating chemical reactions (Rehman *et al.*, 2013:1393; Suslick, 1989:83).

According to Rehman *et al.* (2013:1394), the following three factors have the most important influence on substrate modification and are also interdependent: ultrasonication time (t) in hours (h), power (P) in watt (W) and amplitude (A) in micrometers (μm). These factors determine the amount of energy (E) in kilowatt-hour per ton (kWh/t) transmitted to the medium. Other factors, such as the processing temperature, the frequency of the ultrasound and the properties of the biomass that

will be ultrasonicated, may also have an influence, but not to the same extent as the factors listed above (Rehman *et al.*, 2013:1394).

Many studies have been done on the time-based effect of ultrasonication (Huang *et al.*, 2007; Haung *et al.*, 2011; Montalbo-Lomboy *et al.*, 2010; Nikolic *et al.*, 2010; Sun & Tomkinson, 2002; Sun *et al.*, 2002). Increasing the ultrasonication time increases the total energy transmitted to the medium. The elevated energy level increases the amount of modification of the biomass and it has also been observed that more sugars are released from the substrate. However, increasing the ultrasonication time beyond a certain maximum reduces the efficiency of the treatment: a longer ultrasonication time will only modify the biomass up to a certain point, where after the modification will reach a plateau.

The power of the ultrasound, applied at any specific time, directly affects the cavitation phenomenon by influencing the quantity of cavitation bubbles produced, the lifetime of the bubble and the implosion pressure (Rehman *et al.*, 2013:1394). Greater power will result in more bubbles forming near the tip of the sonotrode, which means there will be more implosions. However, it is also stated that the formation of more bubbles may impede the transfer of the power from the transducer to the liquid medium (Gogate *et al.*, 2011:1088). The lifetime of the bubbles is believed to lengthen, while the implosion pressures are higher due to the bubble collapse intensity increasing (Gogate *et al.*, 2011:1088).

It has been stated that the amplitude of the ultrasonic waves influences the treatment intensity on the medium (Chen *et al.*, 2011:1807). Large amplitudes result in more cavitation bubbles, more severe cavitation and higher ultrasonication power (Josefsson, 2010:5). Since the dimensions and output frequency of any sonotrode remain constant, changes in amplitude are associated with increased power. The increased power is still transferred over the same surface area, resulting in higher intensity. Intensity is important for mechanical fibre modification. The refining intensity is used to describe the impact on the fibres and the extent of their treatment (Lumiainen, 2010: 4). The refining intensity can be measured by looking at the specific edge load (SEL) as can be seen in Equation 1. The change in amplitude hence has the potential to affect the fibres in the same way as the intensity of mechanical refining.

In some ultrasonication treatments, it was found that the ultrasonication power and processing time required are inversely proportional to the energy needed (the higher the power, the shorter the processing time required to achieve the necessary energy transfer to the medium) (Rehman *et al.*, 2013:1395). A schematic representation of this finding can be seen in Figure 2.5.

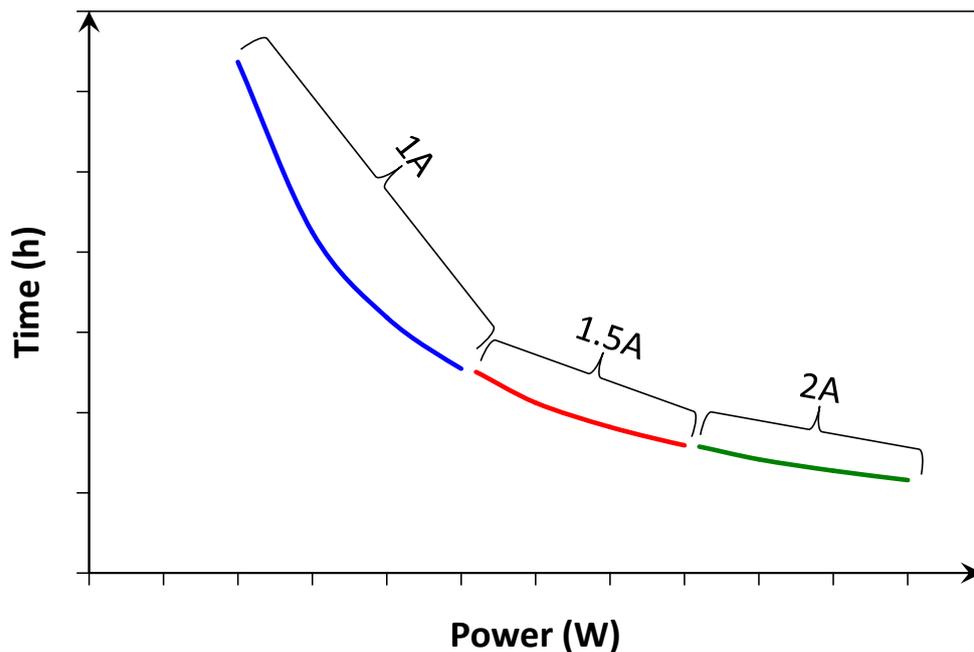


Figure 2.5: Relationship between the power required over time at a constant energy level and constant frequency, but at different amplitudes (A).

The ultrasonication power and amplitude are inter-dependent. When the amplitude is increased, the power transmitted to the medium is also increased. Therefore, the amplitude is also inversely proportional to ultrasonication time: the lower the amplitude, the less power is transmitted to the medium and the longer the ultrasonication processing time required to achieve the desired energy input.

The processing temperature influences the cavitation intensity at which cavitation bubbles implode (as a less important parameter), which in turn influences the ultrasonication intensity (Prabhu, 2004:4997). As a result, an increase in temperature causes a reduction in implosion intensity due to the effect of reduced bubble collapse. It was expected that the higher vapour pressure in the cavities should increase the

cavitation intensity, but this is not the case (Sutkar & Gogate, 2009:33). There is reason to believe that the density changes associated with the rise in temperature plays a role in the reduced intensity. When the temperature of the medium rises, the density decreases, which in turn causes the internal pressure of the medium to decrease. The pressure gradient between the cavitation bubble and the medium will be smaller, which will lower the intensity at which the cavitation bubble implodes. No studies have yet been done on this subject, and at this stage it is only speculation.

The frequency of the ultrasound influences the power, which, in turn, impacts cavitation (Rehman *et al.*, 2013:1396). Altering the frequency either prolongs or shortens the time intervals between rarefaction and compression. Increasing the frequency will inhibit the separation of molecules before they are compressed again, hence the formation of cavities is reduced (Joseffson, 2010:5, Santos *et al.*, 2009:3). Sonicators are built to produce sound waves at a specific frequency; for high intensity ultrasonication, which is used to modify biomass, the frequency is set between 20 kHz and 100 kHz (Khaltsa *et al.*, 2013:882; Rehman *et al.*, 2013:1392; Shanmugan *et al.*, 2012:252), meaning the frequency is not an adjustable variable (Shanmugan *et al.*, 2012:252).

The properties of the biomass are also important. To achieve efficient modification, the viscosity of the medium should be kept low, while the surface tension of the mixture and the presence of impurities should be high (Rehman *et al.*, 2013:1398; Joseffson, 2010:4). Although it is not explicitly stated, there is reason to believe that the pH of the mixture is another factor in the efficiency of the ultrasonication. It may be that a more alkaline solution is more susceptible to the effects of ultrasonication (Manfredi *et al.*, 2013:300).

While the science behind ultrasonication stays the same, the equipment may be either laboratory- or pilot-scale sonicators. The two major variables are the power and intensity. The power is mainly distributed across the tip surface, hence smaller diameter probes generate a more focused cavitation field and a higher intensity. A higher ultrasonic intensity (expressed in power per area) typically results in a higher processing efficiency (Hielscher Ultrasonics, 2006:5). The laboratory-scale sonicator has a low power output of 585 W, operates at a frequency of 20 kHz and has interchangeable sonotrode tips varying between 10 mm and 15 mm. The ultrasonic

waves are transmitted in pulses of six seconds duration each, at one second intervals. The pilot-scale sonicator transmits continuously rather than in pulses. The maximum output power is 1 kW, while the sonicator also operates at 20 kHz. Its interchangeable sonotrode tips go up to 40 mm.

An example of a typical laboratory-scale ultrasonicator can be seen in Figure 2.6, while Figure 2.7 shows a pilot-scale ultrasonicator with a flow cell attached.

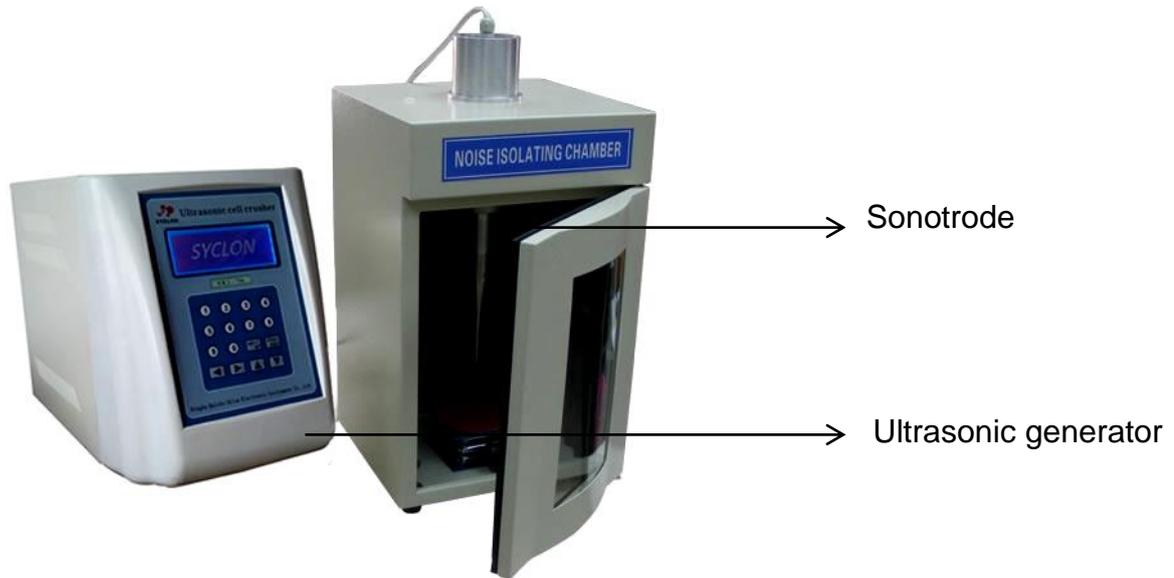


Figure 2.6: SKL-IIND series laboratory-scale ultrasonicator (Syclon, 2011).

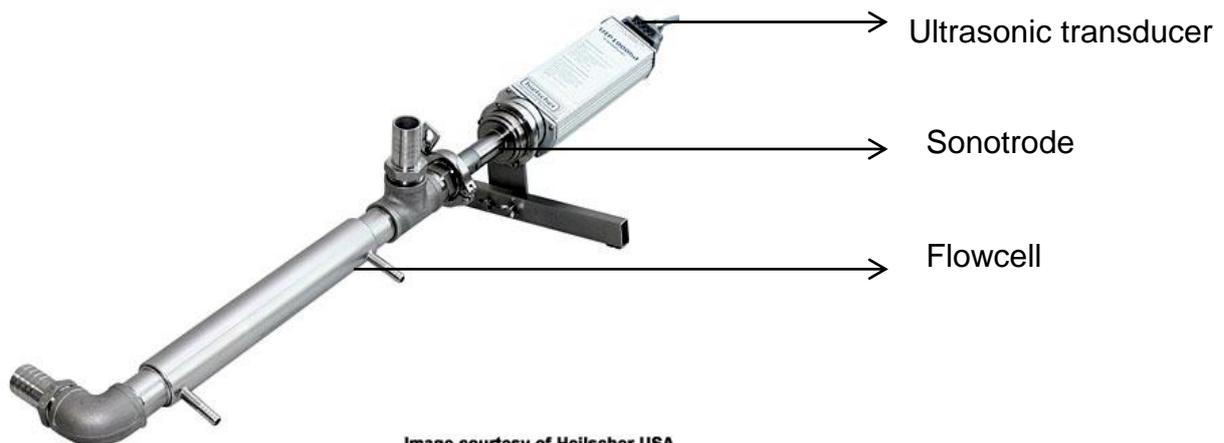


Image courtesy of Heilscher USA

Figure 2.7: Heilscher UIP 1000HD pilot scale ultrasonic processor (Heilscher, 2006).

2.5 Enzymes

Blomstedt *et al.* (2010) states that enzymes are biological catalysts with elevated efficiency, selectivity and reaction speed. Enzymes are used to modify the cellulosic fibre wall to enhance refining efficiency by promoting fibrillation and fibre collapse (Josefsson, 2006:11). Furthermore, enzymes can be used to increase the drainage rate by degrading the colloidal material in the pulp (Steel & Wolfaardt, 2010:2). The two enzymes that may be investigated in this project are xylanase and endoglucanase. While enzymes have been shown to improve and change fibre properties, it has also been shown that an excessive cellulase dosage can cause pulp strength properties to deteriorate (Oksanen *et al.*, 1997:337; Pere *et al.*, 1995:76).

Xylanase is used to degrade xylan, which is one of the hardwood hemicellulose components that lower the effectiveness of bleaching agents on lignin (Goncalves *et al.*, 2007:159). The xylanase acts on the relocated and re-precipitated xylan that occurs on the surface of the pulp fibres. The structure of the fibres is targeted and rendered to become more permeable through enzymatic hydrolysis. This enhanced permeability allows a more thorough extraction of residual lignin from the fibres. The hydrolysis of hemicellulose in the inner fibre layers also plays a role in its enhanced susceptibility to bleaching (Buchert *et al.*, 1994:70).

The removal of xylan has also been proven to facilitate the removal of water from the pulp. Since pulp freeness increases, the drainage properties of the pulp are also enhanced.

Endoglucanases are the enzymes that initiate the creation of a degrading pathway in cellulose (Tomme *et al.*, 1995:5). The opened active site arrangement of endoglucanases restricts them to the amorphous part of cellulose, because their activity has little effect on highly crystalline cellulose (Dashtban *et al.*, 2010:4).

A typical structure of cellulose can be seen in Figure 2.8.

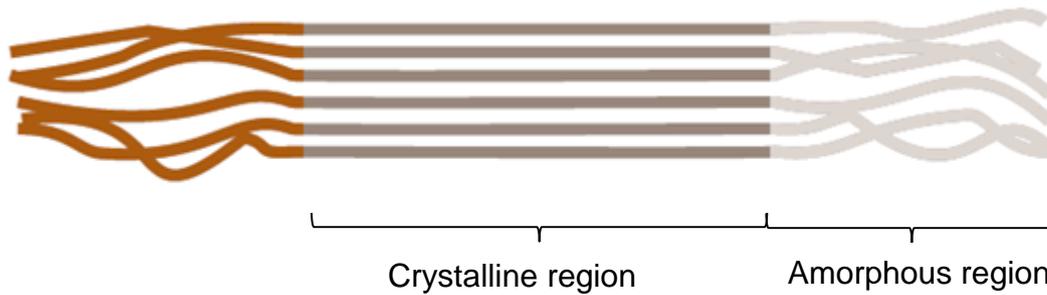


Figure 2.8: Difference between the amorphous and crystalline regions of cellulose (Cotton Inc., 2014).

Endoglucanases randomly attack the internal chain of cellulose and hydrolyses it to produce cello-oligosaccharides (Li *et al.*, 2012:9775; Lars *et al.*, 2005:387).

Peter Josefsson (2006) found that the endoglucanases cause external fibrillation of fibres and swelling of cellulose, enhancing the strength properties of the paper and making it more susceptible to exo-glucanase-enzymes, which can effectively degrade the cellulose. When the fibres were pre-treated with endoglucanase and refined, the tear strength of the paper decreased significantly. The tensile index of the pre-treated paper increased at low refining levels, but decreased when high refining levels were applied, compared to an untreated control. A schematic of endoglucanase is given in Figure 2.9.

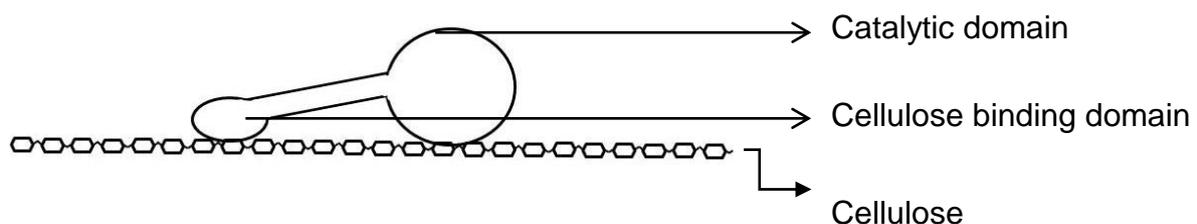


Figure 2.9: Endoglucanase with cellulose binding module (Re-drawn from Gwinner, 2013).

Bench-scale experiments on old corrugated containers (OCC) proved that endoglucanase from AB Enzymes (Ecopulp R) increased the drainage of the pulp without negatively affecting the pulp properties (De Goede & Wolfaardt, 2011:2). Further tests on secondary fibres, at pilot scale, revealed that Ecopulp R had the greatest positive impact on drainage, SCT and Scott Bond (De Goede *et al.*, 2012:3).

2.6 Previous findings

Anna Joseffson (2010) treated never-dried and dried hard- and softwood pulp samples with ultrasonication. Some of the samples were pre-treated using PFI laboratory refining at 0.5 and 100 kWh/t, while the rest was only defibrillated before ultrasonication treatment. The samples had a 1 % consistency and were treated at a frequency of 20 kHz, amplitude 35 μm , pressure of 1 bar and power of 500 W. The ultrasonication times ranged from 1 minute to 15 minutes.

Joseffson's (2010) conclusion was that ultrasonication is not an alternative to conventional refining, due to the high energy demand. She did find that fibre modifications, such as fibre collapse and fibrillation, were obtained when samples were treated with ultrasonication, but without mechanical pre-treatment the ultrasonication had little effect.

Da Silva *et al.* (2013) worked on combining enzymatic treatment with ultrasonication to improve the properties of recycled pulps. The tests were conducted on post-consumer cardboard scraps. The samples had a 3 % consistency and were pre-treated with cellulase and hemicellulase enzymes. The sonicator was run at 190 W at 10 minute intervals for 30 minutes. The result was compared to a PFI mill refiner.

Da Silva *et al.* (2013) concluded that the PFI mill refining combined with enzymatic pre-treatment had better inter-fibre bonding increases, but that the ultrasonication and enzymatic pre-treatment acted more mildly on the pulp fibres. The combination of ultrasonication and enzymatic pre-treatment also had a larger positive effect on the intrinsic fibre strength properties compared to the PFI mill refining and enzyme pre-treatment. The results show that ultrasonication is not a viable alternative for mechanical refining.

Manfredi *et al.* (2013) tested the refining effects of ultrasonication on unbleached old corrugated containers at different pulp consistencies, ultrasonication times and mixture pH. The pulp consistency ranged from 0.5 % to 4 % and the ultrasonic treatment was done at 190 W and a frequency of 20 kHz. The pH ranged between 7 and 10 and the ultrasonication treatment was done in 5, 10 and 20 minute increments. The pulp was also refined in a PFI mill refiner, and the results were compared to that of the ultrasonication treatments.

Manfredi *et al.* (2013) concluded that the effect of ultrasonic treatment was much higher in alkaline solutions (specifically at pH 10). Based on these results, ultrasonication is efficient in developing fibre properties and can replace mechanical refining.

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CHAPTER 3: Materials and Methods

3.1 Introduction

Mechanical refining is an energy-intensive process and therefore alternative methods have been investigated to save energy and modify the fibres without damaging them (Josefsson, 2010:1). Work has been done on the modification effects of ultrasonication on pulp fibres, but to my knowledge the effects of energy, power, amplitude, enzyme dosage and treatment sequence have not been fully described. Some of these factors are dependent on each other, and the combination of factors may interact to result in new fibre properties. It is, therefore, essential to design an experiment that will indicate how fibres will react to various combinations of these factors.

The present project was designed to evaluate the result of ultrasonication and enzyme treatment on pulp fibres and compare it to the effect of mechanical refining. The variables in ultrasonication were amplitude and applied energy, and for the enzyme treatment it was the enzyme dosage and treatment order. The frequency of the sonicator was set at 20 kHz.

Bleached paper sheets (hardwood and softwood pulp) were re-pulped, enzyme-treated and sonicated. During the ultrasonication treatment, samples were taken at set energy levels and the Canadian Standard Freeness (CSF) test was done on them to determine the pulp's drainage properties. Following the CSF test, the pulp was converted to hand-sheets and left to condition for 24 hours, after which strength tests were done. The strength tests were followed by a fibre morphology test.

3.2 Pulps

Softwood, hardwood and recycled pulps, created by pulping the bleached paper sheets, were evaluated. The typical length of hardwood fibres is short, with an average length of between 0.9 mm and 1.5 mm. Hardwood pulps are used to increase the smoothness, bulk and opacity of paper. Due to these properties, hardwood is mostly used to make writing, printing and tissue paper (Bierman, 1996:16). The bleached softwood is produced from *Pinus radiata* and obtained from the Tasman pulp and

paper mill in the Bay of Plenty, New Zealand. The fully bleached hardwood pulp is produced from *Eucalyptus globulus* and obtained from the Sante Fe pulp mill in Chile. The reason that no South African pulps were used in this study was due a number of factors: The research institution had done extensive research on the hardwood and softwood pulp mentioned above, and was also producing products based on these pulps. Due to the mutual agreement of the university and the institution, the conducted research had to benefit the institution.

The unbleached OCC pulp used in the project is from unused recycled containers. The containers were collected, cleaned, sorted to create comparable pulp samples, cut to pieces and pulped.

A morphology test was done on the three pulp species. The results can be seen in Table 3.1.

Table 3.1: Comparison of hardwood, softwood and OCC fibre properties.

Description	Hardwood	Softwood	OCC
Fibre content (millions/g of pulp)	28.2	3.6	8.7
Mean weighted fibre length (μm)	792.0	2 115.0	1009.7
Mean fibre width (μm)	18.0	31.7	21.6
Mean fibre coarseness (mg/m)	0.1	0.2	0.2

The Santa Fe (*E. globulus* hardwood) species has the shortest, thinnest and smoothest fibres (Table 3.1). The reason for the shorter fibre length, compared to the average of 0.9 mm, is that the fibres have gone through the bleaching process. The bleaching process tends to weaken the fibres and release colloidal cellulose material into the pulp slurry (Bierman, 1996:123; Miao *et al.*, 2013). The Tasman (*P. Radiata* softwood) fibres were the longest, coarsest and widest. The OCC fibres had already been refined multiple times, causing the longer fibres to break into shorter lengths and fines. The OCC pulp was unbleached, which means that the lignin had not been removed and explains why, after multiple refining runs, the fibres were not shorter than the bleached hardwood fibres. The presence of lignin in this pulp may cause enzyme modification problems, because the enzyme binds to the lignin (Wolfaardt, 2014a).

These characteristics explain why the fibres are longer than the hardwood fibres, but shorter than the softwood fibres.

3.3 Enzyme

The enzyme used to treat the wood fibres is a Cellulose Binding Module (CBM) containing cellulase known as endoglucanase. The cellulose binding domain increases the enzymatic efficiency (Müller, 2014). This enzyme was selected due to its refining properties and because it presented positive results on both bench scale and pilot scale (Wolfaardt, 2014b). The enzyme works optimally between a pH of 4.5 and 8.5 and within a temperature range of 45°C and 85°C, with a recommended dosage of 50 g/t (AB Enzymes, 2014). These levels were monitored closely using the control interface of the pilot refiner. The temperature was kept in this range by regulating the cooling jacket and ventilation. In the case that the pH varied, a process was in place to add acids or basis to the pulp to regulate the pH. The endoglucanase was bought from AB Enzymes under the commercial name of Ecopulp R. For the present project the dosages will be at 0 g/t for the control, 50 g/t and 200 g/t for the pre-treatments, and 100 g/t for the post-treatment. This increments were chosen because it consisted of a recommended dosage, and two dosages where there have been mechanical refining tests –which would lead to comparable results. The mechanical refining research used the high dosage to examine the effect of increasing the dosage by 2x increments, and if there were any benefits regarding colloidal cellulose removal.

Based on previous studies done on the same pulp, it was found that the enzyme was deactivated once refining commenced. As a precaution, a second process was put into place to ensure deactivation. The pulp was placed in a refrigerator at 5 °C. Due to the constant sample size, sample container, similar temperatures, location within the refrigerator and the regulated refrigerator temperature, it was assumed that enzyme deactivation time, if there was any after ultrasonication, would be similar between samples.

3.4 Pulp preparation

The re-pulping process was similar for ultrasonication and mechanical refining. Because the consistency of the dry sheets varied for the hardwood, softwood and OCC pulps, the moisture content of the different pulps was determined gravimetrically to accurately prepare pulp slurries at a consistency of 3 %. The hardwood and softwood pulps were easy to prepare due to the consistent properties of the provided bleached sheets. The OCC, however, was more difficult as old corrugated containers had to be acquired, and the different containers had different properties. The initial solution was to create one sample of OCC, where all containers would be pulped at the same time, and samples would be extracted to be refined and sonicated. The long treatment times, however, meant that the samples that was not refined and sonicated would be in pulp form for too long, leading to a change in fibre properties. The best solution at the time was to collect OCC, cut it into similar sizes, and distribute it evenly between the samples needed for each treatment. The proposed method would lead to more uniform samples, but some differences where still expected.

A total volume of 214 L pulp slurry had to be prepared. Re-pulping was done by adding the dry sheets to impeller-induced churning water at 50°C. The hardwood pulp slurry was made by mixing 7.1 kg of dry Santa Fe sheets with 207 L of water, the softwood slurry used 6.8 kg dry Tasman sheets and the OCC slurry used 6.9 kg of dry recycled containers.

The pulp slurry was left to re-pulp for 5 min., where after enzyme was added. The enzyme was added in three dosages: 0 g/t as control, 50 g/t and 200 g/t. The re-pulper was closed following the enzyme addition and left to re-pulp and incubate for 25 min.

3.5 Mechanical refining

The mechanical refining was done by Sappi, and the data used for comparing with the present project. The pilot equipment consisted of a 12" single-disc refiner (Matech) with a 400 L re-pulper. The refiner was operated with recirculation to reach different specific refining energies. The hardwood refining was done using plates with bars that

were 2 mm wide and 4 mm high. The grooves were 2 mm wide. The bars were set at a 5° angle, and the refining intensity for the hardwood was 0.4 Ws/m.

The plates used for the softwood refining also had 5° bar angles, but the bars were 3 mm wide and 4 mm high, with groove widths of 3 mm. The refining was done at an intensity of 1.6 Ws/m.

The hardwood and softwood refining was done by Stephen Swart at the Sappi Technology Centre in Pretoria. Stephen also contributed to the OCC mechanical refining runs. The re-pulping was done in the same way as the ultrasonication runs, to generate a pulp with 3 % consistency. The valves on the ultrasonication loop were shut, to direct the flow through the mechanical refiner. The refiner utilised the auto-sampler to take samples at pre-specified times, thus ensuring that samples were taken at accurate energy levels.

After mechanical refining, the same procedure as with ultrasonication was followed to make and condition the hand-sheets and do CSF, strength and morphology tests.

3.6 Ultrasonication

A Hielscher UIP 1000hd ultrasonic transducer with a 40 mm sonotrode, flow cell and cooling jacket was installed in series with the refiner. The maximum output of the sonotrode was 1 kW and it operated at a set frequency of 20 kHz. The unit can be operated at variable amplitudes, controlled from the ultrasound generator (Hielscher UIP 1000hd), while reading power consumption from a Brennenstuhl PM 230 electricity meter. The ultrasonicator was installed in such a way that the pulp slurry could be pumped directly from the re-pulper through the ultrasonicator flow cell and back into the re-pulper, thereby creating a recycling loop. The pulp slurry had to pass through the mechanical refiner, but by increasing the refiner gap, the effect of mechanical fibre modification was removed. The heat generation of the sonicator caused safety concerns, which motivated the decision to keep the treatment temperature below 80°C. The cooling water used was at 20°C. A graphic representation of the pilot plant can be seen in Figures 3.1 and 3.2.

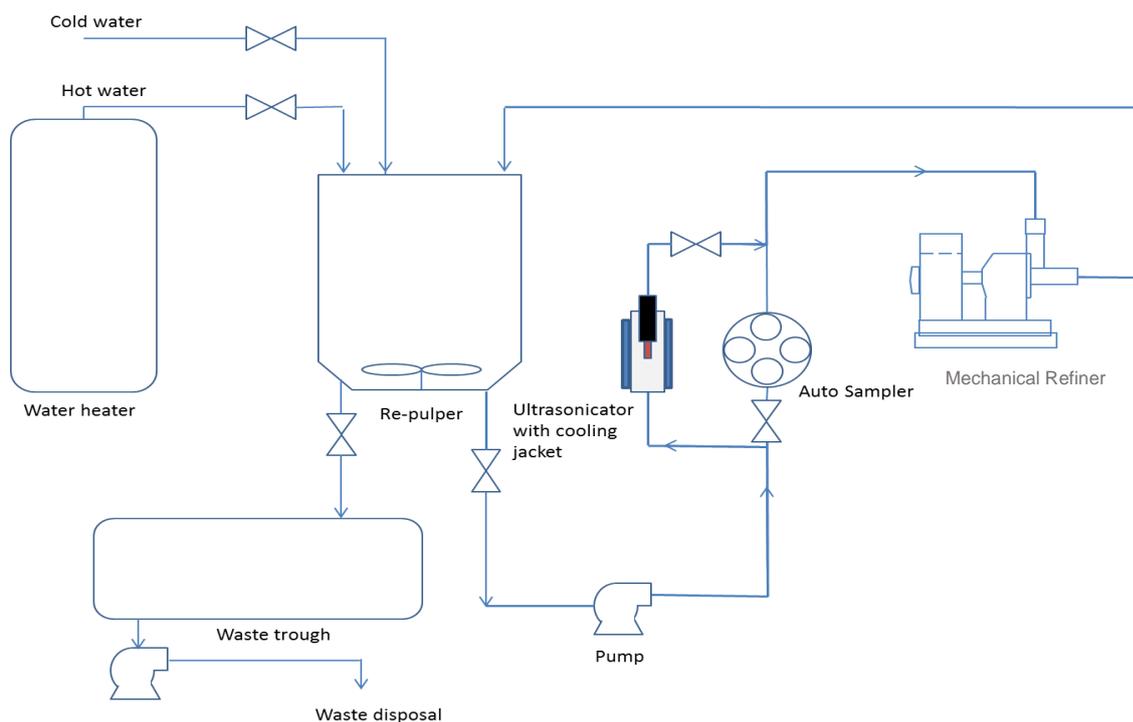


Figure 3.1: Process flow diagram of installed ultrasonicator with flow direction and highlighted recycling loop.



Figure 3.2: Installation of ultrasonicator in the pilot plant.

Following the installation, twenty commissioning runs were done with Santa Fe hardwood pulp to determine the influence of the flow rate on the pump speed and pressure profile. The runs were done at 1 %, 2 % and 3 % consistencies (solids content). Due to the low consistencies, the density of the mixtures remained constant, resulting in comparable pressure profiles and pump speeds. The pulp slurry in mechanical refining was close to 3 % consistency, and literature also claims that pulp slurry at this consistency is optimal for ultrasonication treatment (Da Silva *et al.*, 2013:654). The runs at 3 % were monitored and it was concluded that a flow speed of 7 m³/h was most effective. At this flow speed, steady state was reached quickly and no pressure changes were recorded.

Based on this flow rate and consistency, calculations were done to determine the energy transmitted to the pulp slurry. The length of the flow cell (L in m), diameter (D in m) and area (A in m²) was measured. The volumetric flow speed of the pulp slurry (v in m³/h) was determined and was used to calculate the residence time (in hours) of the pulp in the flow cell applying Equation 2.

$$t = L / \left(\frac{v}{A} \right) \dots \dots \dots (3)$$

The power (P in kW) transmitted by the ultrasonicator was measured using a Brennenstuhl PM 230 electricity meter and the dry weight of the pulp (W_{dry} in ton) was recorded. The residence time, along with the measured power and the dry weight of the pulp, was used to calculate the energy (E in kWh/t) which is transmitted to the pulp per single pass in Equation 3.

$$E = (P * t) / W_{dry} \dots \dots \dots (4)$$

The time to complete a single pass (t_p in hours) was calculated by dividing the total volume of pulp (V in m^3) by the volumetric flow (Equation 4).

$$t_p = \frac{V}{v} \dots \dots \dots (5)$$

The moisture content of different pulps was determined gravimetrically to prepare pulp slurries accurately at a consistency of 3 %.

It must be noted that the pilot plant runs were quite energy-intensive, and due to limited resources, the different treatments were done only once each. To provide for possible experimental error, Tappi (1996) was used to determine the experimental precision for the hand sheet conditioning (T402), grammage (T220), tear (T414), tensile (T494) and freeness (T227) tests.

3.6.1 Enzymatic treatment sequence 1

In the first set of treatments, the enzyme was used as a pre-treatment, followed by ultrasonication. The paper sheets were re-pulped and put through the recycle loop, where samples were taken. The Canadian Standard Freeness test was done on the samples before they were refrigerated. After 24 hours, the samples were removed from the fridge and the hand-sheets made and conditioned for 24 hours. After this, strength and morphology tests were done to determine the properties of the modified pulp fibres.

After re-pulping, the pulp slurry was put through the fibre modification process. The gap between the mechanical refiner plates was increased and the pilot plant was put through the start-up process.

In the start-up, the mechanical refiner was switched on to create a pressure drop, so that the pulp slurry could start moving through the pump. Once the pulp slurry started

moving, the pump was switched on and the flow monitored until it reached steady state.

Once steady state was achieved, the amplitude on the ultrasonic processor control box was set and the ultrasonic transducer switched on. The power transmitted to the pulp slurry was monitored via the electric meter. The time needed to reach the desired energy when a certain amount of power is transmitted to the pulp slurry was calculated using Equation 2. Table 3.2 was used in combination with a timer, to ensure that accurate energy treatments are applied to the pulp.

Table 3.2: Residence time (min) to achieve the transfer of the required energy (E) at different power settings (P).

P (W)	E (kWh/t)					
	10	20	30	40	50	60
50	76	153	229	306	382	459
100	38	76	115	153	191	229
150	25	51	76	102	127	153
200	19	38	57	76	96	115
250	15	31	46	61	76	92
300	13	25	38	51	64	76
350	11	22	33	44	55	66
400	10	19	29	38	48	57
450	8	17	25	34	42	51
500	8	15	23	31	38	46

The high temperature associated with ultrasonication limited the treatment time due to safety concerns. The cooling jacket and water could not keep the temperature of the pulp slurry from exceeding 50°C for longer than 90 minutes, which was considered dangerous by the Sappi Technology Centre safety representative. This was however not a problem, since previous experiments indicated that ultrasonication was much more effective at lower energies. The focus was therefore on the energy range up to 60 kWh/t.

One-litre pulp samples were collected in 10 kWh/t increments from the re-pulper without stopping or altering the flow rate. These relatively small samples did not have an influence on the flow rate, but were large enough to allow all of the required tests to be done. After each sample was collected, its drainage properties were tested before it was refrigerated at 5°C. The refrigeration was also used to ensure that the enzymes were deactivated. A schematic of the procedure can be noted in Figure 3.3.

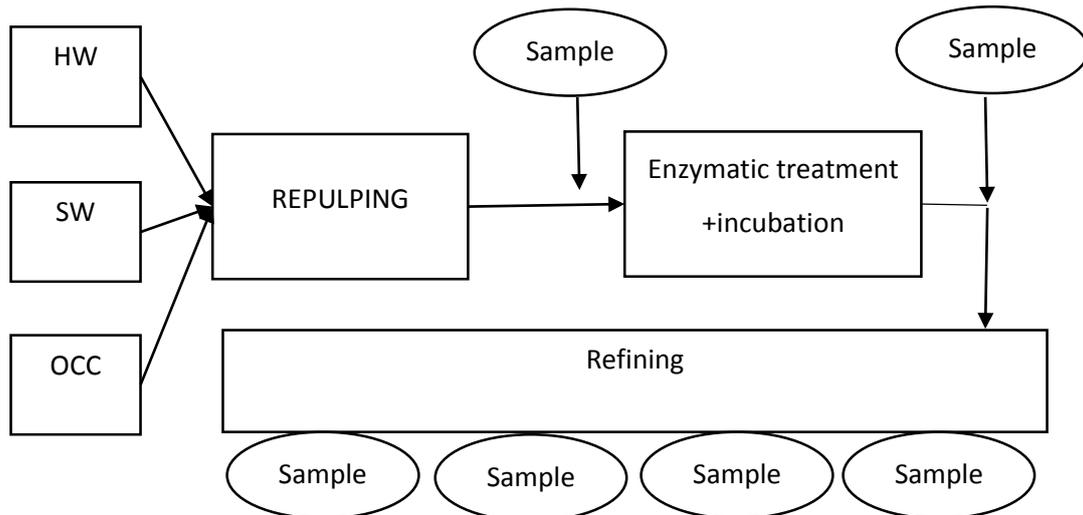


Figure 3.3: Schematic representation of sequence 1 process.

3.6.2 Enzymatic treatment sequence 2

The second sequence consisted of sonicated pulp, post-treated with enzyme. The paper sheets and recycled containers were re-pulped for 5 minutes and subjected to ultrasonication. After ultrasonication, a total of 20 litres of pulp slurry was taken at four different energy treatments, and put into heating baths at 70 °C to control the temperature and keep the pulp at 50°C. Overhead stirrers were installed to agitate the samples and 100 g/t enzyme was added. After 25 minutes the Canadian Standard Freeness test was done on the pulp, where after the samples were refrigerated. The procedure followed in the first sequence was repeated to do the strength and fibre morphology tests. A schematic of the process can be e tests should be carried out at 20 °C (Tappi, 1996:T227). Water was added to 100 g of treated pulp to make a one-litre sample. It must be noted that the pulp had a consistency noted in Figure 3.4.

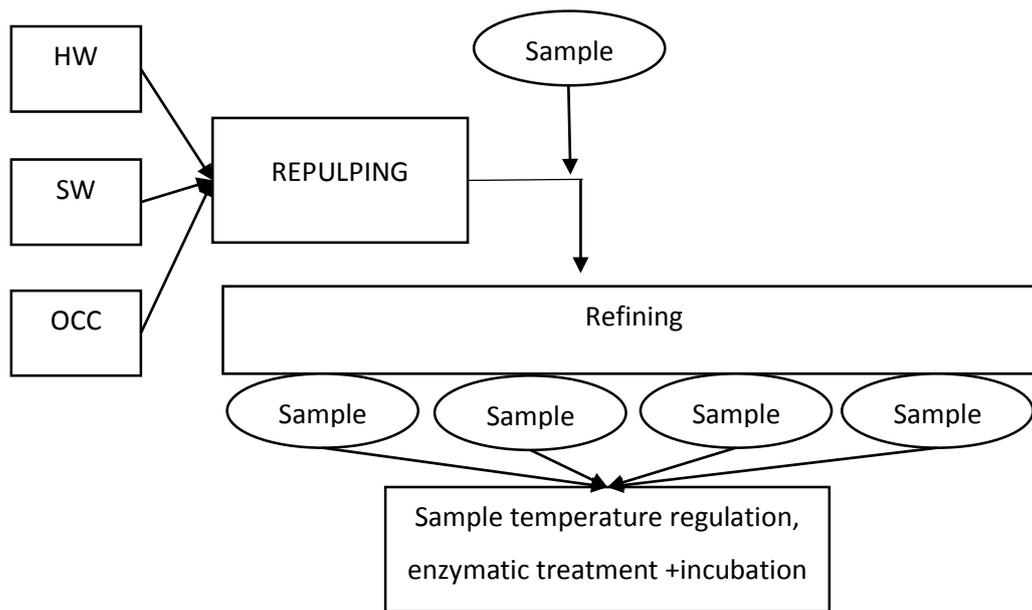


Figure 3.4: Schematic representation of sequence 2 process.

3.7 Tests conducted on modified pulp

The Canadian Standard Freeness (CSF) test was used to determine the drainage properties of the pulp. The freeness of pulp is a measure of the rate at which 0.3 % consistency pulp can be drained. It is important to note that th

of 3 %. The Canadian standard method, Tappi T227, was followed (Tappi, 1996:T227). After the drainage properties were recorded, the modified pulp samples were refrigerated to immobilize the enzyme. The modified pulp that was not enzyme-treated was also refrigerated. The apparatus used is shown in Figure 3.5.

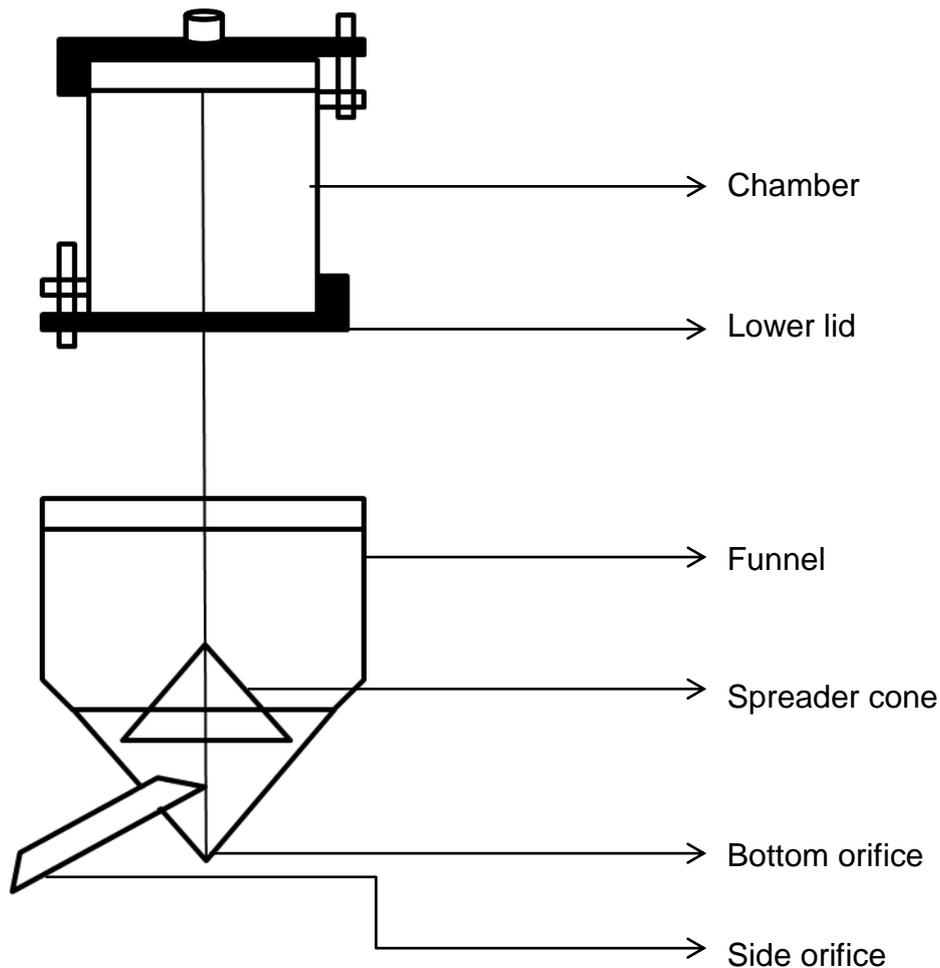


Figure 3.5: CSF tester (Redrawn from Tappi, 1996).

Hand-sheets were prepared using a Battbildner Rapid Köthen System PTI hand-sheet maker in accordance with ISO 5269/2. With the hardwood and OCC pulps, 100 g of pulp was used to make the hand-sheets, while 70 g was used from the softwood pulp. These pulp amounts were calculated to ensure that the mass per area of paper (grammage) for the hand-sheets would be as close to 90 g/m² as possible. Four hand sheets were prepared per sample.

The hand-sheets were thoroughly dehydrated, so that they rapidly absorbed the water vapour in the air. If the hand-sheets had been kept in a room where the temperature and humidity were not controlled, the fluctuations would have had an effect on the properties of the paper and board. The Tappi T402 standard was consequently followed and the hand-sheets were kept in a conditioning laboratory at a temperature of 23°C and humidity of 50 % for a minimum of 24 hours.

The mass per unit area of the hand-sheet is known as the grammage. The hand-sheets were round with a diameter of 205 mm. The Tappi T220 standard was applied, except that the weight of each hand-sheet was determined by using a Precisa XT620M scale. The grammage was then calculated using Equation 4.

$$\text{Grammage} = \frac{W_{HS}}{A_{HS}} \dots \dots \dots (4)$$

Where W_{HS} refers to the mass of the hand sheet, and A_{HS} refers to the area of the hand sheet.

The conditioned hand-sheets were cut with a guillotine. The Tappi T220 standard was used to cut the appropriate strips for the tensile and tear tests. Every hand-sheet was divided into four tear test blocks and two tensile strength strips. A schematic can be seen in Figure 3.6.

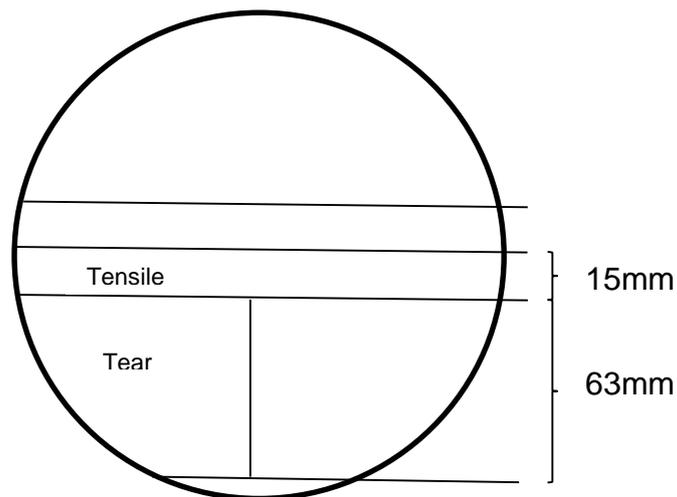


Figure 3.6: Hand-sheet division for tear and tensile tests.

The internal tearing resistance reflects the force perpendicular to the plane of a paper sheet that is required to tear it. The Elmendorf type tester consists of a pendulum that applies a force and measures the loss in potential energy of the pendulum as it tears the paper (Tappi, 1996:T414). The result is measured in mN (mili-Newton). An example of a tear-resistance tester can be seen in Figure 3.7.

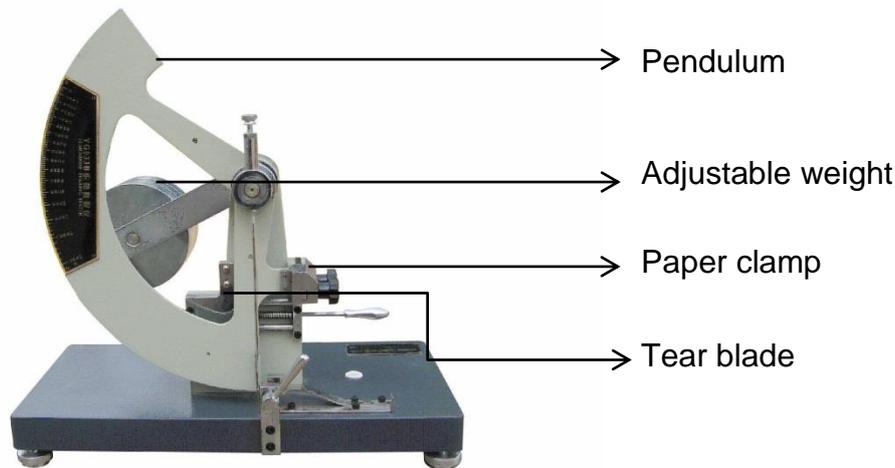


Figure 3.7: Elmendorf-type tear tester (Eclplaza, 2014).

The tear tests were conducted by applying the Tappi T220 standard. Four squares per hand-sheet were clamped into the machine, with the smooth sides facing the axis of the instrument. A weight of 1 600 g was attached to the pendulum, the hand-sheets were torn halfway through using the tear blade and the tests were conducted. The energy range in which these experiments were completed was low in comparison to industry standards, therefore it was expected to only see an increase in tear strength. When looking at a larger energy range, the initial tear index increase followed by a decrease could be noted, unfortunately ultrasonication could not reach the high energies due to safety concerns and time constraints.

The tensile test uses constant-rate-of-elongation equipment. The data generated by this test include tensile strength, tensile strain, tensile energy absorption, breaking length and tensile index (Tappi, 1996:T494).

Tensile strength is the maximum force (tensile stress) per unit width required to rupture the test specimen. *Tensile strain* is the percentage elongation that the test specimen can withstand before rupturing due to the induced tensile strain. *Tensile energy absorption* (TEA) is the amount of work done when the test specimen is stressed to the point of rupture, and is expressed as energy per unit of area. The *breaking length* is the length which will cause the test strip to break due to its own weight, if it were suspended from one end. *Tensile index* is the tensile strength divided by the

grammage (weight per area) of the test specimen (Tappi, 1996:T494). A typical tensile-strength test machine is shown in Figure 3.8.

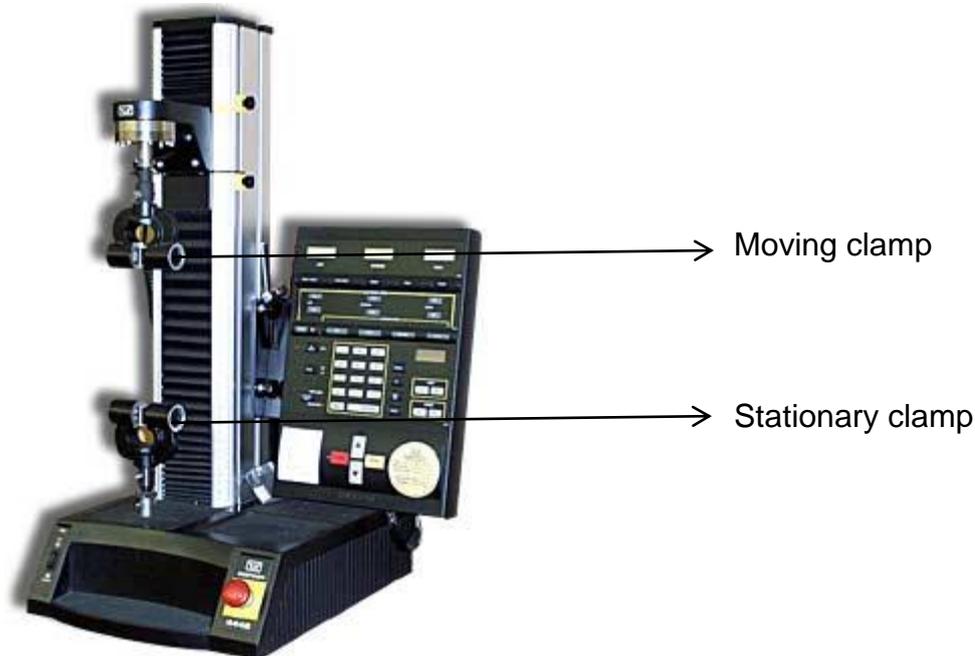


Figure 3.8: Tensile strength tester (H. Cross Company, 2014).

The tensile strength tests were conducted in accordance with the Tappi T220 and Tappi T494 standards. Two strips per hand-sheet were used to test the abovementioned properties.

The fibre analysis was done using a Techpap automated morphological analyser. The Morfi module was specifically designed for optimal optics and flow cell measurements and can give accurate readings on fibre, fine elements and shive properties. Samples at specific consistencies were prepared, and fed into the Morfi machine. These samples passed through a measuring cell, where a high resolution camera would photograph the sample as it passes through. The Morfi used programming to extract all the above mentioned information from these photographs using algorithms, and displayed the results on a user interface. This data was then exported to an Excel sheet, where it could be structured and investigated. In the fibre analysis the focus was on the fibre content and fines content (in millions/gram), mean fibre length and width (in μm) and fibre coarseness (in mg/m). The kinked fibre content, mean fibre curl index, macro-fibrillation index, broken fibre content and fine content were measured and expressed as percentages (%).

It is important to note that a single ultrasonication experiment requires substantial resources to complete; therefore, the experiments could not be repeated to determine the experimental error. Testing procedures was repeated to the extent that the limited resources allowed, however, the Tappi standard was used to determine the error margins for freeness (T227), tear strength (T414) and tensile strength (T494) and is reported as expected errors in Chapters 4, 5 and 6.

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CHAPTER 4: Results of ultrasonication and enzymatic treatment of *Eucalyptus globulus* pulp

The influence of ultrasonication and enzymatic treatments on the *Eucalyptus globulus* (Santa Fe) pulp was investigated. These results were compared to mechanical refining to determine whether ultrasonication and enzymatic treatment may be a viable alternative. The untreated ultrasonication and mechanical refining were taken as the control treatments, which were compared to the enzymatic treatments to investigate the effect of combining ultrasonication or mechanical refining and enzymatic treatment. The treatment and testing procedures described in Chapter 3 were applied to re-pulp, treat and test the Santa Fe hardwood pulp.

4.1 Measurement of the development of untreated, sonicated hardwood pulp

In the first set of experiments the untreated pulp was developed by means of ultrasonication. The resulting pulp was tested for the degree of freeness, and the hand-sheets, made from the sonicated pulp, were tested for tensile strength and tear strength.

4.1.1 Freeness of untreated sonicated hardwood pulp

To test the freeness of the pulp, a sample was taken immediately after the ultrasonication treatment was completed. This sample was cooled rapidly to 20°C before the test was done. The freeness results can be seen in Figure 4.1.

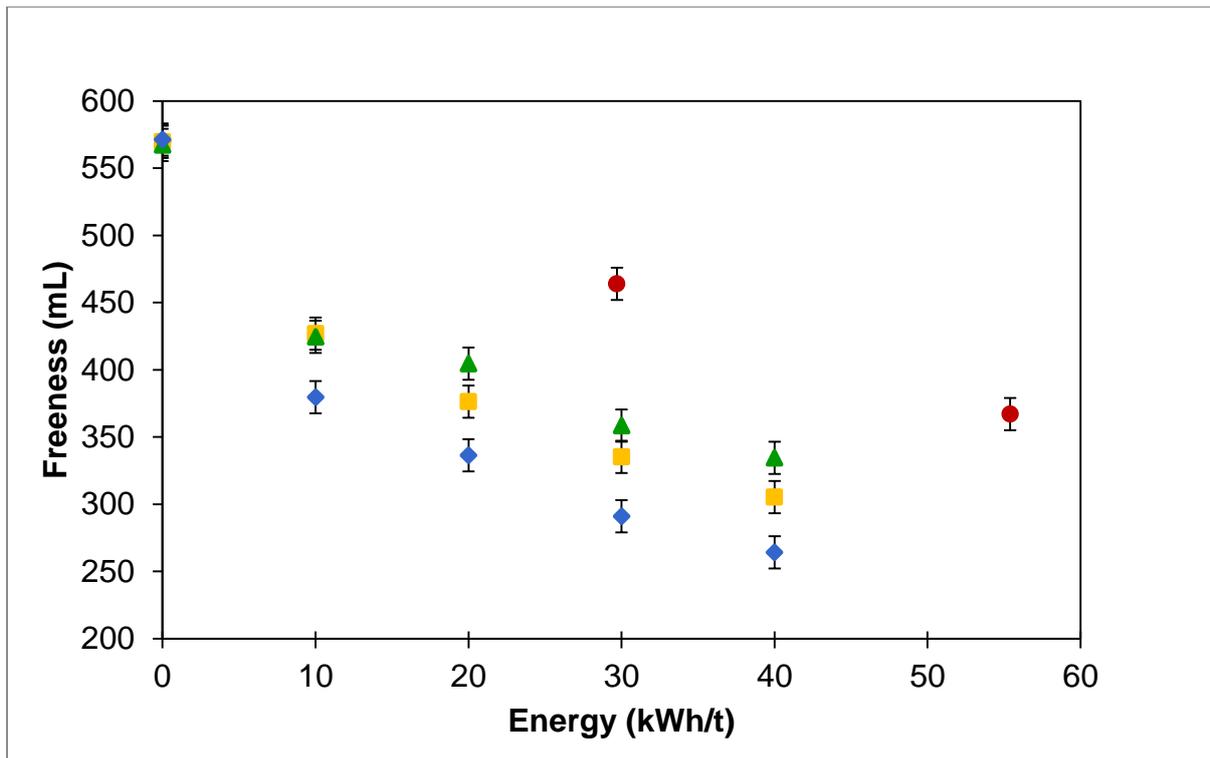


Figure 4.1: Hardwood pulp freeness after treatments with mechanical refining and ultrasonication respectively at different energy levels (● Mechanical refining, ◆ Untreated ultrasonication at 53 μm, ▲ Untreated ultrasonication at 80 μm, ■ Untreated ultrasonication at 106 μm).

Ultrasonication caused a significant decrease in freeness between 0 kWh/t and 10 kWh/t, where after the decrease was almost linear. This compared to mechanical refining, where the decrease seemed to be linear from 0 kWh/t to 55.4 kWh/t. High-amplitude ultrasonication (80 and 106 μm) seemed to result in higher freeness values when compared to ultrasonication at a low amplitude (53 μm). The reason for this could be that the low-amplitude ultrasonication was more effective in transferring energy to the pulp due to the treatment time being slightly longer, causing the resulting fibre development effect to be more apparent. Previous studies suggested that an increase in ultrasonication treatment time increased the modification effect on the medium (Huang *et al.*, 2007; Haung *et al.*, 2011; Montalbo-Lomboy *et al.*, 2010; Nikolic *et al.*, 2010; Sun & Tomkinson, 2002; Sun *et al.*, 2002), but did not find that the transfer of energy was more effective when applying lower amplitudes.

When comparing mechanical refining to ultrasonication, it transpired that an increase in energy input decreased the pulp freeness. This change in fibre properties supported

Rehman's (2013) and Suslick's (1989) findings indicating that fibre development in ultrasonication and mechanical refining were similar in that both increase the fibre contact area, which caused the freeness to decrease. Furthermore, the freeness of the sonicated pulps was lower than that of the pulps obtained by means of mechanical refining for all amplitudes. This could support the theory of higher energy transfer efficiency through ultrasonication (Rehman *et al.*, 2012:1393; Suslick, 1989:83). Fibre morphology results (Appendix A: Tables A1.1, A1.4 and A1.7) indicated higher fibrillation and increased fines production during ultrasonication when compared to mechanical refining, which explained the difference in freeness between mechanical refining and ultrasonication. The influence of different amplitudes on the morphology of the fibres was similar, which explains why the levels of freeness at higher amplitudes match. Slightly higher fines content at 53 μm explained the decreased freeness when compared to the 80 and 106 μm ultrasonication treatments. Another factor that may have caused the freeness to decrease, was the amount of colloidal cellulose material (crill) that was produced during ultrasonication (Miao *et al.*, 2013:1432). However, since there was no known feasible method to test the amount of colloidal cellulose, this was only an assumption.

4.1.2 Tensile strength of untreated hardwood pulp

The second aspect evaluated for untreated hardwood pulp was the average tensile strength. The effect of ultrasonication and mechanical refining is presented in Figure 4.2.

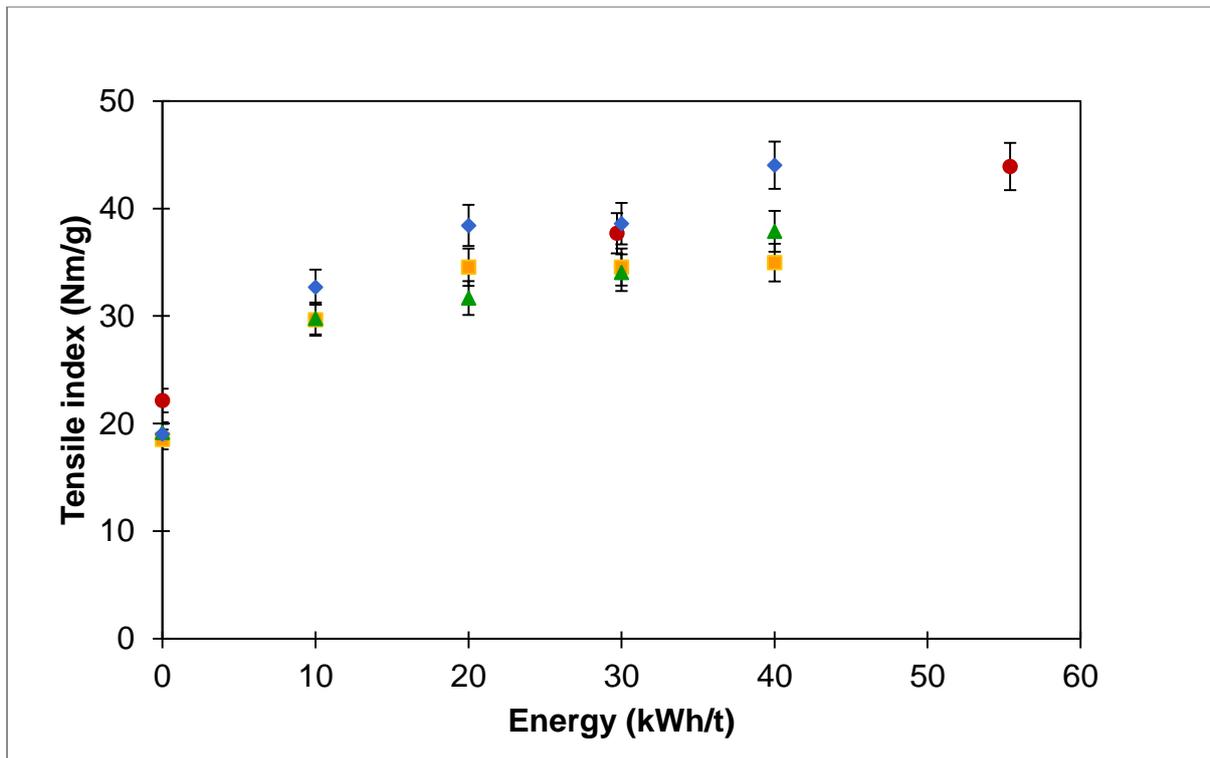


Figure 4.2: Tensile strength results for hardwood fibres after different levels of energy treatment (● Mechanical refining, ◆ Untreated ultrasonication at 53µm, ▲ Untreated ultrasonication at 80 µm, ■ Untreated ultrasonication at 106 µm).

When the ultrasonication energy input was increased, the tensile strength also improved, which supported the findings of Rehman (2013) and Suslick (1989), who found that ultrasonication and mechanical refining induced similar fibre development effects. Increasing the ultrasonication energy input resulted in a large initial increase in the tensile strength, but once the energy input exceeds 10 kWh/t, the change in tensile strength was less pronounced. An increased ultrasonication time was effective in modifying the medium, but Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002) and Sun *et al.* (2002) noted that a maximum time limit exists, beyond which treatment efficiency deteriorates. Ultrasonication at 53 µm resulted in constantly higher tensile strength values when compared to ultrasonication at high amplitudes. This result supports the freeness findings, where it was established that energy was transferred more effectively when ultrasonication treatment times were slightly longer and the transferred energy was lower. The highest tensile strength of 44 ± 2.2 Nm/g was achieved by applying ultrasonication at 53 µm with an energy input of 40 kWh/t. Higher amplitude ultrasonication did not seem to affect fibrillation and fibre collapse. Based

on the freeness and tensile strength, it was possible that more colloidal cellulose (crill) was produced. Colloidal cellulose is largely undetectable when using a MorFi instrument, and the resultant small differences in the fibre width and fines (Appendix A: Tables A1.1, A1.4 and A1.7) produced supported the theory of colloidal cellulose production.

When comparing ultrasonication and mechanical refining, the tensile strength results were similar, with ultrasonication at higher amplitudes producing slightly lower tensile strength results. This indicated that ultrasonication at a low amplitude was effective at lower energy inputs. It also indicated that low-amplitude ultrasonication may have caused fibre collapse and that the slightly higher fibrillation played a role in the increased tensile strength (Appendix A: Figure A1).

4.1.3 Tear strength of untreated hardwood pulp

The third aspect of the study was the tear strength, as shown in Figure 4.3.

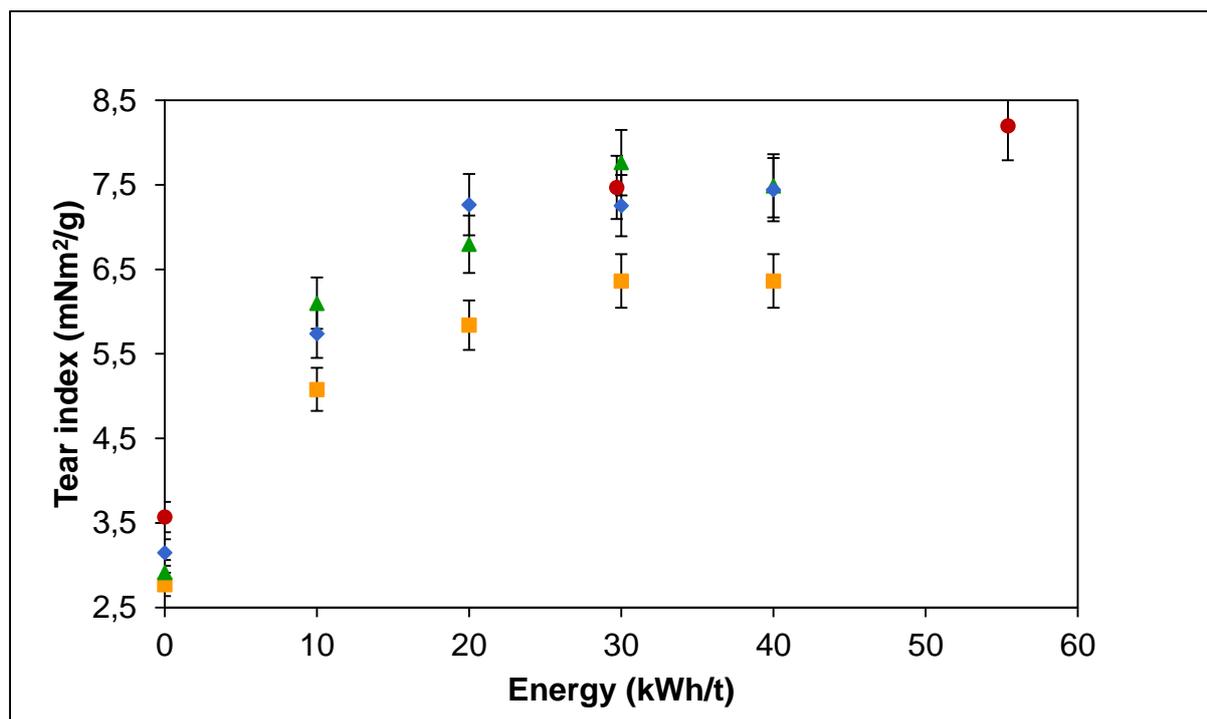


Figure 4.3: Tear strength of hardwood fibres at different treatment-energy levels (● Mechanical refining, ◆ Untreated ultrasonication at 53 µm, ▲ Untreated ultrasonication at 80 µm, ■ Untreated ultrasonication at 106 µm).

There was a large initial increase in tear strength when applying ultrasonication. The lack of tear strength decrease was due to the low energy ranges used in

ultrasonication, a clear tear strength decrease was noted with mechanical refining at high energy levels, which was expected (Chen *et al.*, 2010:7041). The increase indicated that the fibres remained strong, and that ultrasonication possibly caused less fibre damage and cutting than mechanical refining. The lack of fibre cutting can also be observed when looking at the fibre length (Appendix A: Figures A1.1, A1.4 and A1.7), where ultrasonication produced less fibre cutting compared to mechanical refining. It seemed that ultrasonication at low and medium amplitudes was the most effective in developing tear strength. This also supported the theory that slightly longer treatment times and lower amplitudes were more effective in treating the hardwood fibres. The highest tear strength (7.7 ± 0.3 mNm²/g) was achieved at 40 kWh/t while applying ultrasonication at 80 μ m.

Ultrasonication at low and medium amplitudes followed the same trend as mechanical refining. The high-amplitude treatment produced notably lower tensile strength results compared to mechanical refining. The lower results could be because the power produced by the high amplitude was detrimental to the fibres.

During mechanical refining, tear strength will increase at lower energy levels due to limited fibre damage, but as the applied energy increases, more fibres will be damaged, and the tear strength will decrease (Chen *et al.*, 2010:7041). Ideally the tear strength decrease should be as low as possible.

4.1.4 The relationship between tear and tensile strength for untreated hardwood pulp
The relationship of the tear and tensile indices is presented in Figure 4.4 and will provide a basis for comparing the overall strength of the paper after being either mechanically refined or sonicated.

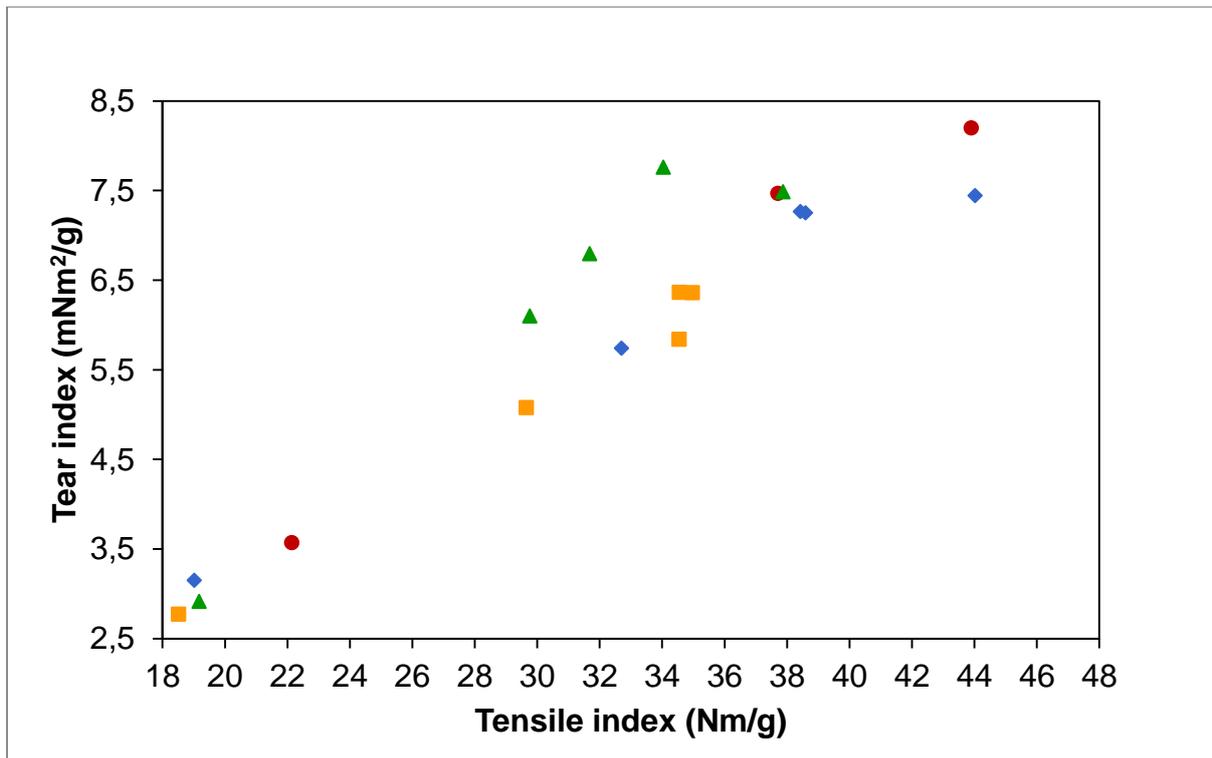


Figure 4.4: Tear and tensile strength relationship of untreated hardwood fibres (● Mechanical refining, ◆ Untreated ultrasonication at 53 µm, ▲ Untreated ultrasonication at 80 µm, ■ Untreated ultrasonication at 106 µm).

Overall, the tear versus tensile strength relationship of the mechanically refined pulps was higher than that of the sonicated pulps, but ultrasonication still showed a steady increase (Appendix A: Tables A1.1, A1.4 and A1.7). This meant that the tear strength of the fibres increased without negatively affecting the tensile strength.

Ultrasonication at amplitude 80 µm showed potential when compared to mechanical refining and the other amplitudes, with the highest tear strength at a tensile strength of 34 Nm/g.

4.1.5 The relationship between freeness and tensile strength for untreated hardwood pulp

The relationship between freeness and tensile strength was important, because it showed the interaction between the apparent fibre modification (freeness) and the ideal fibre modification (tensile strength). This interaction can be seen in Figure 4.5.

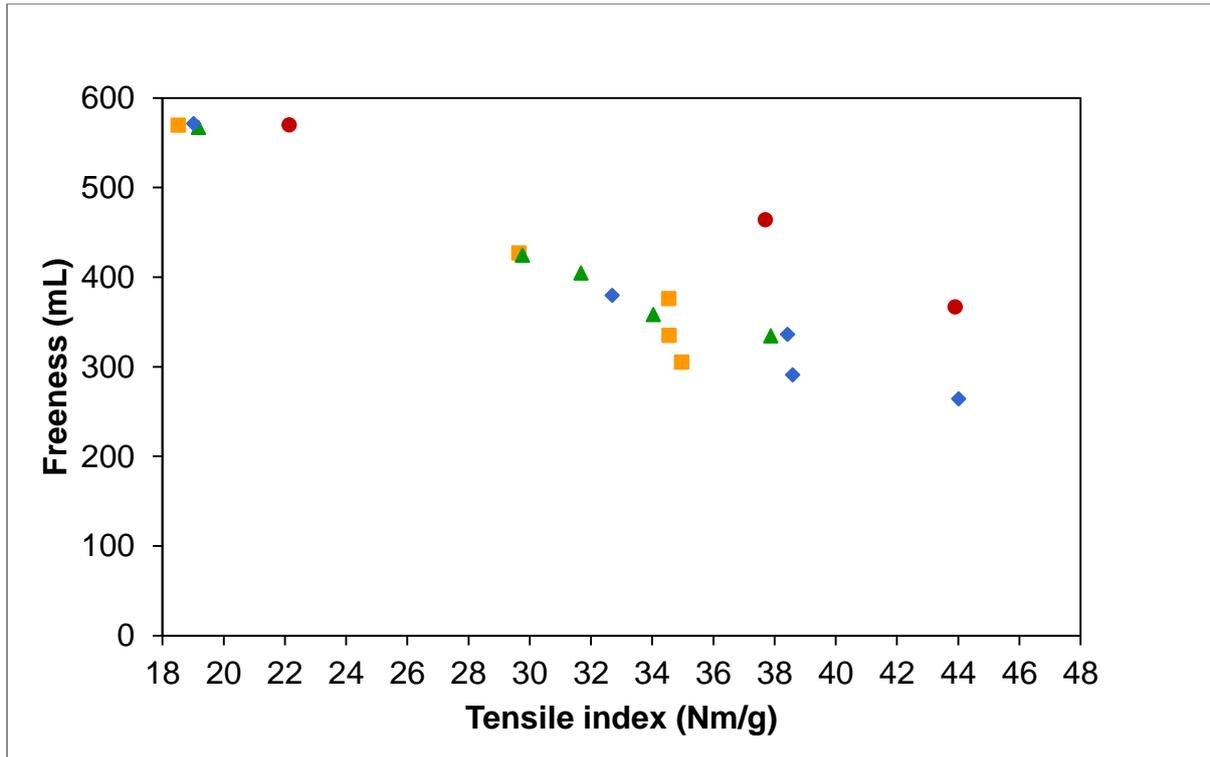


Figure 4.5: The relationship between freeness and tensile strength for hardwood (● Mechanical refining, ◆ Untreated ultrasonication at 53 μm , ▲ Untreated ultrasonication at 80 μm , ■ Untreated ultrasonication at 106 μm).

The freeness of the pulp needs to be high to ensure the minimum of blockages and constant flow in the paper machine process (Miao *et al.*, 2013:1432). A high tensile strength would have confirmed that the fibres were ideally modified, rather than being merely damaged.

The significant reduction in drainage for the sonicated pulps was a large drawback. Mechanical refining was effective in increasing the tear and tensile strength of the fibres without a significant loss of freeness.

In summary, at low energy inputs ultrasonication was more effective at developing fibres than mechanical refining. Ultrasonication at amplitude 53 μm had the potential to induce the desired fibre modification effects, while using less energy than mechanical refining. The main drawbacks in using ultrasonication were the considerable decrease in pulp freeness and the inefficiency in modifying the fibres at higher energy inputs. The inability to induce continuous fibre modification effects through a range of energy inputs supported the findings of Joseffson (2010) that ultrasonication can modify fibres, but not to the same extent as mechanical refiners.

4.2 Ultrasonication and refining of enzymatically-treated hardwood at low dosages

In order to address the shortcomings of ultrasonication with regard to freeness, an enzyme was added to the system and the tests were repeated. The enzyme, endoglucanase, was found to increase the freeness of fibres in previous studies (Steel & Wolfaardt, 2010:2). For the next sets of experiments, the recommended dosage of 50 g/t was used to treat the hardwood fi

bres and slow the rate of freeness reduction.

4.2.1 Freeness of enzymatically-treated hardwood at low dosages

The effect of the enzymatic pre -treatment can be seen in Figure 4.6.

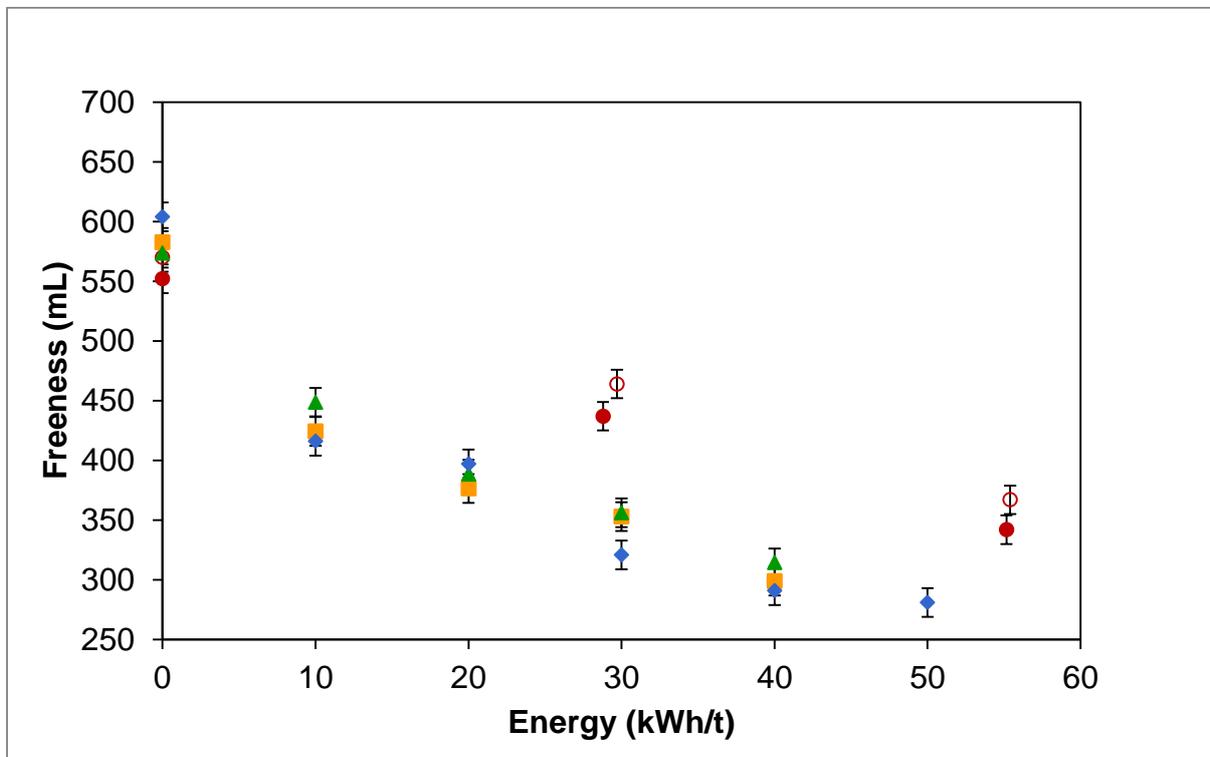


Figure 4.6: Hardwood pulp freeness after 50 g/t enzymatic pre-treatment at different energy levels with mechanical refining and ultrasonication respectively (○ Untreated mechanically refined, ● Enzymatically treated and mechanically refined, ◆ Enzymatically treated with ultrasonication at 53 μm, ▲ Enzymatically treated with ultrasonication at 80 μm, ■ Enzymatically treated with ultrasonication at 106 μm).

The freeness of both the enzymatically treated, mechanically refined pulp and the sonicated pulp decreased. When comparing the untreated and enzymatically treated, mechanically refined pulp, the enzymatically treated pulp had a lower freeness.

Initially, the freeness of the enzymatically treated sonicated pulp was higher than that of the enzymatically treated and untreated mechanically refined pulp, but it subsequently decreased notably. This significant decrease in freeness of the sonicated pulp indicated a possible different mechanism of fibre modification, compared to mechanical refining. It was expected that the freeness of all pulps would decrease at a slower rate when treated with the enzyme, because previous studies by Wolfaardt and Steele (2010) indicated a reduction of fines and, possibly, colloidal cellulose. When comparing the morphology of the untreated sonicated fibres to the enzymatically treated sonicated fibres (Appendix A: Tables A1.2, A1.5 and A1.8), there was a considerable decrease in the fines content. This proved that the fines removal theory holds. The decrease in freeness, on the other hand, was supported by Josefsson (2006), who noted that endoglucanase treatment resulted in external fibrillation and swelling of fibres, which caused the freeness to decrease. Another theory was that prolonged enzymatic pre-treatment times may cause the freeness of the fibres to deteriorate (Oksanen *et al.*, 1997; Pere *et al.*, 1995). This theory was more feasible, since ultrasonication required more time to reach comparable energy levels than mechanical refining, meaning that the enzymes were in contact with the fibers for a longer period. At lower energy inputs ultrasonication was much more effective in decreasing the freeness, which indicated possible fibre modification results. The enzymatically treated and sonicated pulp achieved a freeness of between 310 ± 7 mL and 350 ± 7 mL using the same amount of energy that mechanical refining used to achieve a freeness of 450 ± 12 mL. However, as the energy increased, the difference between the enzymatically treated, mechanically refined pulp and the sonicated pulp decreased, and the freeness of the sonicated fibres matched that of the mechanically refined fibres.

The freeness of the three sonicated pulps was largely similar. The 80 μ m amplitude treatment caused a marginally higher freeness than the other amplitude treatments, while the 53 μ m amplitude treatment had an overall lower freeness.

A comparison of untreated and enzymatically treated sonicated fibres can be seen in Figure 4.7.

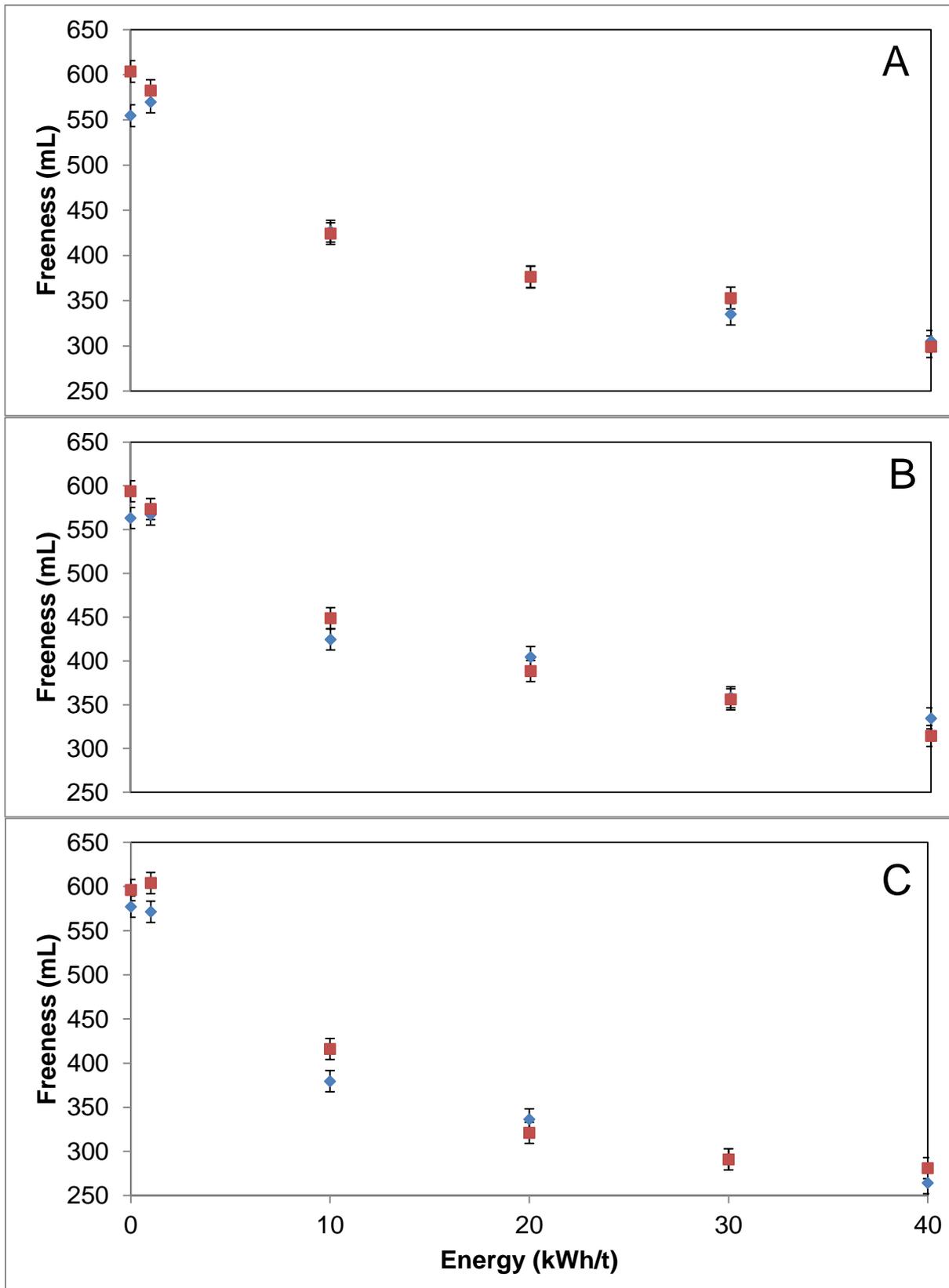


Figure 4.7: Freeness (mL) of untreated and enzymatically treated sonicated hardwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; ◆ Untreated, ■ 50 g/t Enzymatically treated).

The freeness of the untreated sonicated pulp was similar to that of the enzymatically treated fibres. This similarity also supported the findings of Oksanen *et al.* (1997) and Pere *et al.* (1995) that modification ceased once the enzymatic pre-treatment time was prolonged beyond a certain point.

4.2.2 Tensile strength of low-dosage enzymatically treated hardwood

The tensile strength results for the enzymatically treated sonicated pulp can be seen in Figure 4.8.

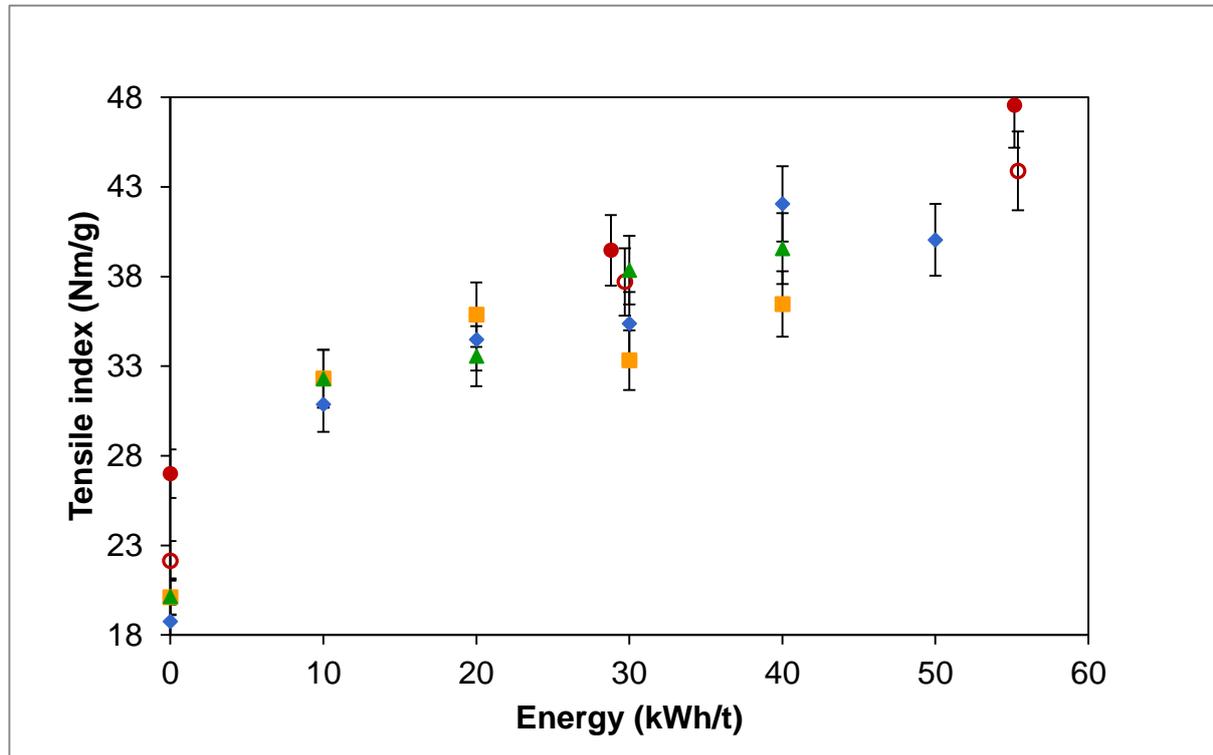


Figure 4.8: Tensile strength results for enzymatically treated hardwood fibres after different levels of energy treatment with mechanical refining and ultrasonication respectively (○ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm, ▲ Enzymatically treated ultrasonication at 80 μm, ■ Enzymatically treated ultrasonication at 106 μm).

There was a significant increase in tensile strength for all treatments. The enzymatically treated, mechanically refined pulp did, however, display the highest tensile strength results, closely followed by the enzymatically treated sonicated pulp.

The tensile strength of the enzymatically treated, mechanically refined fibres was slightly higher than that of the untreated mechanically refined fibres and enzymatically treated sonicated fibres. The comparable tensile strength results could be explained

when looking at the morphology (Appendix A: Tables A1.2, A1.5 and A1.8), where the fibre width and fibrillation were quite close. At low energy inputs the tensile strength of the enzymatically treated, sonicated fibres increased faster than the mechanically refined fibres, but as the energy increased, the tensile strength started to level out. The ultrasonication of enzymatically treated fibres indicated potential when compared to untreated mechanical refining, but it seemed that mechanically refined, enzymatically treated fibres had the highest tensile strength.

The 53 μm sonicated, enzymatically treated fibres had the highest tensile strength of the sonicated samples ($42 \pm 2.1 \text{ Nm/g}$ at $40 \pm 2 \text{ kWh/t}$), but the 80 μm treatment had an even increase and was higher at the lower energy inputs. The 106 μm enzymatically treated fibres did not show any potential, except at 20 kWh/t, where it had the highest tensile strength ($35.9 \pm 1.8 \text{ Nm/g}$). In Figure 4.9 the tensile strength of the untreated sonicated fibres are compared to the enzymatically treated sonicated fibres.

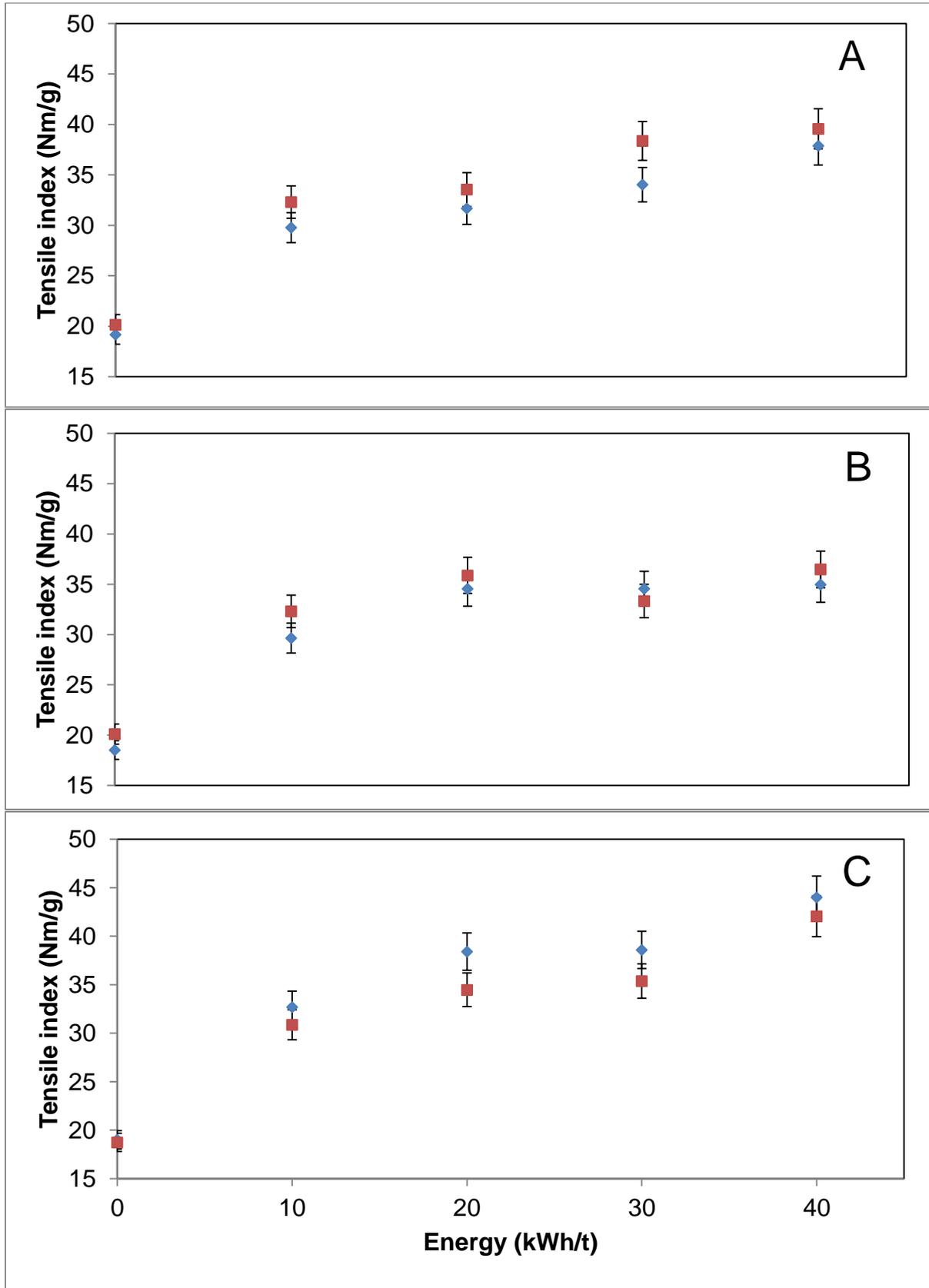


Figure 4.9: Tensile strength of untreated and enzymatically treated sonicated hardwood fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm amplitudes [C]; ♦ Untreated, ■ Enzymatically treated at 50 g/t).

At the 106 μm amplitude, the tensile strength of the enzymatically treated fibres were consistently higher than the untreated fibres. The same was true for the tensile strength of the 80 μm enzymatically treated fibres at low energies. A clear change was noted once the energy was higher than 20 kWh/t, where the untreated fibres displayed a higher tensile strength. The untreated fibres at the 53 μm treatments had a consistently higher tensile strength when compared to the enzymatically treated fibres. The lower tensile strength results noted at 53 μm and the higher-energy range of the 80 μm treatment may be explained by the compilation of two findings. It was found that increased ultrasonication time may have resulted in fibres reaching a maximum point of modification, as noted by Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002) and Sun *et al.* (2002). Furthermore, prolonged enzymatically treated times may have resulted in damaged fibres, as seen by Josefsson (2006). These two findings explained why the longer treatment times at 53 μm had a negative effect on the tensile strength of the fibres.

4.2.3 Tear strength of low-dosage enzymatically treated hardwood

The tear strength of the enzymatically treated fibres can be seen in Figure 4.10.

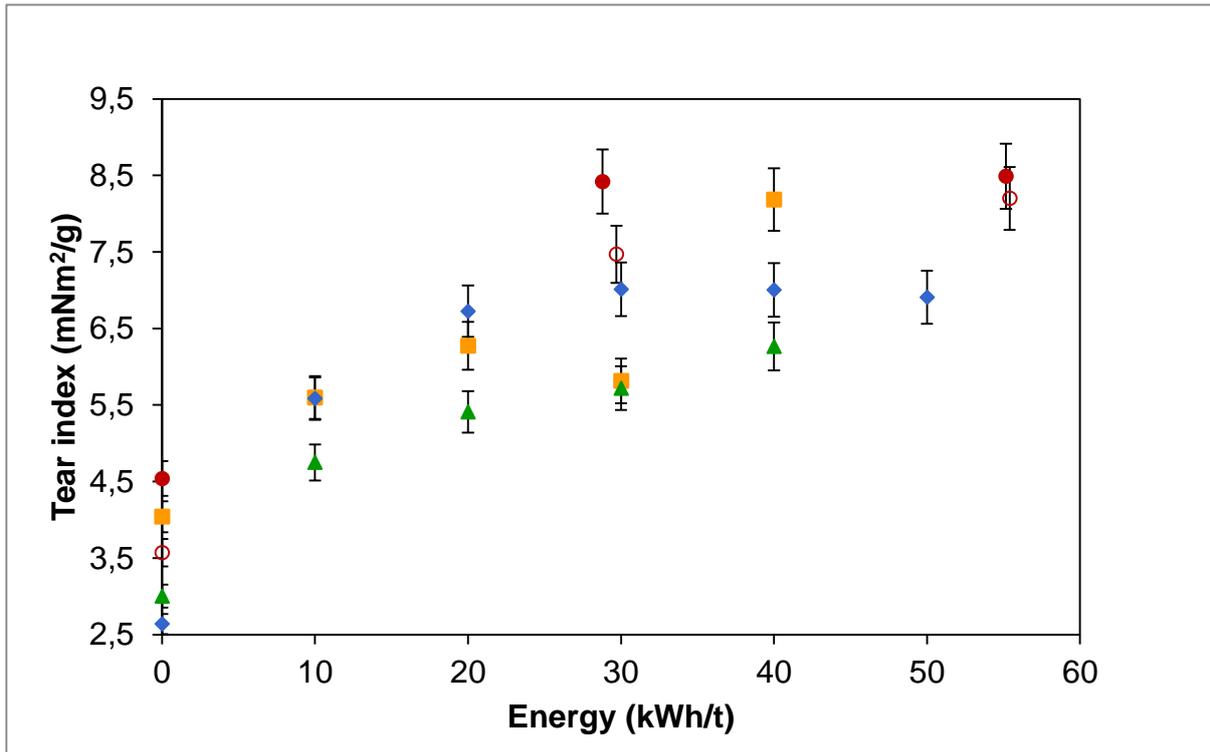


Figure 4.10: Tear strength results of enzymatically treated hardwood fibres after mechanical refining or ultrasonication (○ Untreated mechanical refining, ● Enzymatically treated, mechanical refining, ◆ Enzymatically treated, ultrasonication at 53 µm, ▲ Enzymatically treated, ultrasonication at 80 µm, ■ Enzymatically treated, ultrasonication at 106 µm).

The tear strength of the enzymatically treated, mechanically refined fibres was notably higher than for any of the other treated fibres. As noted earlier, no tear strength decrease was noted due to the low energy ranges where ultrasonication was used. It seemed that the 106 µm enzymatic ultrasonication treatment caused a rapid increase in tear strength at energy inputs above 30 kWh/t, but the data were insufficient for proving this beyond doubt. It should also be noted that the enzymatic ultrasonication treatment caused a large increase in tear strength at lower energy inputs. The morphology (Appendix A: Tables A1.2, A1.5 and A1.8) indicated that the sonicated fibres retained their length well when compared to the mechanically refined fibres, which could explain why the tear strength was higher at the lower energy inputs. It was also an indication that the ultrasonication process was less harsh on the fibres, and that less fibre cutting occurs. After a 10 kWh/t ultrasonication treatment, the tear

strength of the 106 μm sonicated fibres increased by 38 %, the 80 μm fibres increased by 58 % and the 53 μm increased by 111 %.

The three ultrasonication amplitudes gave very different results. At 106 μm the tear strength increased initially, then decreased steadily, until it increased again by 40 % between 30 kWh/t and 40 kWh/t. The 80 μm treatment resulted in a steady increase in tear strength throughout the energy range, while at 53 μm tear strength increased rapidly at the low energy inputs, then stabilized at $7 \pm 0.3 \text{ mNm}^2/\text{g}$.

A comparison between the tear strength of untreated sonicated fibres and that of the enzymatically treated sonicated fibres can be seen in Figure 4.11.

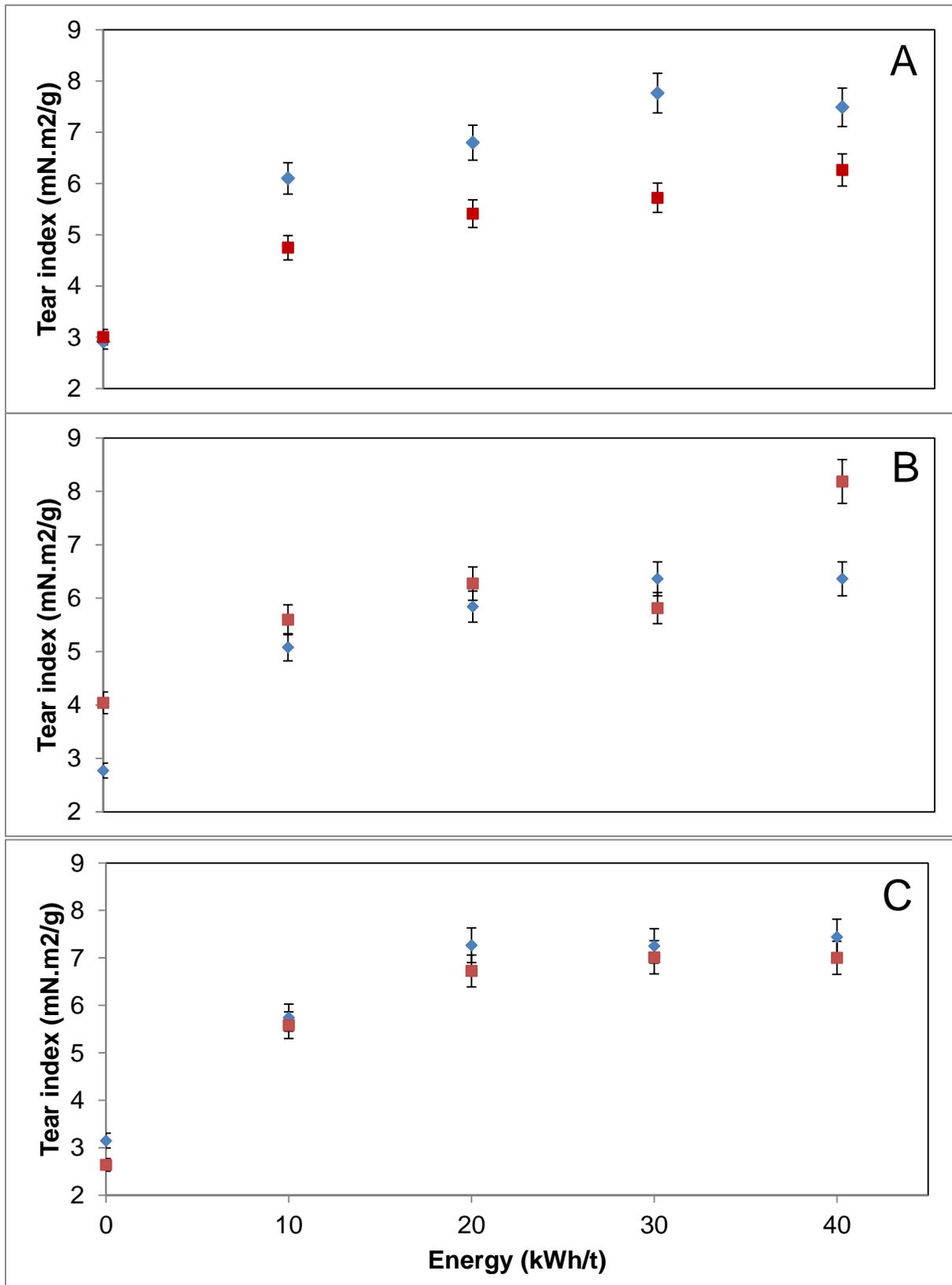


Figure 4.11: Tear strength of untreated and enzymatically treated sonicated hardwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; ♦ Untreated, ■ Enzymatically treated at 50 g/t).

When comparing the tear strength of the untreated sonicated fibres with the 50 g/t enzymatically treated fibres, it appeared that the enzymatic pre-treatment seemed to have the effect of reducing the tear strength of the paper. At the 53 μm treatment, the tear strength of the treated and untreated fibres was similar, but at 80 μm a distinct difference between the two treatments became evident. The tear strength of the enzymatically treated fibres was higher at 106 μm , but the total change in tear strength was lower when compared to the untreated fibres.

4.2.4 The relationship between the tear and tensile strength of low-dosage enzymatically treated hardwood

Figure 4.12 shows how tear and tensile strength relate.

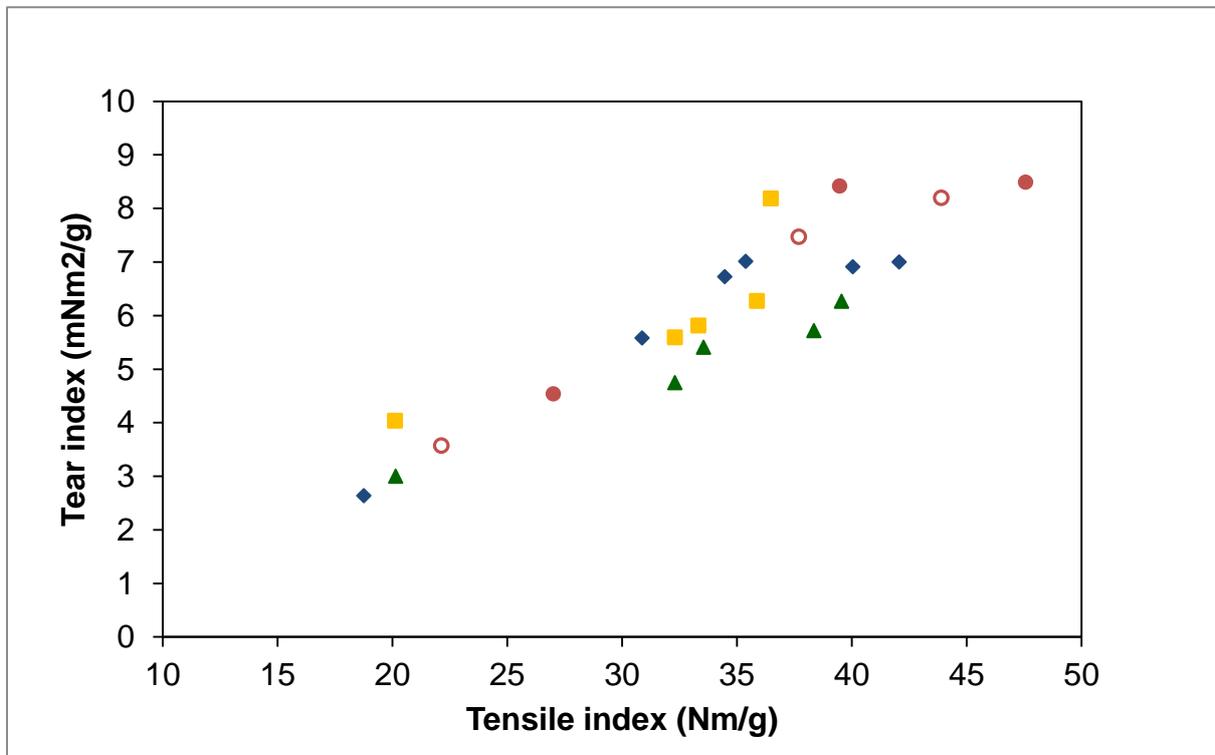


Figure 4.12: The relationship between the tear and tensile strength of 50 g/t enzymatically treated hardwood fibres (○ Enzymatically treated and mechanically refined, ● Mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

In all ultrasonication cases there was an increase in tear strength along with an increase in tensile strength. However, ultrasonication could not improve the tear and tensile relationship to the same extent as mechanical refining, which seemed to have a linear effect on the relationship at lower tensile strength, before reaching an

equilibrium point. The enzymatically treated, mechanically refined fibres showed a constant increase in the relationship, but it was lower than the untreated mechanically refined fibres. Ultrasonication at 106 μm displayed positive results at tensile indices of $20 \pm 1 \text{ Nm/g}$ and $36 \pm 1.8 \text{ Nm/g}$, with corresponding tear indices of $4 \pm 0.2 \text{ mNm}^2/\text{g}$ and $8.1 \pm 0.3 \text{ mNm}^2/\text{g}$. The relationship of ultrasonication at 53 μm was similar to the mechanically refined samples, but it reached a maximum at a tensile strength of $35 \pm 1.5 \text{ Nm/g}$.

4.2.5 Freeness and tensile strength relationship of low-dosage enzymatically treated hardwood

The tensile strength and freeness relationship of the enzymatically treated fibres can be seen in Figure 4.13.

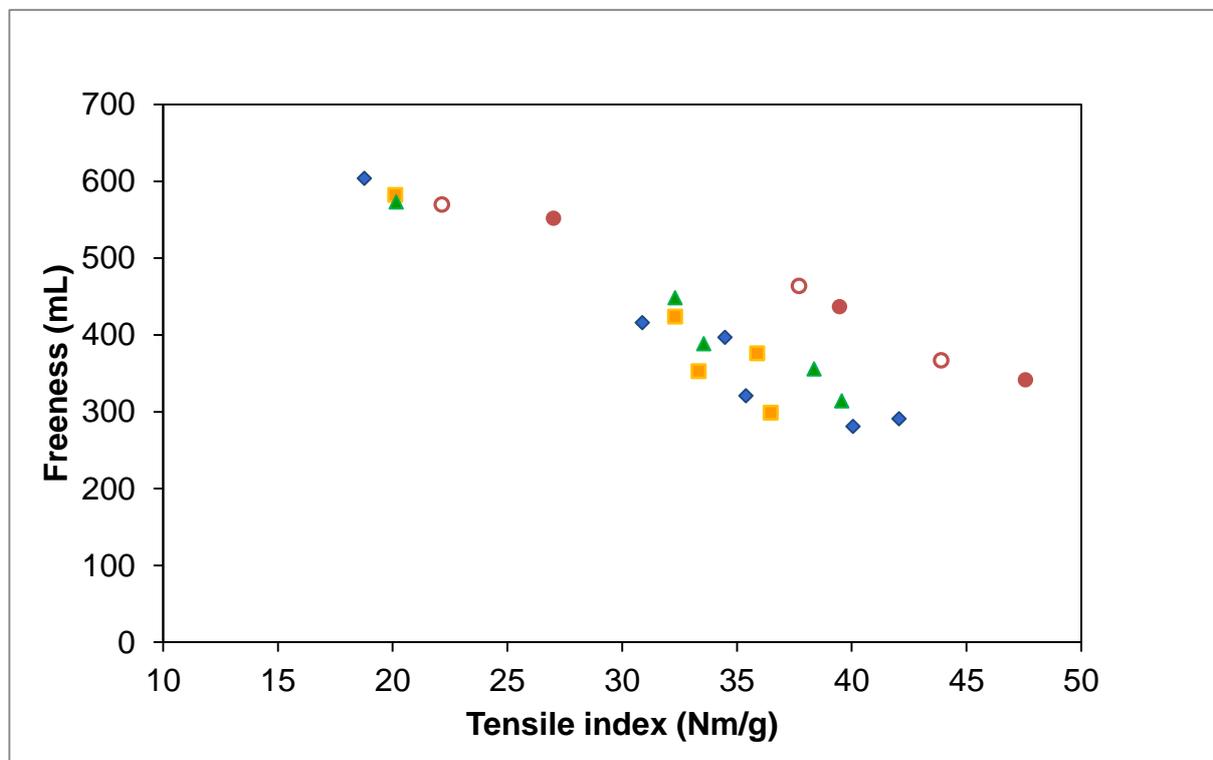


Figure 4.13: Freeness (in mL) and tensile strength relationship of 50 g/t enzymatically treated hardwood fibres (○ Enzymatically treated, mechanically refined, ● Mechanical refining, ◆ 53 μm enzymatically treated ultrasonication treatment, ▲ 80 μm enzymatically treated ultrasonication treatment, ■ 106 μm enzymatically treated ultrasonication treatment).

In all cases the tensile strength of the fibres could not be increased without losing freeness. There was a higher loss in freeness during ultrasonication than during mechanical refining. Figure 4.13 shows that ultrasonication and enzymatic pre-

treatment combined could not develop the tensile strength of the fibres without negatively impacting the freeness.

In summary, ultrasonication and enzymatic pre-treatment were successful at modifying fibres at low energy inputs, but beyond a certain point in time began to have a negative impact on the properties of the fibres. This negative impact confirmed the findings of Josefsson (2006), Oksanen *et al.* (1997) and Pere *et al.* (1995) that ultrasonication was effective in modifying fibres, but becomes detrimental to the fibre properties once the ultrasonication period was too long. The enzymatically treated fibres, however, displayed more promise after mechanical refinement. The freeness of the enzymatically treated fibres did not improve as expected; it was similar for the sonicated fibres and lower than the mechanically refined fibres. The strength properties of the mechanically refined fibres improved when compared to the untreated mechanically refined fibres.

4.3 Ultrasonication and refining of high-dosage enzymatically treated hardwood

In an attempt to solve the marked decrease in freeness, higher enzymatic dosages were investigated. An experiment was consequently done to determine the result of enzymatically treating the pulp at 200 g/t before introducing ultrasonication.

4.3.1 Freeness of high-dosage enzymatically treated hardwood

The same treatment procedure as with the 50 g/t enzymatic pre-treatment was followed for the 200 g/t dosage enzymatic pre-treatment, and the freeness results can be seen in Figure 4.14.

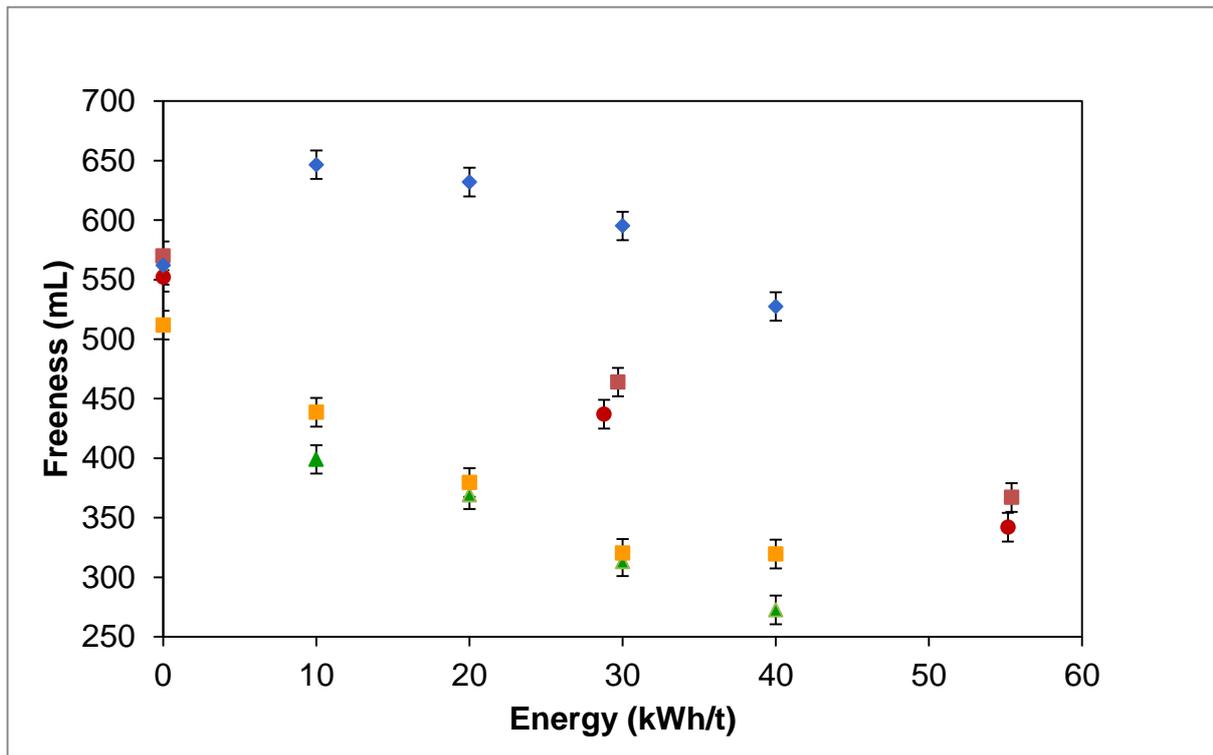


Figure 4.14: Hardwood pulp freeness after 200 g/t enzymatic pre-treatment at different energy levels with mechanical refining and ultrasonication respectively (■ Untreated mechanically refined, ● Enzymatically treated, mechanically refined, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The higher enzymatic dosage seemed to have little effect on the freeness, except in the low-amplitude ultrasonication test. The untreated and enzymatically treated, mechanically refined pulp had similar levels of freeness, with that of the untreated pulp slightly higher than the enzymatically treated pulp. A combination of ultrasonication at high amplitudes and the high enzymatic dosage treatment resulted in similar freeness profiles. The 53 μm treatment, however, resulted in a significant freeness improvement. The initial freeness increase indicated colloidal-cellulose removal by the enzymes, before it started decreasing as fines were produced at higher energy levels. These freeness changes indicated less harsh conditions at 53 μm ultrasonication, which allowed the enzymes to remove colloidal cellulose at a faster rate than it was being generated. Due to the lack of literature regarding high-dosage endoglucanase treatments, it was difficult to compare these results to previous studies. The results of ultrasonication at higher amplitude (106 μm and 80 μm) looked similar to the control and 50 g/t enzymatic experiments. The 80 μm and 106 μm

treatments resulted in much lower freeness values (313 ± 7 mL and 320 ± 7 mL) at 30 kWh/t, when compared to the mechanically refining runs.

The freeness comparison of sonicated untreated, 50 g/t and 200 g/t enzymatic pre-treatment is presented in Figure 4.15.

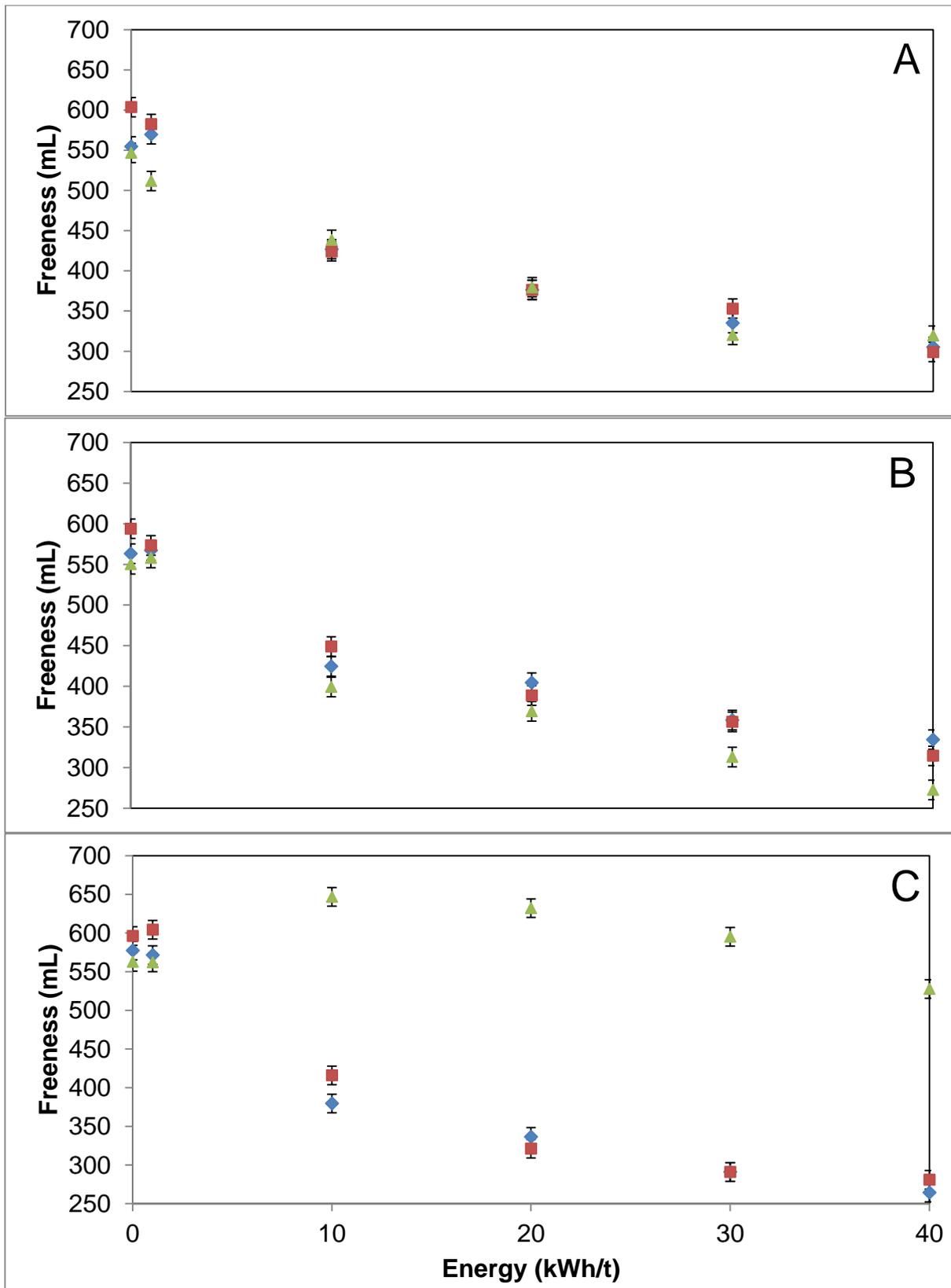


Figure 4.15: Freeness comparison of untreated and enzymatically treated sonicated hardwood fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm [C] amplitudes; ♦ Untreated, ■ Enzymatically treated at 50 g/t, ▲ Enzymatically treated at 200 g/t).

When comparing the freeness of the ultrasonication control, namely 50 g/t enzymatic pre-treatment and 200 g/t enzymatic pre-treatment, the results were very similar, except for the 53 μm amplitude experiments. It seemed that the combination of the enzymatic and ultrasonication treatment had no notable effect on the freeness of the fibres. A possible explanation may be that the enzymes were immobilized by the considerable temperature increases at the sonotrode tip commonly associated with ultrasonication. A higher amplitude resulted in more power being transferred to the pulp (Rehman *et al.*, 2013:1395), which meant that the temperature at the sonotrode was higher.

Another explanation may have been that the prolonged enzymatic pre-treatment time caused a maximum point of fibre modification as seen by Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lomboy *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002). The maximum point of modification explained why the different enzymatic dosages had little effect on the freeness.

4.3.2 Tensile strength of high-dosage enzymatically treated hardwood

The tensile strength results from the 200 g/t enzymatic pre-treatment can be seen in Figure 4.16.

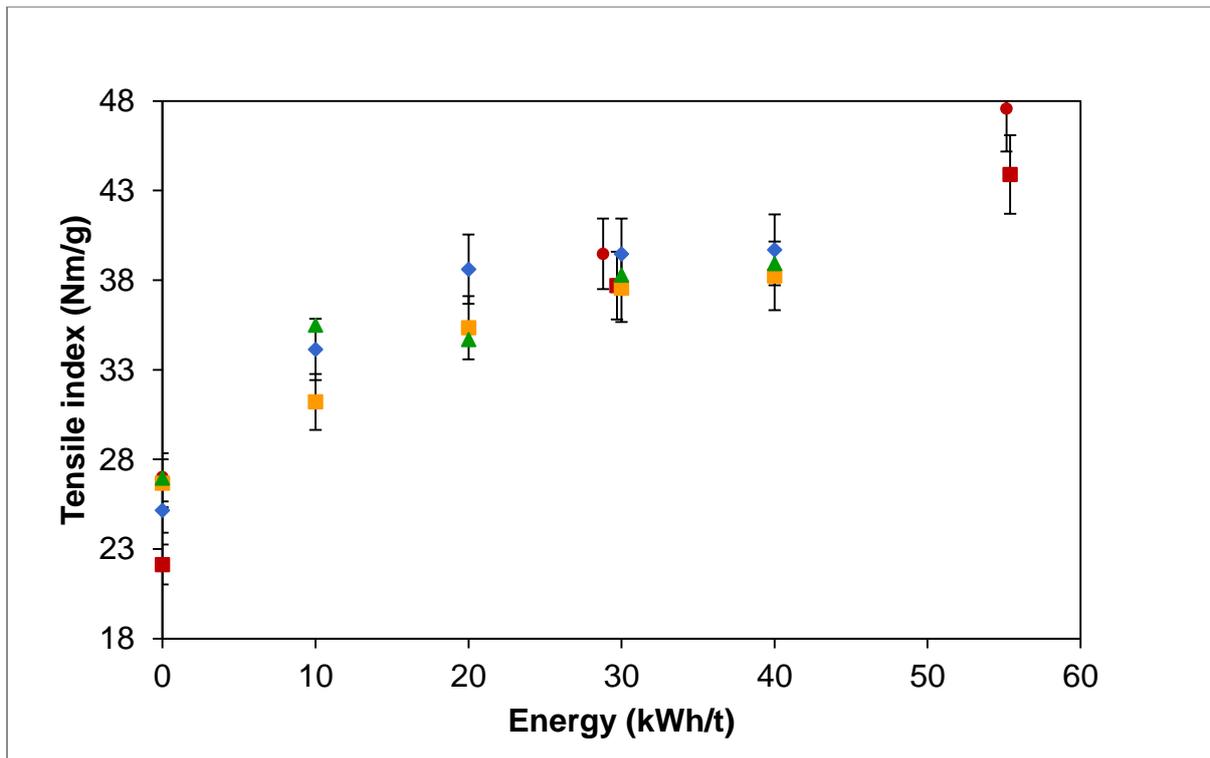


Figure 4.16: Tensile strength results for 200 g/t enzymatically treated hardwood fibres at different levels of energy treatment with mechanical refining and ultrasonication (■ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

The 200 g/t enzymatic ultrasonication treatment increased the tensile strength of the fibres rapidly at lower energy inputs (0 to 20 kWh/t). It was also noted that the tensile strength of the enzymatically treated fibres was higher than the untreated mechanically refined fibres at 0 kWh/t. The tensile strength at 0 kWh/t energy represents the effect of re-pulping and enzymatic pre-treatment with no additional fibre modification effects. The difference in tensile strength supported the findings of Josefsson (2006), who found that the enzymatic pre-treatment alone had the capacity to induce fibre modification effects such as fibrillation and fibre collapse. The 53 µm 200 g/t enzymatic ultrasonication treatment had a tensile strength of 39.5 ± 2 Nm/g at 30 kWh/t, which was very similar to the enzymatically treated, mechanically refined fibres. The two mechanical refining experiments resulted in notably higher tensile strengths at energy levels above 30 kWh/t when compared to ultrasonication (which seemed to reach a plateau after 30 kWh/t). The different amplitude ultrasonication treatments

had similar effects on 200 g/t enzymatically treated pulp, but the 53 μm treatment showed the most promise.

A comparison of the tensile strength of sonicated fibres at different enzymatic dosage treatments can be seen in Figure 4.17.

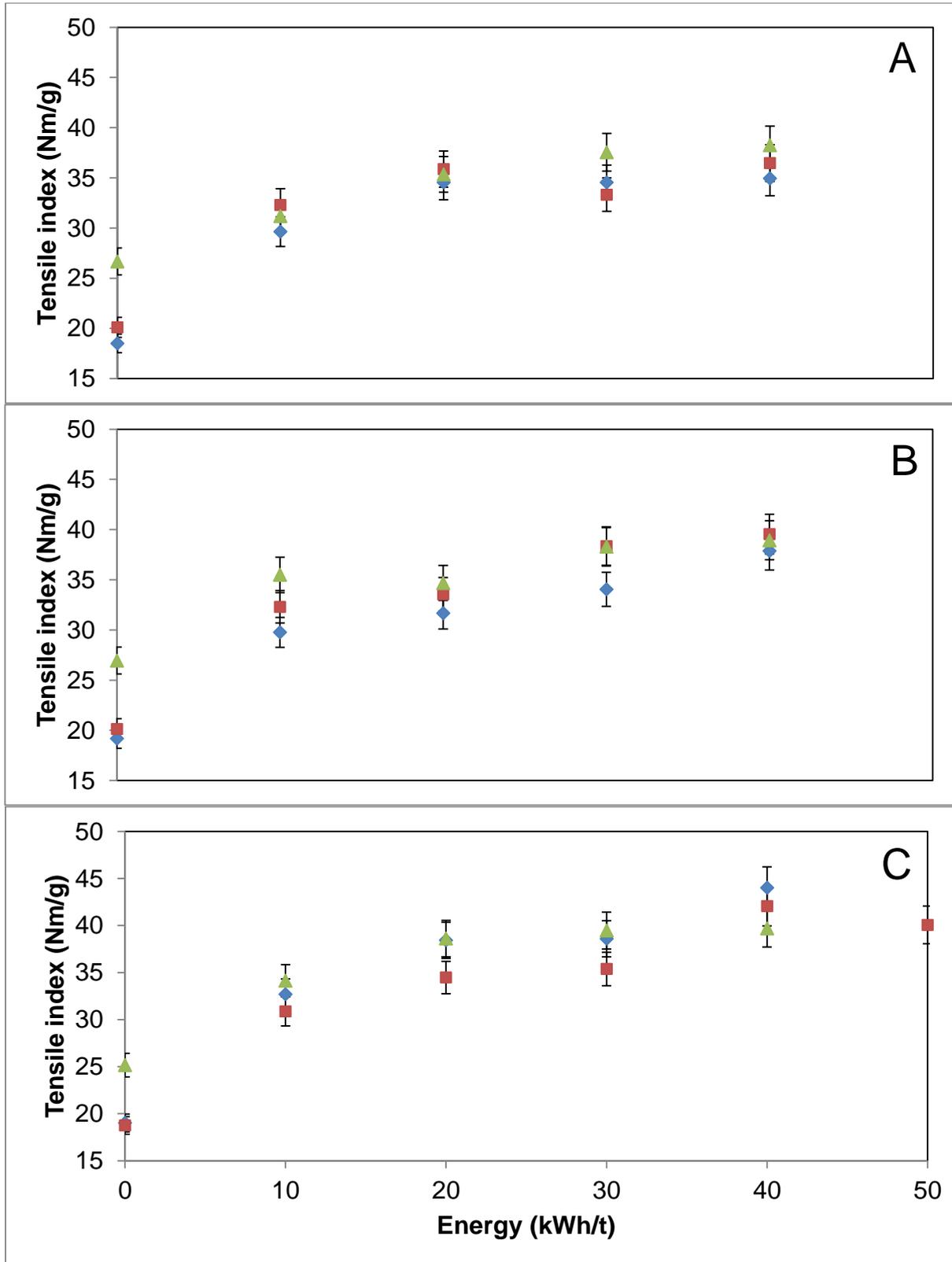


Figure 4.17: Tensile strength comparison of untreated and enzymatically treated sonicated hardwood fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm [C]; ♦ Untreated, ■ Enzymatically treated at 50 g/t, ▲ 200 g/t Enzymatically treated).

Very little change was apparent when comparing the tensile strength of the different sonicated enzymatic dosages, but the tensile strength of the enzymatically treated fibres was constantly higher than that of the control directly after the 25 min enzymatic incubation period (seen at 0 kWh/t). It was clear that the tensile strength of the 200 g/t enzyme dosage was higher than the 50 g/t enzyme dosage and control. These tensile strength results supported the findings of Oksanen *et al.* (1997) and Pere *et al.* (1995) that ultrasonication and enzymatic pre-treatment have a positive modification effect on the fibres for a finite period of time.

4.3.3 Tear strength of high-dosage enzymatic-treated hardwood

The tear strength results for the 200 g/t enzymatically treated pulp can be seen in Figure 4.18.

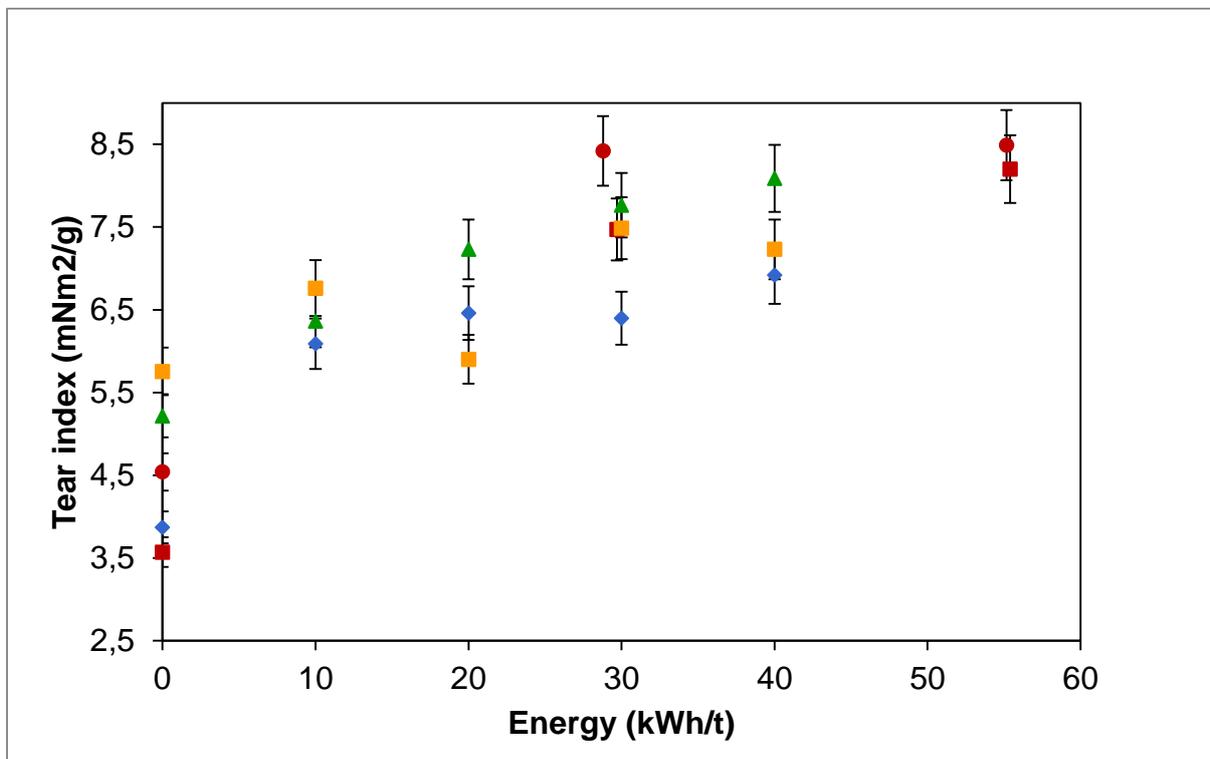


Figure 4.18: Tear strength results for 200 g/t enzymatically treated hardwood fibres after different levels of energy treatment with mechanical refining and ultrasonication (■ Untreated mechanical refining, ● Enzymatically treated, mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

The low energy range used for ultrasonication resulted in a steady increase in tear strength, as can be expected due to the limit fibre damage at lower energies. The tear

strength seemed to increase for the 200 g/t enzymatically treated, sonicated pulp. However, when compared to the tear strength of the 50 g/t enzymatically treated, mechanically refined pulp, there was no added benefit for the sonicated pulp. The sonicated pulp seemed to produce similar results to the untreated, mechanically refined pulp. Although this theory could not be validated by previous studies, the explanation for the low tear strength may have been that the higher enzymatic dosage caused the sonicated pulp to reach its maximum point of modification faster, which could support the findings of Oksanen *et al.* (1997) and Josefsson (2006). Ultrasonication at higher amplitudes (80 μm and 106 μm) produced higher tear strength results when compared to ultrasonication at a low amplitude.

In Figure 4.19, the comparison of tear strengths for different enzymatic dosages can be seen.

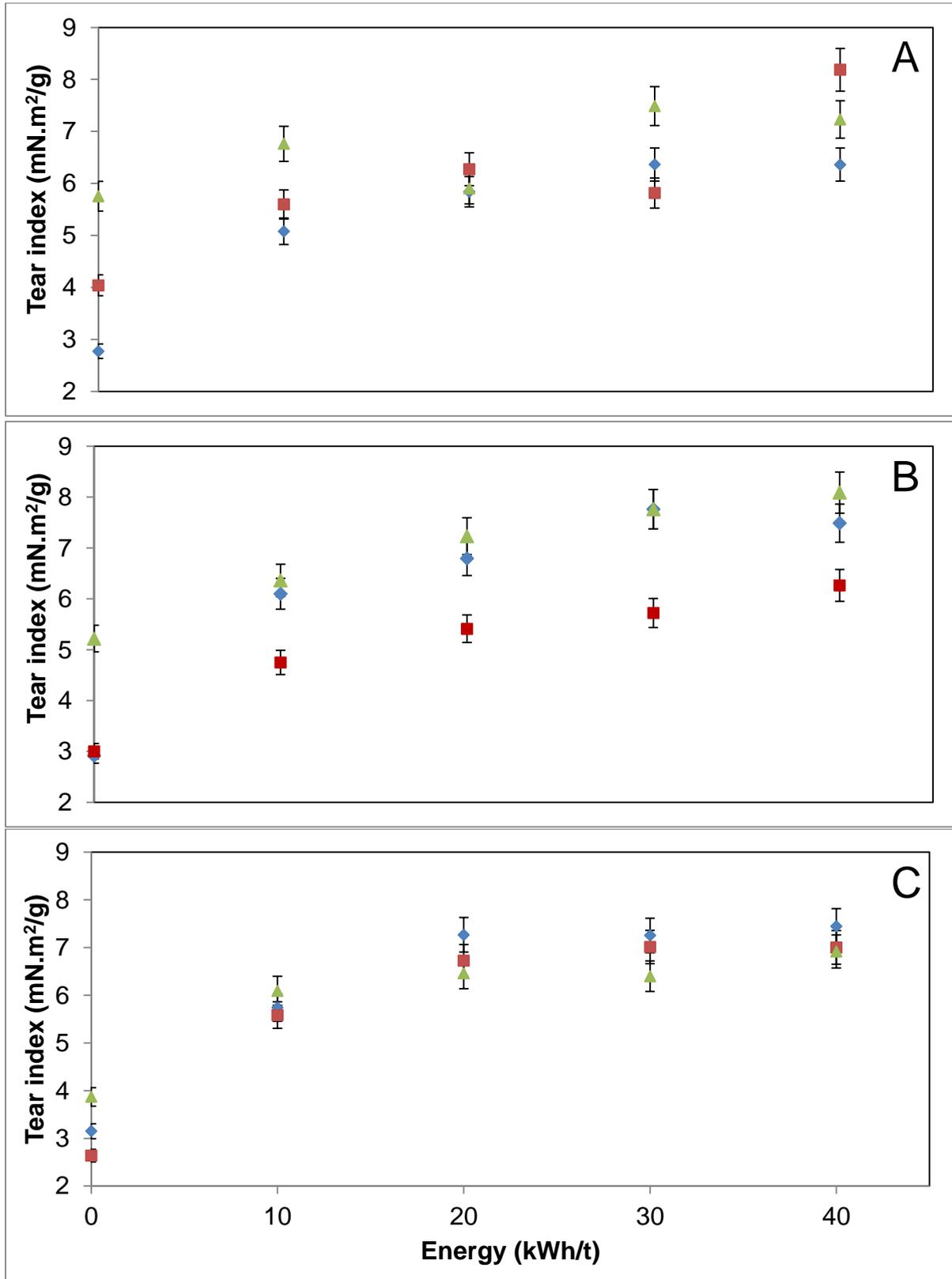


Figure 4.19: Tear strength of untreated and enzymatically treated, sonicated hardwood fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm [C]) ♦ Untreated, ■ Enzymatically treated [50 g/t], ▲ Enzymatically treated [200 g/t].

When comparing the different enzymatic dosages and ultrasonication, the results were similar, except at the 0 kWh/t treatment, where the 200 g/t enzymatic dosage was notably higher. These tear strength results supported the findings of Peter Josefsson (2006). What it proved additionally was that higher enzymatic dosages caused enhanced fibre modification. The tear strength results above indicated that the enhanced fibre modification effect was only for a finite period of time. Once a certain time has passed, there was no added benefit from the higher dosage, which supported the findings of Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lombay *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002).

4.3.4 Tear and tensile strength relationship for high-dosage enzymatically treated hardwood

The tear and tensile strength relationship of the 200 g/t enzymatically treated pulp can be seen in Figure 4.20.

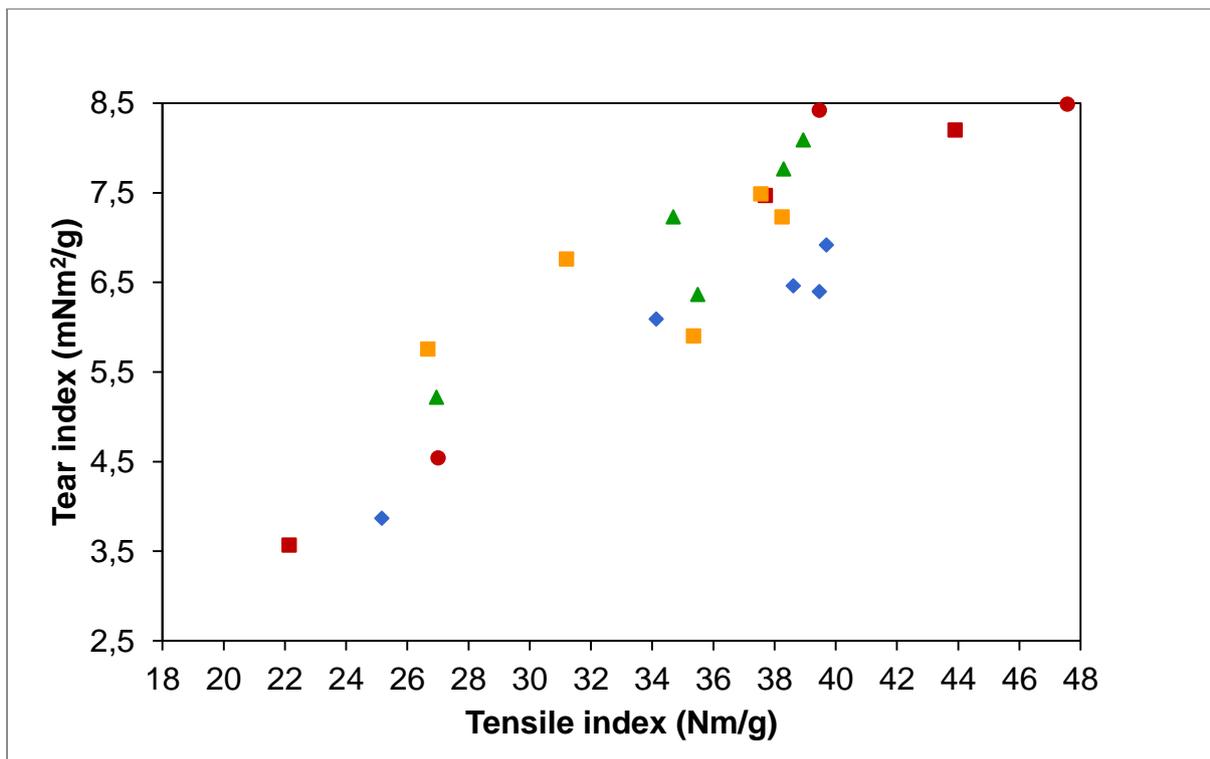


Figure 4.20: Tear and tensile strength relationship of 200 g/t enzymatically treated hardwood fibres after different levels of energy treatment with mechanical refining and ultrasonication. (■ Untreated mechanical refining, ● Enzymatically treated, mechanical refining, ◆ Enzymatically treated ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm.)

The tear-tensile strength relationship of the mechanically refined experiment was the highest, but it was closely followed by the 200 g/t, 80 μm ultrasonication experiment. The 200 g/t, 80 μm ultrasonication experiment yielded the most promising results of the ultrasonication treatments, meaning that the tensile strength of the hand-sheets was increased without negatively affecting the tear strength.

4.3.5 Freeness and tensile strength relationship for high-dosage enzymatically treated hardwood

The freeness and tensile strength relationship is presented in Figure 4.21.

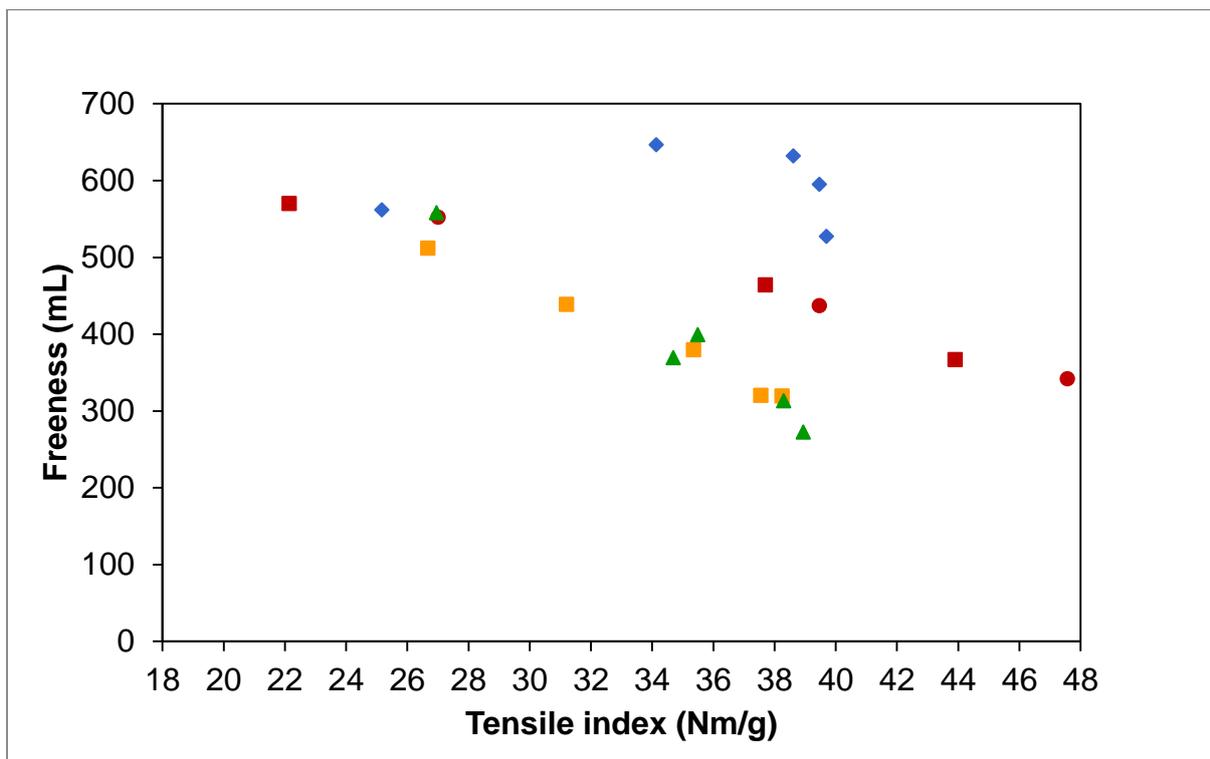


Figure 4.21: Freeness and tensile strength relationship of 200 g/t enzymatically treated hardwood fibres after different levels of energy treatment with mechanical refining and ultrasonication (■ Untreated mechanical refining, ● Enzymatically treated, mechanical refining, ◆ Ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The 200 g/t enzyme-treated ultrasonication at 53 μm displayed the optimum relationship of freeness and tensile strength when compared to the ultrasonication and mechanical refining experiments. The other ultrasonication experiments displayed a lower freeness and tensile strength relationship compared to the mechanical refining experiments.

In summary, the combination of ultrasonication and high enzyme dosage (200 g/t) did not result in any added strength benefits when compared to mechanical refining. Nevertheless, the only positive result regarding an increase in freeness was recorded at this high enzyme treatment. The 200 g/t enzyme pre-treatment resulted in a definite advantage with regard to the strength properties of the hand-sheets prior to the ultrasonication treatment (at 0 kWh/t). Once ultrasonication was introduced, the strength properties became similar to the control and 50 g/t enzyme-ultrasonication experiments.

4.4 Ultrasonication and refining of hardwood followed by 100 g/t enzymatic treatment

The 100 g/t enzymatic post-treatment was done as described in Chapter 3, followed by the same pulp and strength tests as with the other hardwood experiments. The ultrasonication amplitude selected was 53 μm , based on the more consistently good results obtained throughout the control, 50 g/t and 200 g/t experiments.

4.4.1 Freeness of hardwood followed by 100 g/t enzymatic treatment

The freeness of the 100 g/t enzymatic post-treated pulp can be seen in Figure 4.22.

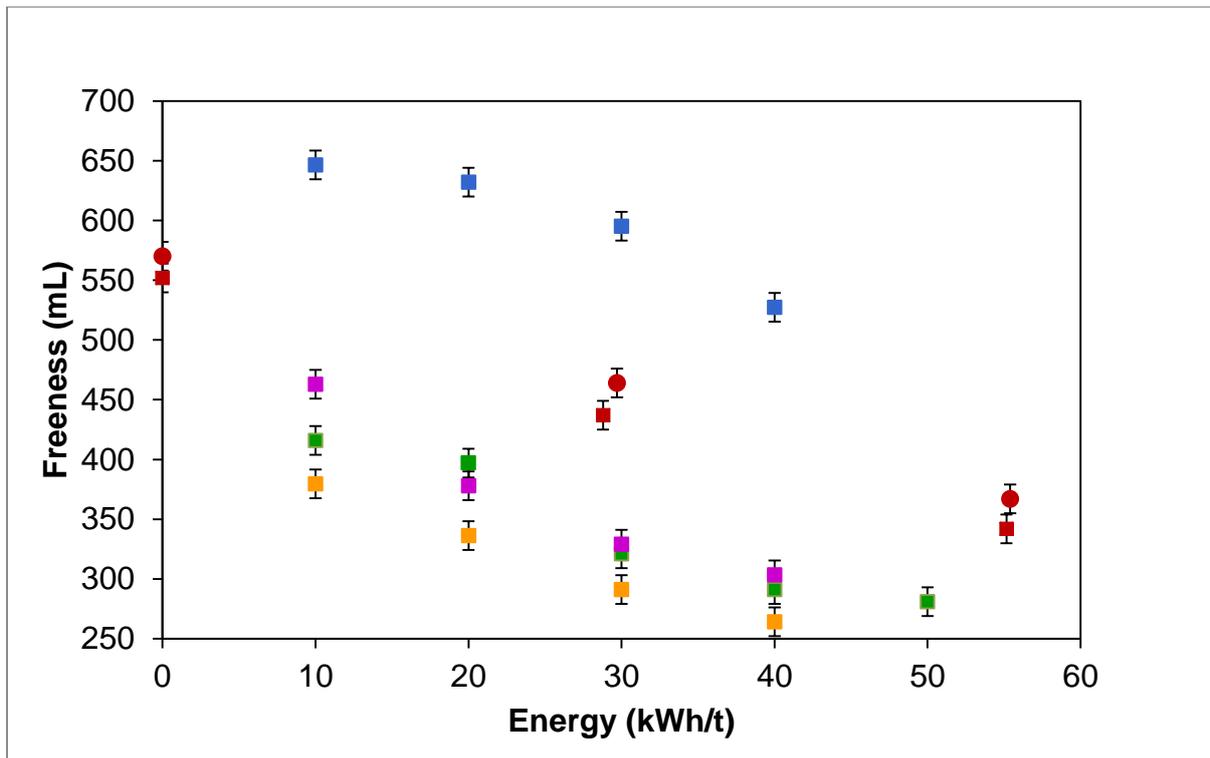


Figure 4.22: Freeness comparison of all hardwood ultrasonication experiments at 53 μm (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Enzymatically treated, mechanically refined [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The freeness of the sonicated sample that was post-treated with 100 g/t enzyme was lower than the mechanically refined control and enzymatically treated pulp, but it was higher than the sonicated pulp control and similar to the 50 g/t enzymatically pre-treated sonicated pulp. A reason for the higher freeness might be that the enzyme wasn't effectively deactivated by the ultrasonication treatment as was seen in previous work, meaning that there might have been more enzymatic activity in the experiments where there was enzymatic pre-treatment, resulting in longer enzymatic treatment time. If this was the case, it would support the previous studies by Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lomboy *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002), stating the enzyme treatment time was one of the largest factors influencing refining effects. However, as this process mimics the refining process in industry, the longer enzymatic pre-treatment time was taken as an added benefit for pre-treating paper pulp, meaning that by default enzymatic pre-treatment was more viable than enzymatic post treatment. The higher freeness could

mean that the sonicated fibre modification effect was lower than the control, 50 g/t and 200 g/t enzymatic pre-treatments, or that the shorter enzymatic contact time and 100 g/t dosage was effective in removing colloidal cellulose.

4.4.2 Tensile strength of hardwood followed by 100 g/t enzymatic treatment

The tensile strength of the 100 g/t enzymatic post-treated pulp can be seen in Figure 4.23.

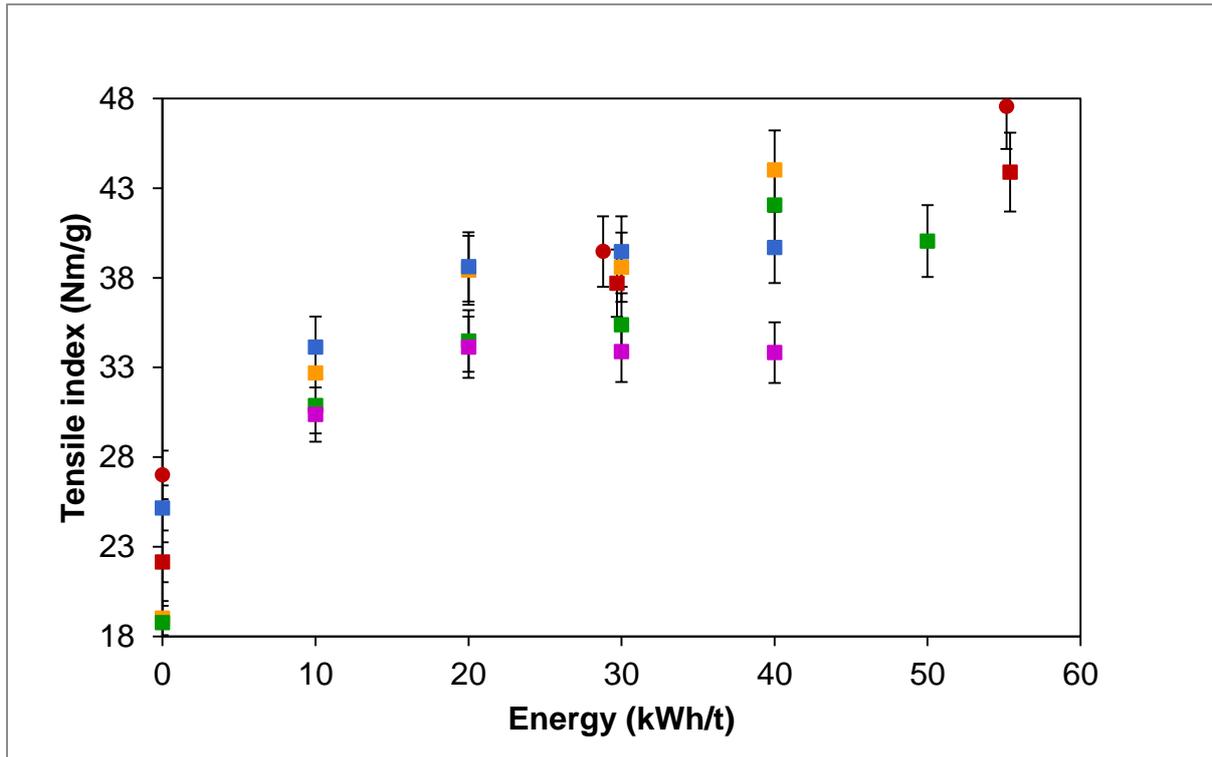


Figure 4:23. Tensile strength of all ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatic treated mechanical refining (\blacksquare Ultrasonication with enzymatic pre-treatment [200 g/t], \bullet Mechanically refined control, \blacksquare Mechanically refined enzymatic treated [50 g/t], \blacksquare Ultrasonication with enzymatic post-treatment [100 g/t], \blacksquare Ultrasonication with enzymatic pre-treatment [50 g/t], \blacksquare Ultrasonication control).

The enzymatic post-treated sample had the overall lowest tensile strength. This freeness result proved that the higher freeness (Figure 4.22) indicated a lower level of fibre modification, rather than a more effective method of removing colloidal cellulose. At the low energy inputs (0-20 kWh/t) the tensile strength of the 100 g/t enzymatic post-treatment was similar to the 50 g/t enzymatic pre-treatment, but reached a plateau after 20 kWh/t. Once again, the shorter enzymatic post-treatment time may

have played a role in effectively modifying the fibres, which supports Anna Joseffson's (2010) findings that ultrasonication on its own was not efficient enough to induce the same magnitude of results one finds with mechanical refining.

4.4.3 Tear strength of hardwood followed by 100 g/t enzymatic treatment

The tear strength of the 100 g/t enzymatic post-treatment is presented in Figure 4.24.

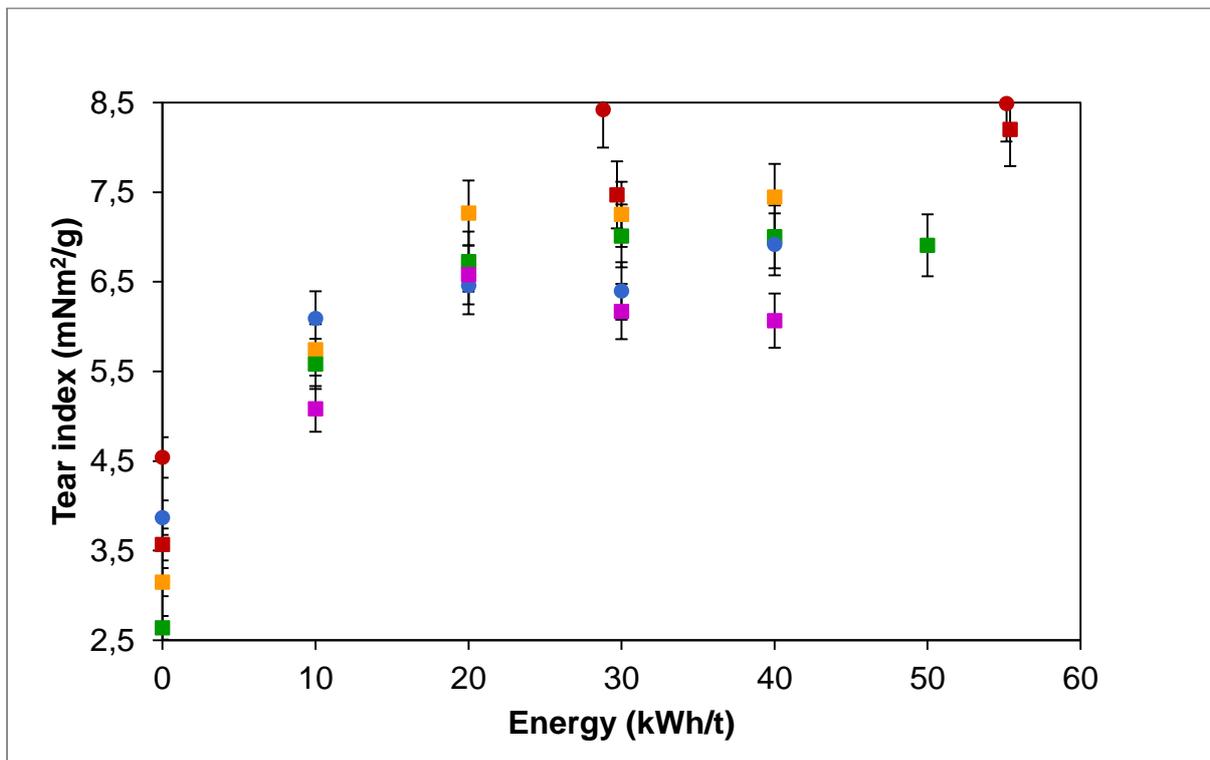


Figure 4.24: Tear strength of all ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining. (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined, enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

Overall, the tear strength of the enzymatic post-treatment was the lowest. The low tear and tensile strength results, together with the higher freeness results, supported the findings of Oksanen *et al.* (1997) and Pere *et al.* (1995), who supported the notion that enzymatic treatment time was a significant factor in fibre modification. When comparing the tear strength of the enzymatic post-treatment to the enzymatic pre-treatment experiments, it was the only treatment to reach a maximum at a low energy

(20 kWh/t) before decreasing by 8 %. Although an 8 % decrease seems trivial, it was the biggest decrease in tear strength recorded in the hardwood experiments.

4.4.4 Tear, tensile and freeness strength relationship of hardwood followed by 100 g/t enzymatic treatment

The tear strength, tensile strength and freeness relationships can be seen in Figure 4.25.

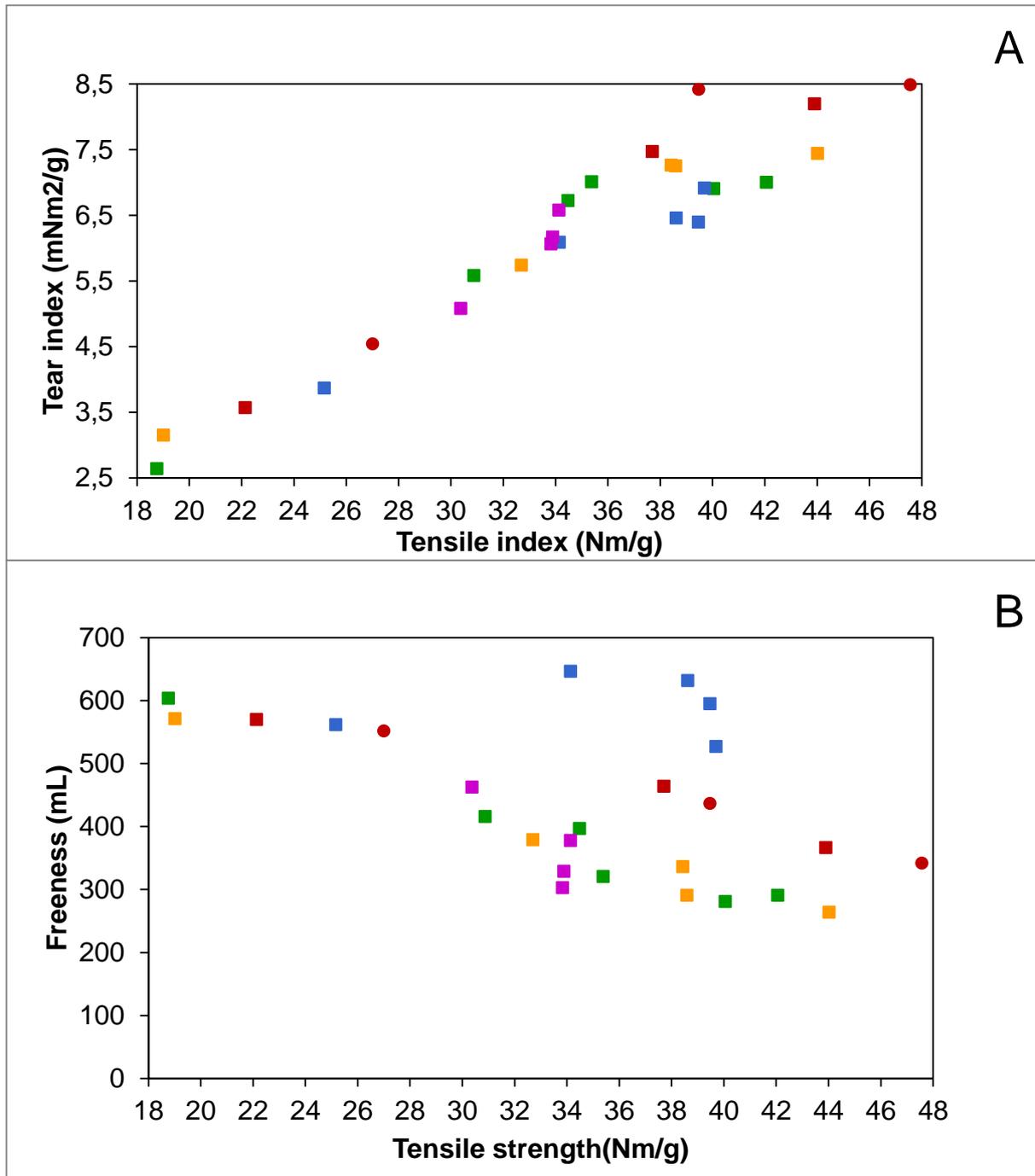


Figure 4.25: Tear and tensile strength relationship (A) and freeness and tear strength relationship (B) of all ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatic treated mechanical refining (■ Ultrasonication with enzymatic post-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined, enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic pre-treatment [100 g/t], ■ Ultrasonication with enzymatic post-treatment [50 g/t], ■ Ultrasonication control).

As expected, the tear and tensile relationship and tensile-freeness relationship of the ultrasonication and enzymatic post-treatment was the lowest of the hardwood experiments. The enzymatic post-treatment results looked similar to the enzymatic pre-treatment results at tensile strengths between 30 ± 1.5 and 34 ± 1.7 Nm/g. The difference was that the enzymatic post-treatment could not modify the fibres beyond a tensile strength of 34 ± 1.7 Nm/g and a tear strength of 6.51 ± 0.3 mNm²/g. Compared to the ultrasonication and enzymatic pre-treatments, which reached values of 44 ± 2.2 Nm/g and 7.49 ± 0.3 mNm²/g respectively, the enzymatic post-treatment was not effective.

In summary, the enzymatic post-treatment had a positive result on the strength properties of the hand-sheets, however, it was notably lower when compared to the enzymatic pre-treatment. The enzymatic post treatment, however, caused a smaller decrease in freeness, which was positive for the paper machines. The post-treatment results were, however, not comparable to the strength results of mechanical refining or the previous enzymatic and ultrasonication experiments. A possible explanation could be that the shorter enzymatic post-treatment time (compared to the enzymatic pre-treatment, where an ineffective deactivation of the enzyme was suspected) caused a smaller fibre modification effect compared to the enzymatic pre-treatment experiments. Applying an enzymatic post treatment was not effective at fibre modification when compared to the enzymatic pre-treatments.

4.5 References

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CHAPTER 5: Ultrasonication of *Pinus radiata* pulp

The influence of ultrasonication and enzyme treatments on the *Pinus radiata* (Tasman) pulp was investigated. The results were compared to mechanical refining to determine whether ultrasonication together with enzymatic treatment may be a viable alternative. Section 5.1 covers the results of the untreated ultrasonication and mechanical refining (control), Section 5.2 covers the data on the 50 g/t enzymatic pre-treatment and Section 5.3 covers the 200 g/t enzymatic pre-treatment. An enzymatic post-treatment with 100 g/t was also done and is summarised in Section 5.4. The treatment and testing procedure described in Chapter 3 was followed to re-pulp, treat and test the Tasman softwood pulp.

5.1 Development of untreated softwood pulp

The same procedure was followed as with the hardwood pulp. In the first set of experiments, ultrasonication was used to develop the untreated pulp, and the resulting freeness was tested. The sonicated pulp was then used to make hand-sheets, as described in Chapter 3, and the hand-sheets were tested for tensile strength and tear strength.

5.1.1 Freeness of untreated softwood pulp

To test the freeness of the pulp, a sample was taken immediately after the ultrasonication treatment was completed. This sample was cooled rapidly, by means of refrigeration, to 20°C before the test was done. It was expected that the freeness of sonicated pulp would decrease, due to the induced fibre modification effect that causes the contact surface area of the fibres to enlarge. According to Bierman (1996), however, softwood fibres are longer and stronger than hardwood fibres, meaning that the fibre modification effect at lower energies would not be as apparent as with hardwood. The freeness results can be seen in Figure 5.1.

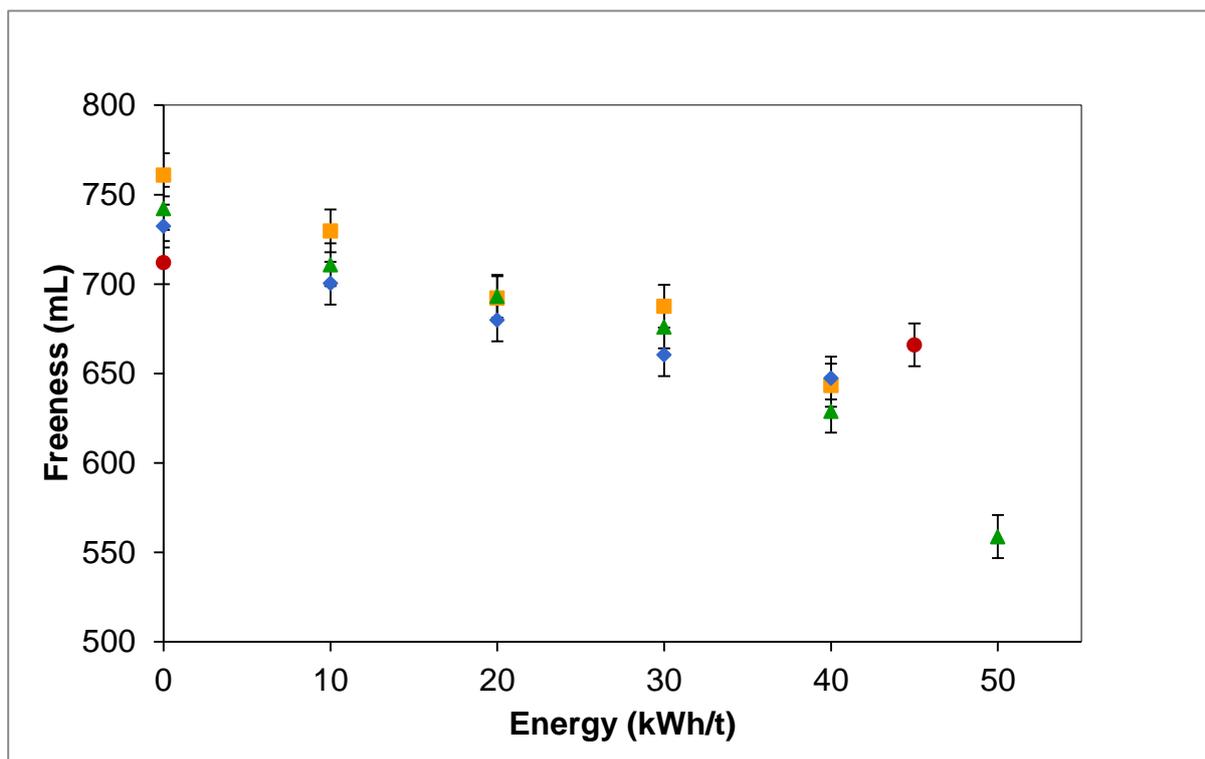


Figure 5.1: Softwood pulp freeness after treatments with mechanical refining and ultrasonication respectively at different energy levels (● Mechanical refining, ◆ Ultrasonication at 53 μm, ▲ Ultrasonication at 80 μm, ■ Ultrasonication at 106 μm).

Although there was an apparent decrease in freeness at higher energies, the rate of decrease was much lower than with hardwood pulp, indicating that the softwood fibres were stronger. The broken fibre content and fine content remained relatively constant through all amplitudes, which supported the freeness results (Appendix A2: Tables A2.1, A2.4 and A2.7). The freeness of the sonicated pulp closely reflected the freeness of mechanically refined pulp up to 40 kWh/t, where after the ultrasonication caused a higher rate of decrease in freeness. The higher rate of decrease at the higher ultrasonication energy may be because ultrasonication used more time than the mechanical refining, thereby subjecting the pulp to a longer treatment. This result is supported by Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002) and Sun *et al.* (2002), who found that extended ultrasonication times resulted in more pronounced modification effects on the medium. The different ultrasonication amplitudes produced similar results, especially when the ± 12 mL. experimental error was taken into account (Tappi, 1996:T227). The reason for the small difference between amplitudes may be that the softwood fibres were stronger than the hardwood fibres, so that the effect of the

different amplitudes was not as apparent as with hardwood pulp. The freeness of the mechanically refined pulp supports this theory, since the freeness also decreased much slower than with hardwood pulp. The lowest freeness of 558 ± 12 mL was recorded at 50 kWh/t, applying ultrasonication at 80 μ m.

5.1.2 Tensile strength of untreated softwood pulp

The average tensile strength of the untreated softwood pulp was evaluated. The effect of ultrasonication and mechanical refining is presented in Figure 5.2.

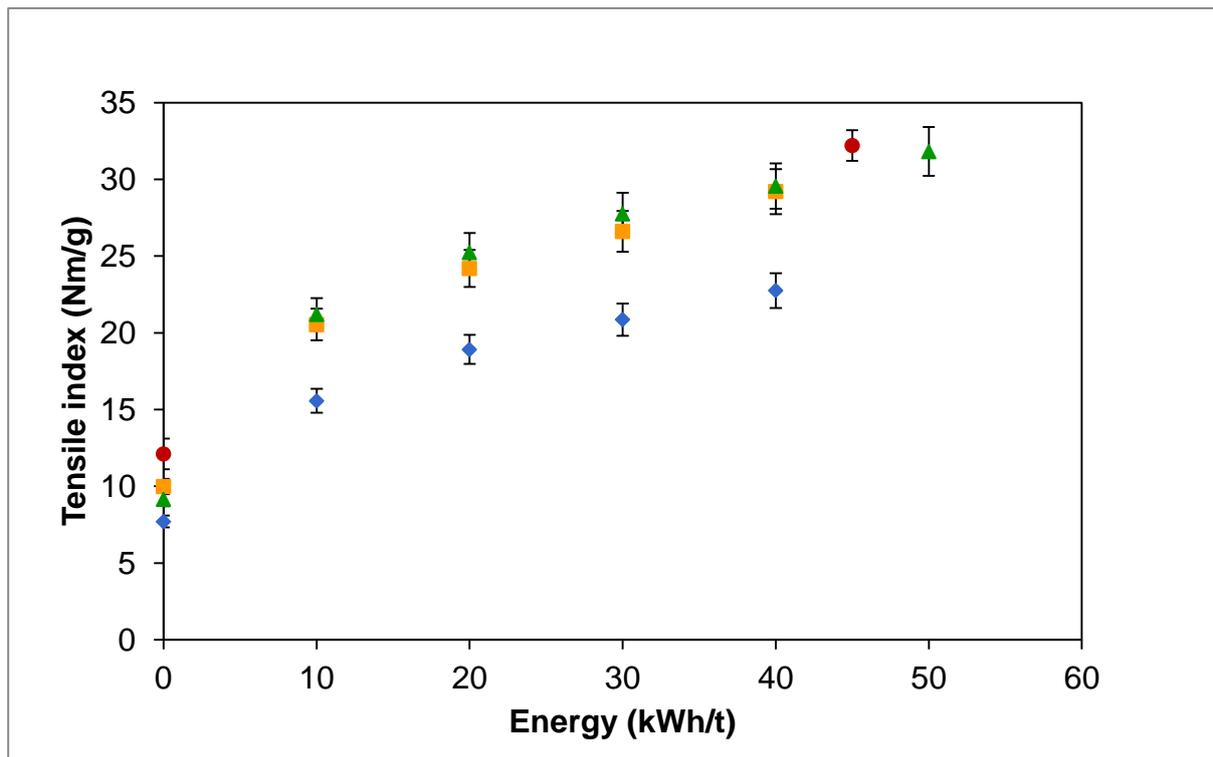


Figure 5.2: Tensile strength of softwood fibres after application of different levels of energy (● Mechanical refining, ◆ Ultrasonication at 53 μ m, ▲ Ultrasonication at 80 μ m, ■ Ultrasonication at 106 μ m).

The improvement of the tensile strength with an increase in ultrasonication or mechanically refining energy was very similar. This similarity supported the findings of Rehman (2013) and Suslick (1989) that ultrasonication and mechanical refining induced similar fibre-development effects. Increasing the ultrasonication energy caused a significant increase in the tensile strength, but once the energy input exceeded 10 kWh/t, the growth in tensile strength was slower. The morphology results offered no explanation as to why the tensile strength increased. This tensile increase was, however, explained by the findings of Huang *et al.* (2007); Haung *et al.* (2011);

Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002); Sun *et al.* (2002), who observed that increased ultrasonication time was effective in modifying the medium, but that there was a time limit, after which treatment efficiency decreased. Ultrasonication at 53 μm resulted in consistently lower tensile-strength values compared to ultrasonication at high amplitudes. This result was the exact opposite of the hardwood results, which meant that the lower intensity of transferred energy was insufficient for adequate treatment of the softwood fibres. The stronger softwood fibres reacted positively with the high-amplitude ultrasonication. Work by Chen *et al.* (2011), found that ultrasonication amplitude and power are interdependent, meaning that higher amplitude ultrasonication will transfer a given amount of energy to the medium much faster than low-amplitude ultrasonication. A stronger fibre, like softwood, would need a higher intensity of transferred power to reach the required level of modification, hence the higher amplitude ultrasonication was much more effective.

The maximum tensile strength of $31 \pm 1.6 \text{ Nm/g}$ was recorded at 50 kWh/t applying ultrasonication at amplitude 80 μm . Mechanical refining reached a tensile strength of $32 \pm 1.6 \text{ Nm/g}$ at 45 kWh/t.

5.1.3 Tear strength of untreated softwood pulp

The third aspect of the testing was the tear strength, as shown in Figure 5.3.

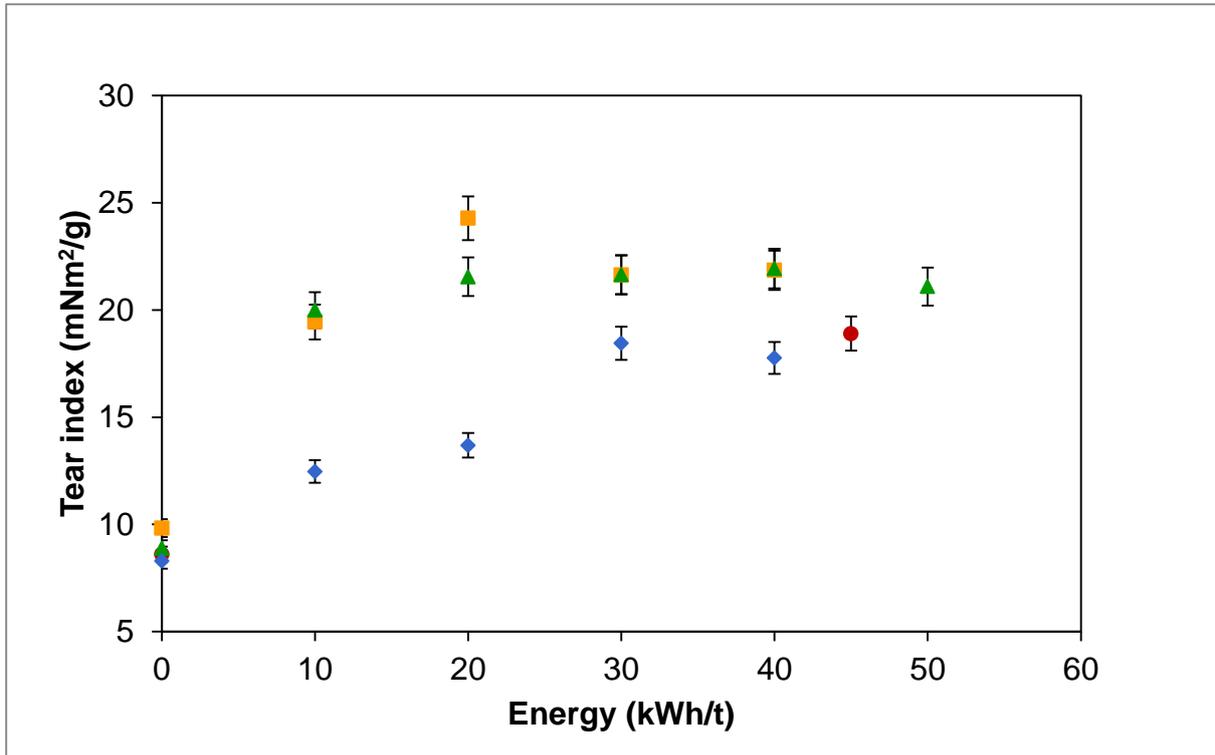


Figure 5.3: Tear strength of softwood fibres (● Mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

The tear strength increased in proportion to the energy transferred. There was a large initial increase in tear strength when applying ultrasonication at higher amplitudes (80 and 106 µm). The increase indicated that the fibres remained strong, and that ultrasonication possibly caused less fibre damage and cutting than mechanical refining – this was mainly due to the low energies at which ultrasonication was used, resulting in limited fibre damage. The morphology results also indicated that the fibre length and broken fibre content remained relatively constant (Appendix A2: Tables A2.1, A2.4 and A2.7). It appeared that ultrasonication at high amplitudes was the most effective in developing the tear strength of the softwood fibres, supporting the theory that a higher treatment intensity was more effective. Mechanical refining appeared to follow the same trend as low-amplitude ultrasonication, and the tear strength was much lower than the high-amplitude ultrasonication. The highest tear strength (24.3 ± 1 mNm²/g) was achieved at 20 kWh/t, applying ultrasonication at amplitude 106 µm. The highest tear strength attained by mechanical refining was 18.9 ± 0.8 mNm²/g at an energy level of 45 kWh/t.

5.1.4 Tear/tensile strength relationship of untreated softwood pulp

The relationship between tear and tensile strength is presented in Figure 5.4 and will provide a basis for comparing the overall strength of the paper after it was mechanically refined or sonicated.

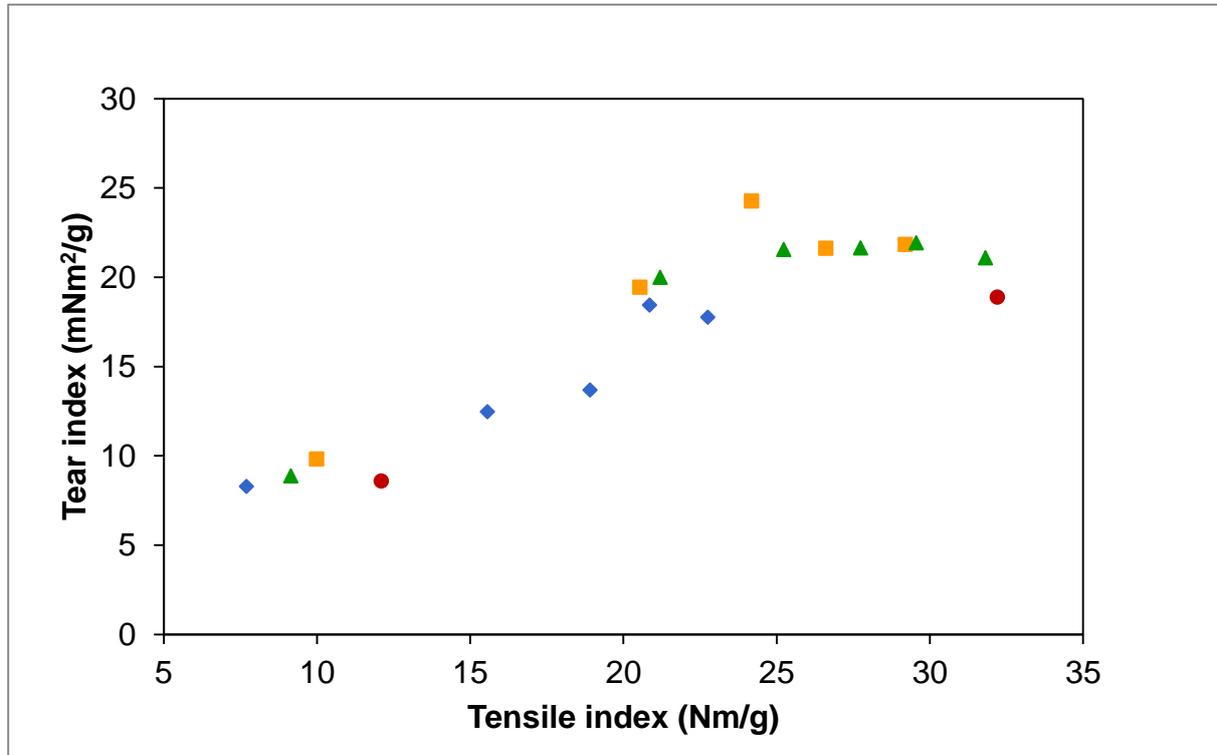


Figure 5.4: Tear and tensile strength relationship of softwood fibres (● Mechanical refining, ◆ Ultrasonication at 50 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

The overall tear and tensile strength relationship of the sonicated pulps was higher than the mechanically refined pulps, possibly indicating that the tear strength of the fibres increased without negatively influencing the tensile strength.

Ultrasonication at high amplitudes showed potential when compared to mechanical refining and low-amplitude ultrasonication, with the highest tear strength of 24.2 ± 1 mNm²/g recorded at a tensile strength of 24 ± 1.2 Nm/g.

5.1.5 Freeness/tensile strength relationship of untreated softwood pulp

The freeness and tensile strength relationship was important, because it showed the interaction between the apparent fibre development (freeness) and actual fibre development (tensile strength). This interaction can be seen in Figure 5.5.

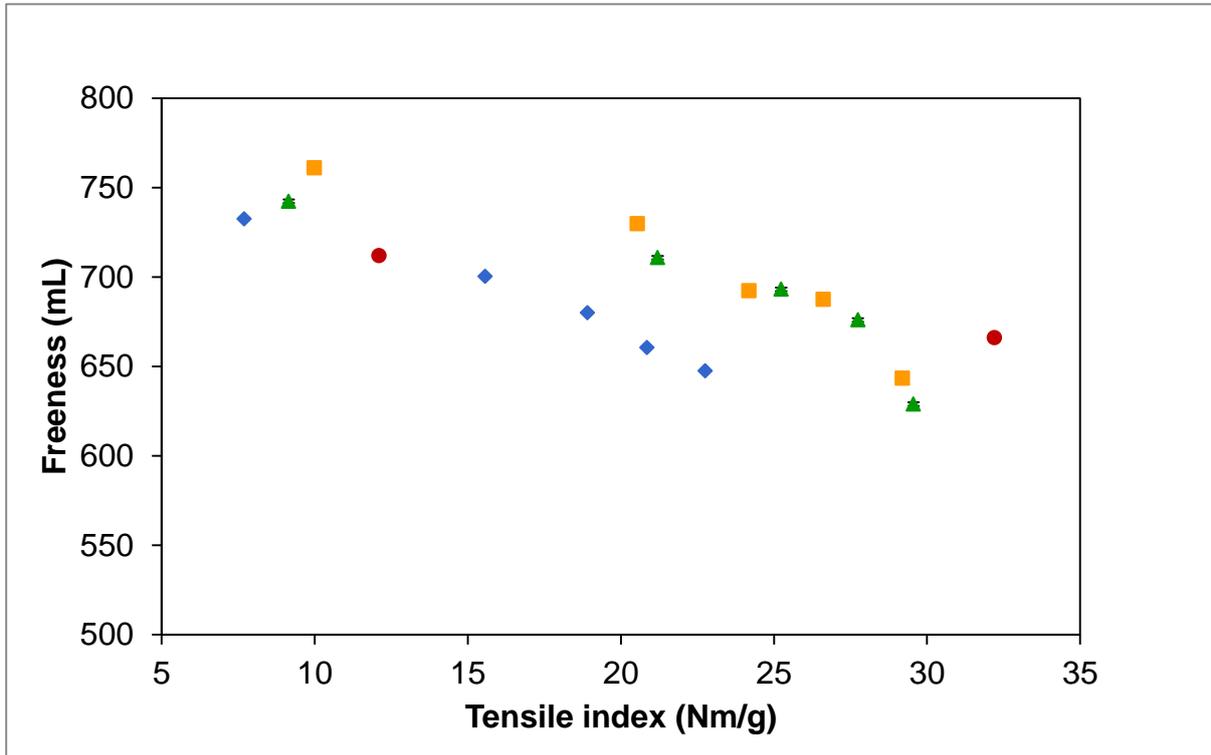


Figure 5.5: Softwood freeness and tensile strength relationship (● Mechanical refining, ◆ Ultrasonication at 50 μm, ▲ Ultrasonication at 80 μm, ■ Ultrasonication at 106 μm).

The freeness of the pulp needs to be high to ensure the minimum of blockages and constant flow in the paper machine (Aikawa Fiber Technologies, 2001:22). A high tensile strength will confirm that the fibres were effectively modified and not just damaged. High-amplitude ultrasonication resulted in notably higher freeness values at low to medium tensile index values. Mechanical refining, however, resulted in the highest tensile index of $32.2 \pm 1.6 \text{ Nm/g}$ at a freeness of $667 \pm 12 \text{ mL}$.

In summary, ultrasonication at high amplitudes was effective in modifying the fibres and resulted in high tensile strength and very high tear strength values without causing a significant decrease in freeness. It seems that the untreated softwood fibres reacted favourably to ultrasonication, especially at amplitude 80 μm.

5.2 Ultrasonication and refining of low-dosage enzymatically treated softwood

In view of the effect of enzymatic pre-treatment in the hardwood experiments, the influence of enzymatic pre-treatment on the stronger softwood fibre was investigated. The potential of more advanced fibre modification was, therefore, investigated.

5.2.1 Freeness of low-dosage enzymatically treated softwood

The result of the enzymatic pre-treatment on the freeness of the softwood pulp can be seen in Figure 5.6.

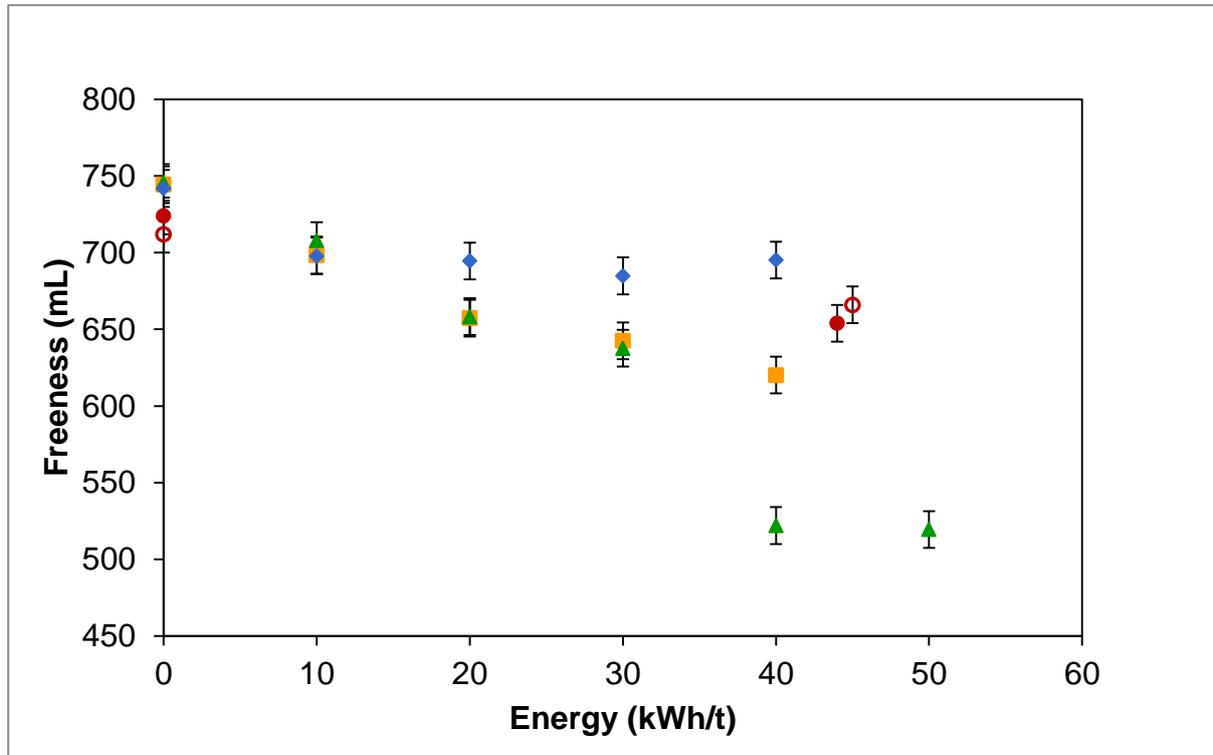


Figure 5.6: Softwood pulp freeness after enzymatic pre-treatment (50 g/t) and mechanical refining or ultrasonication (○ Untreated mechanically refined, ● Enzymatically treated, mechanically refined, ◆ Enzymatically treated ultrasonication at 53 μm, ▲ Enzymatically treated ultrasonication at 80 μm, ■ Enzymatically treated ultrasonication at 106 μm).

The freeness of the enzymatically treated, mechanically refined pulp and sonicated pulp decreased at a slightly higher rate when compared to the untreated mechanical pulp. At low energies (10 and 20 kWh/t), the sonicated pulp had similar freeness throughout the different amplitudes. A clear difference in amplitude was noted at 40 kWh/t, where the low-amplitude (53 μm) ultrasonication resulted in a high freeness (695 ± 12 mL), while the 80 μm ultrasonication resulted in a low freeness (522 ± 12 mL). Ultrasonication at a high amplitude (106 μm) resulted in a freeness between the previously mentioned amplitudes (620 ± 12 mL). This unexpected development can be explained by the difference in treatment times. Ultrasonication at 80 μm required 30 % more treatment time than ultrasonication at 106 μm to reach the same energy.

In the control experiments, where there was no enzymatic pre-treatment, the longer treatment times had little effect on the strong softwood fibres. When pre-enzymatic treatment was introduced, however, the fibre modification effect was increased and the stronger fibres were more susceptible to the effect of longer treatment times. Similar results were noted by Josefsson (2006), Oksanen *et al.* (1997) and Pere *et al.* (1995). The high freeness results at low-amplitude ultrasonication may indicate that the low ultrasonication intensity was still not effective in modifying the softwood fibres. The long treatment times (80 % longer than ultrasonication at 106 μm) and 50 g/t enzymatic pre-treatment had little effect on collapsing and fibrillating the softwood fibres.

A comparison of untreated and enzymatically treated sonicated fibres can be seen in Figure 5.7.

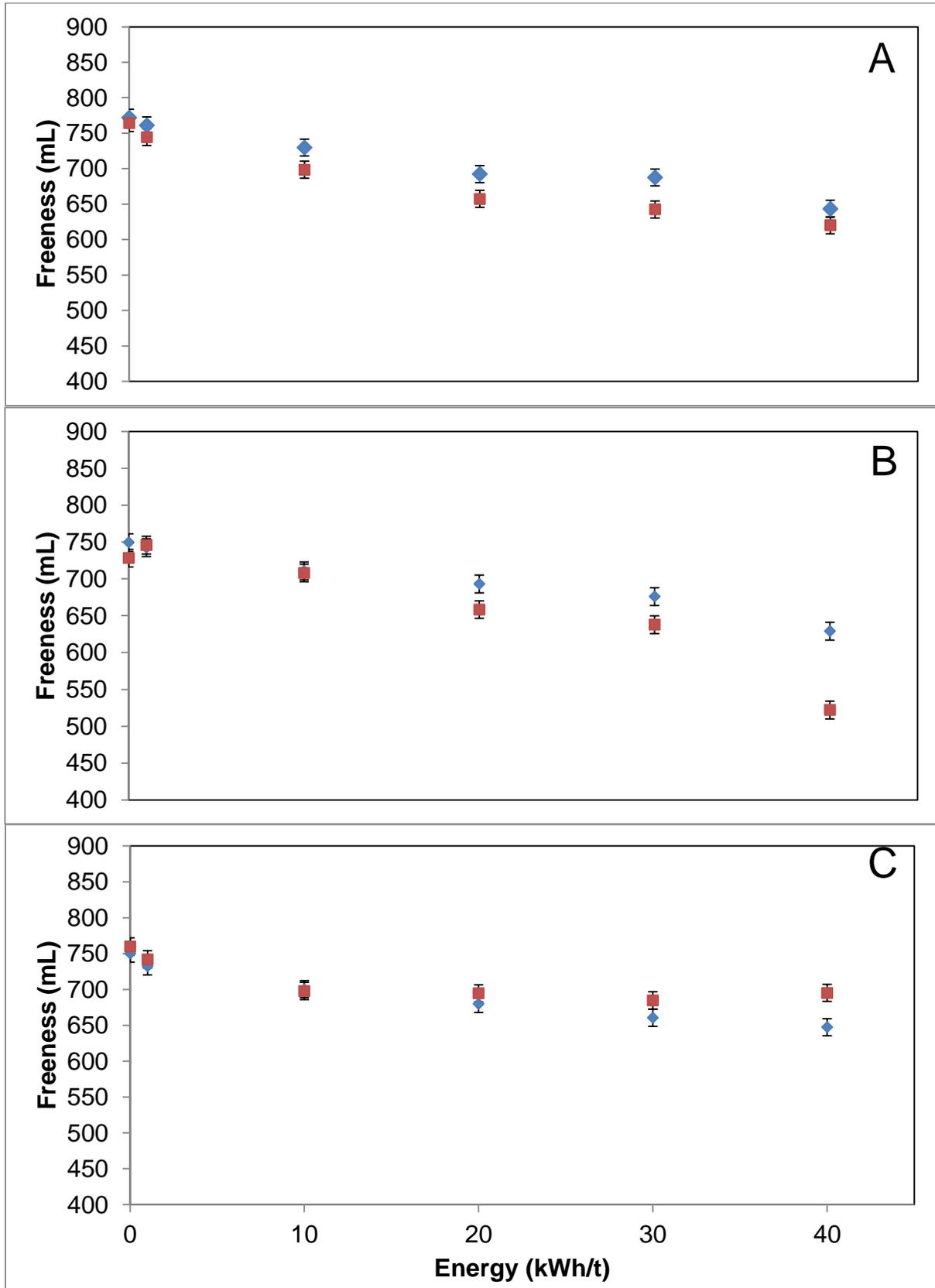


Figure 5.7: Freeness of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C] amplitudes; ♦ Untreated, ■ 50 g/t Enzymatic pre-treatment).

The freeness of the sonicated softwood pulp was similar to that of the enzymatically treated fibres. The comparable results may be due to the stronger softwood fibres being less susceptible to the enzymatic pre-treatment than the hardwood fibres. It must be noted, however, that the freeness of the enzymatically treated fibres was constantly lower than that of the untreated fibres when high-amplitude ultrasonication (80 μm and 106 μm) was applied. The morphology results indicated that the fines content (in millions per gram of pulp) was consistently lower with enzymatically treated pulps (Appendix A2: Tables A2.2, A2.5 and A2.8) when compared to untreated pulps.

5.2.2 Tensile strength of low-dosage enzymatically treated softwood

The tensile strength results for the enzymatically treated sonicated pulp can be seen in Figure 5.8.

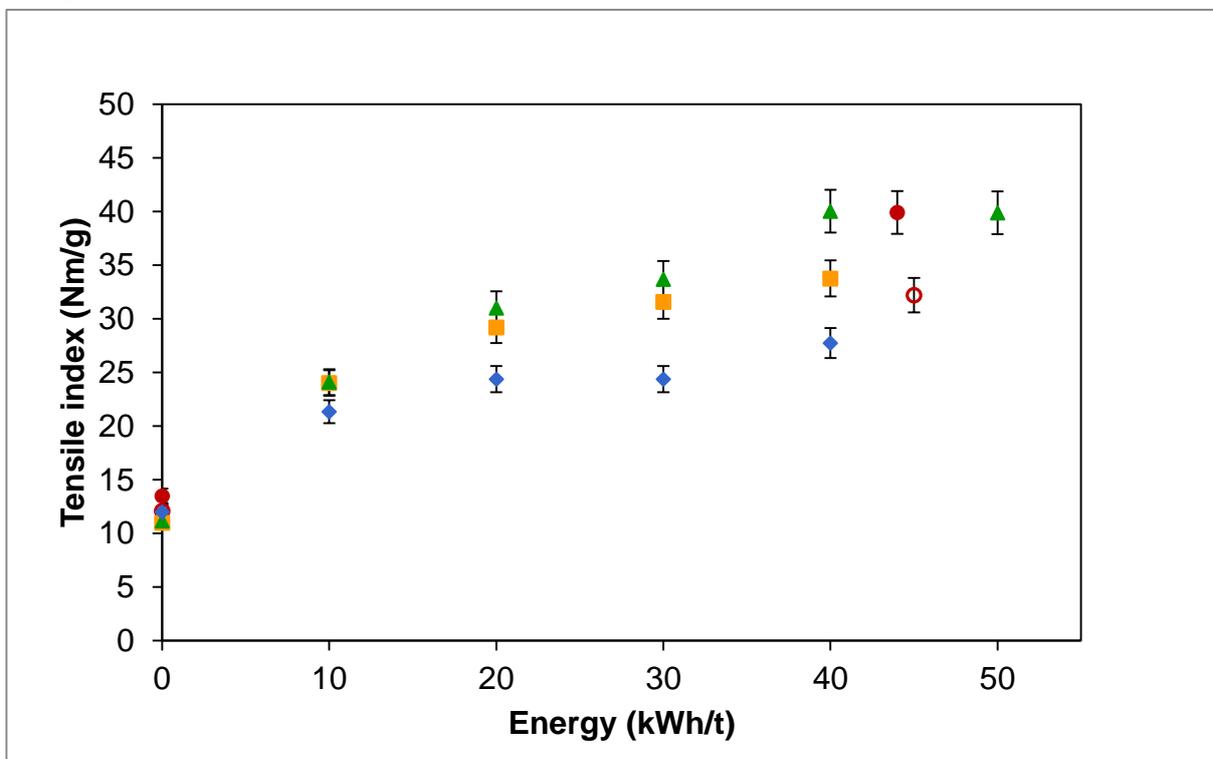


Figure 5.8: Tensile strength results for enzymatically treated softwood fibres after mechanical refining and ultrasonication (○ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

There was a significant increase in tensile strength for all treatments. Ultrasonication resulted in a 90 to 100 % initial increase in tensile strength between 0 and 10 kWh/t. It appeared that ultrasonication at higher amplitudes (80 and 106 μm) followed the

same profile as that of the enzymatically treated, mechanically refined pulp, which was notably higher than the untreated mechanically refined pulp. These tensile strength values support the freeness findings. Ultrasonication at 53 μm had the highest freeness, but also the lowest tensile strength, indicating that the softwood fibres were not modified to the same extent as by the treatments at high amplitudes. The 106 μm ultrasonication treatment had freeness and tensile strength results that were between the 53 μm and 80 μm ultrasonication treatments. The 80 μm ultrasonication had similar tensile strength results when compared to ultrasonication at 106 μm , but at 40 kWh/t, a significant difference was apparent, while the 80 μm treatment resulted in a maximum tensile strength of $40 \pm 2 \text{ Nm/g}$.

Figure 5.9 shows the tensile strength of the untreated sonicated fibres compared to the enzymatically treated sonicated fibres.

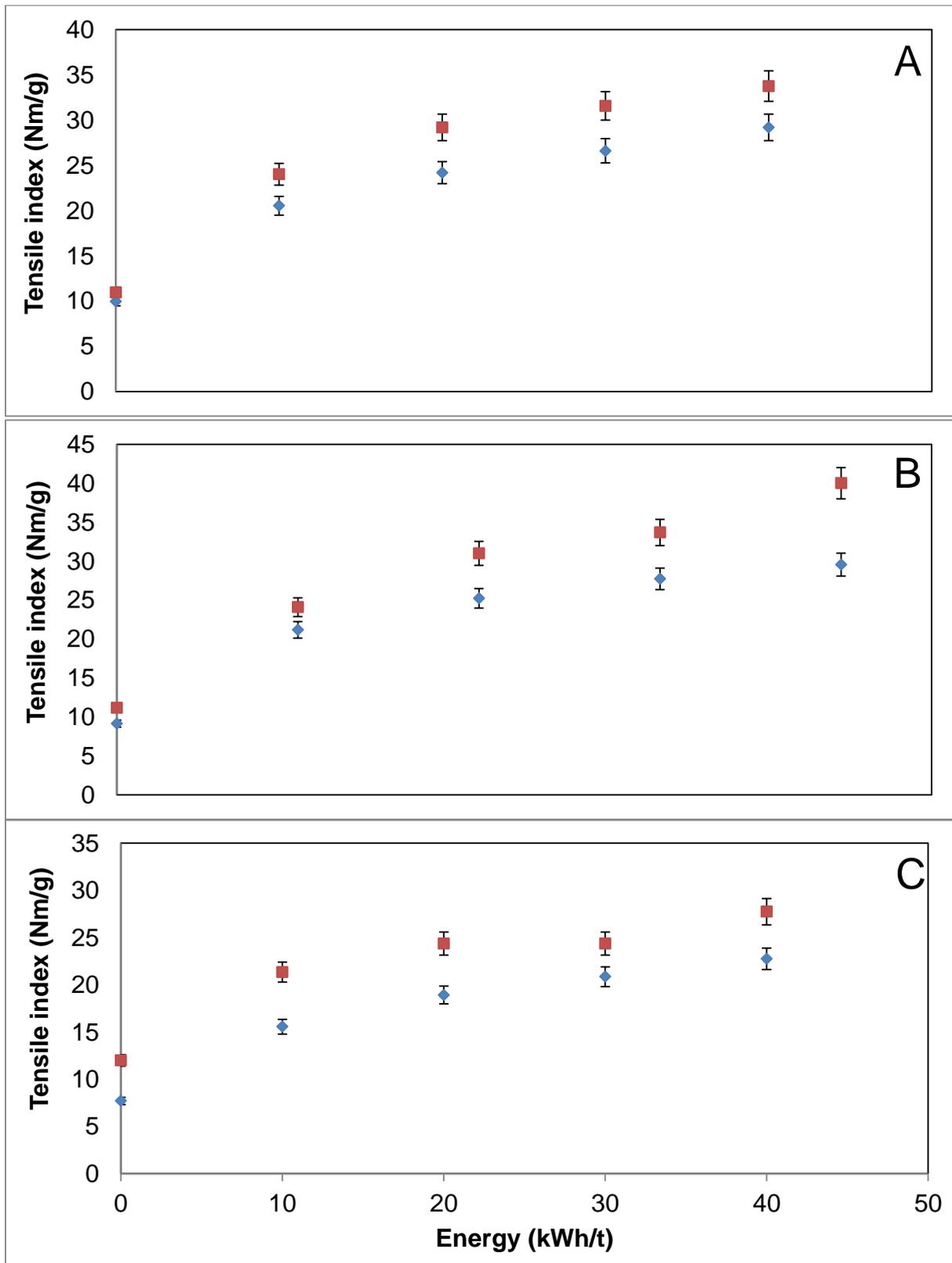


Figure 5.9: Tensile strength of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 [A] μm , 80 μm [B] and 53 μm [C] amplitudes; \blacklozenge Untreated, \blacksquare Enzymatically treated [50 g/t]).

The tensile strength of the enzymatically treated fibres was consistently higher than for the untreated sonicated fibres. It can also be noted that ultrasonication at high amplitudes caused the most significant increase in tensile strength.

5.2.3 Tear strength of low-dosage enzymatically treated softwood

The tear strength of the enzymatically treated fibres can be seen in Figure 5.10.

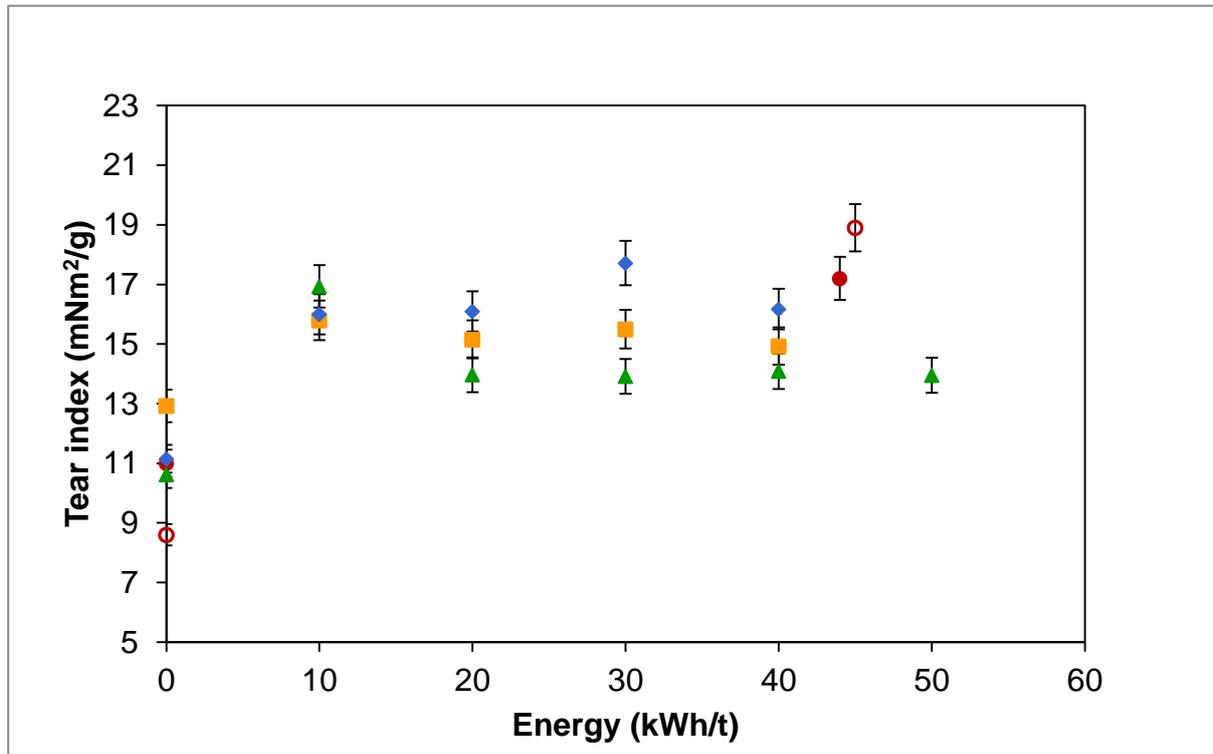


Figure 5.10: Tear strength of enzymatically treated softwood fibres after different levels of energy treatment with mechanical refining and ultrasonication (○ Untreated mechanical refining ● Enzymatically treated, mechanical refining, ◆ Enzymatically treated ultrasonication at 50 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

There was little change in tear strength for all treatments. The tear strength of the enzymatically treated and mechanically refined fibres was lower than that of the untreated fibres. Initially, the enzymatically treated and sonicated fibres resulted in a large tear strength increase, but little change was recorded at energies higher than 10 kWh/t. Ultrasonication and enzymatic pre-treatment caused similar results, regardless of amplitude, but ultrasonication at 53 µm resulted in consistently higher tear strength values compared to the 80 µm and 106 µm treatments.

Ultrasonication at 80 μm resulted in consistently lower values compared to the other two amplitudes, which supports the freeness and tensile strength results as follows: Softwood fibres are used in the paper industry to increase the tear strength of paper (Bierman, 1996:16), but when the fibres were modified the tear strength was generally reduced due to fibre cutting and fibrillation, which weakens the fibres (Chen *et al.*, 2010:7041). These statements by Bierman (2006) and Chen *et al.* (2010) explain that the tear strength of ultrasonication at 53 μm was consistently higher than at the other amplitudes, because the fibre modification effect was not as apparent as with the other amplitudes. Ultrasonication at 80 μm resulted in constantly lower tear strength results compared to the other amplitudes, due to the increased fibre modification effect induced by the balance of ultrasonication intensity and treatment time.

A comparison of the tear strength of untreated sonicated fibres and enzymatically treated sonicated fibres can be seen in Figure 5.11.

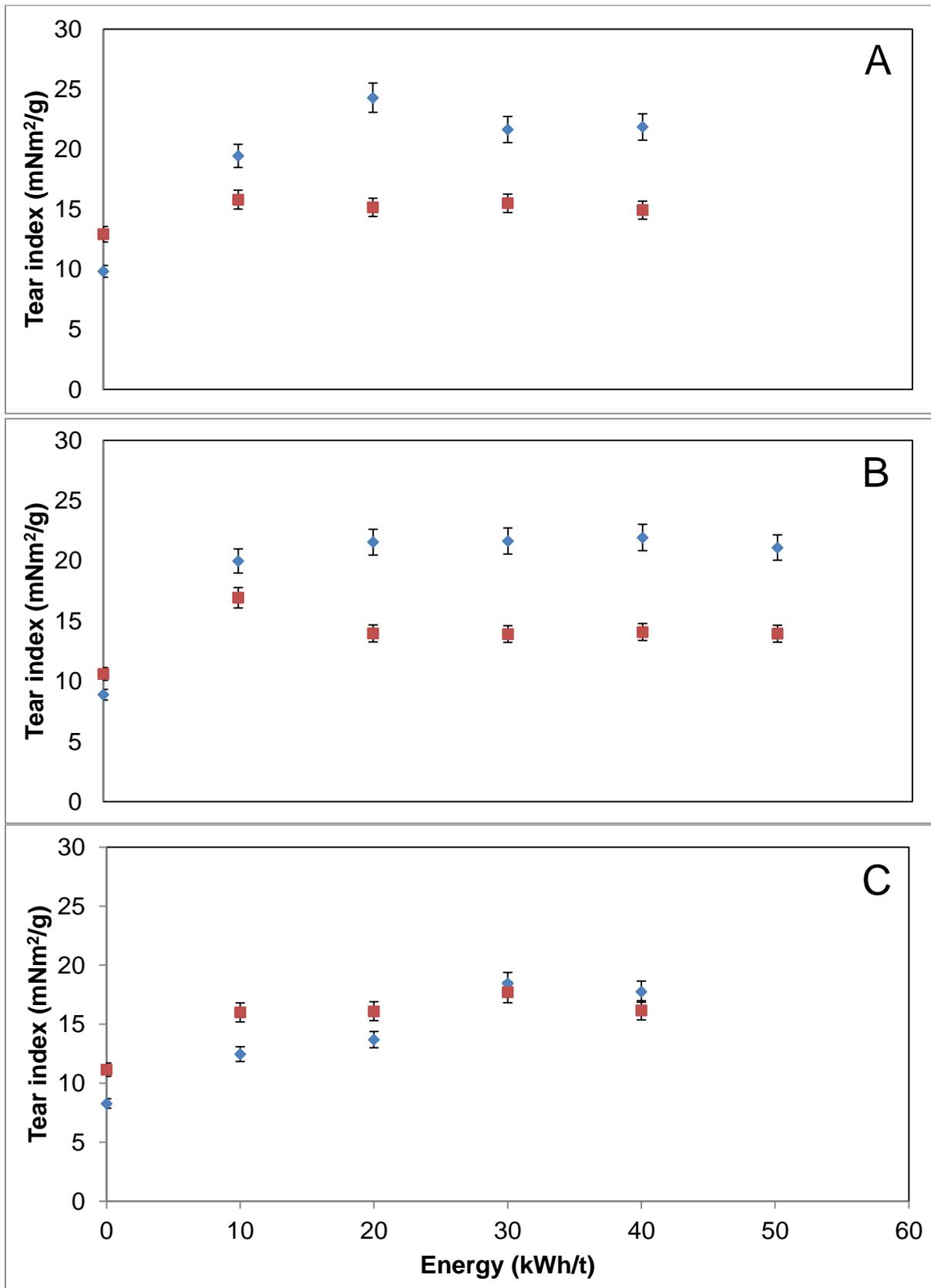


Figure 5.11: Tear strength of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; ♦ Untreated, ■ Enzymatically treated [50 g/t]).

When comparing the tear strength of the untreated sonicated fibres and the 50 g/t enzymatically treated fibres, one can see that the enzymes seem to have a debilitating effect on the tear strength of the paper. At the 53 μm treatment the tear strength of the treated and untreated fibres was similar, but at the 80 μm and 106 μm treatments the enzymatically treated fibres resulted in consistently lower tear strength values. The overall results were very similar to the hardwood results, and could not be explained by the morphology results.

5.2.4 Tear/tensile relationship of low-dosage enzymatically treated softwood

In Figure 5.12, the tear and tensile strength relationship can be seen.

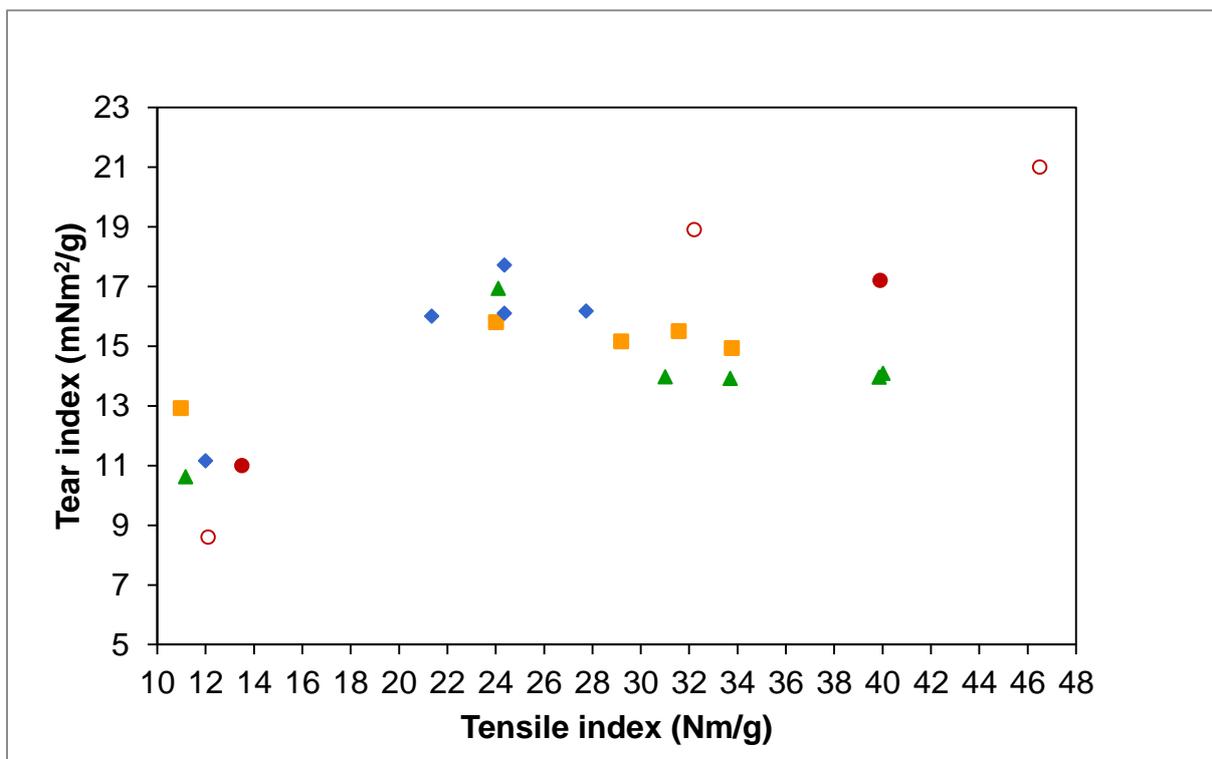


Figure 5.12: Tear and tensile strength relationship of 50g/t enzymatically treated softwood fibres (○ Enzymatically treated, mechanically refined, ● Mechanical refining, ◆ Enzymatically treated ultrasonication at 50 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The tear and tensile relationship was best developed by combining enzymatic pre-treatment with mechanical refining. Ultrasonication, however, seemed to cause a better tear and tensile relationship in the fibres than mechanical refining. The tear and tensile strength relationship graph shows that ultrasonication combined with enzymatic pre-treatment was more effective in developing the tensile index than

mechanical refining, but that mechanical refining could achieve high tensile strength results without losing tear strength. Mechanical refining and enzymatic pre-treatment had the highest tear strength of $21 \pm 0.9 \text{ mNm}^2/\text{g}$ at a tensile strength of $46.5 \pm 2.3 \text{ Nm/g}$. Ultrasonication at $80 \mu\text{m}$ seemed to have the best ultrasonication result with a tear strength of $14 \pm 0.6 \text{ mNm}^2/\text{g}$ at a tensile index of $40 \pm 2 \text{ Nm/g}$.

5.2.5 Freeness and tensile strength relationship of low-dosage enzymatically treated softwood

The tensile strength and freeness relationship of the enzymatically treated fibres can be seen in Figure 5.13.

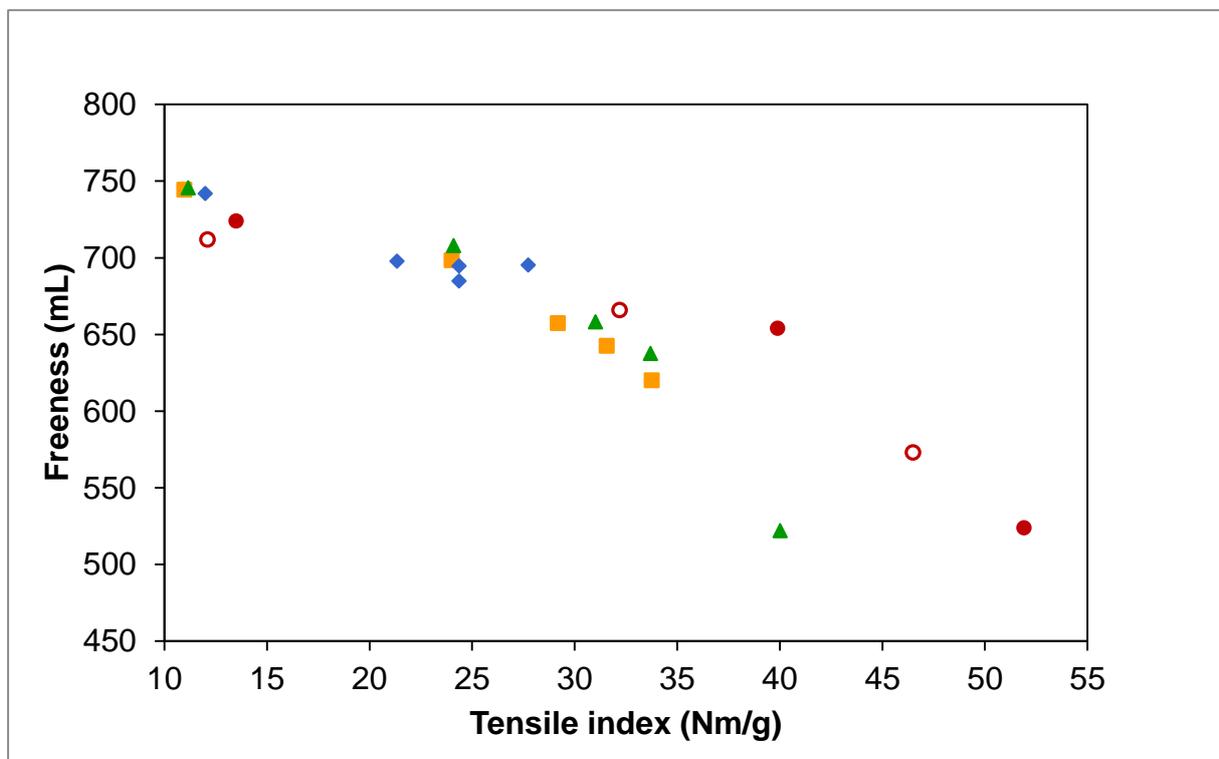


Figure 5.13: Softwood freeness and tensile strength relationship for 50 g/t enzymatically treated fibres (○ Enzymatically treated, mechanically refined, ● Mechanical refining, ◆ Enzymatically treated ultrasonication at $50 \mu\text{m}$, ▲ Enzymatically treated ultrasonication at $80 \mu\text{m}$, ■ Enzymatically treated ultrasonication at $106 \mu\text{m}$).

It was possible to increase the tensile strength of the softwood fibres without losing large freeness amounts up to $34 \pm 1.7 \text{ Nm/g}$. Ultrasonication at $80 \mu\text{m}$ caused a larger decrease in freeness than mechanical refining to achieve a tensile strength of $40 \pm$

2 Nm/g. Mechanically refined fibres achieved a tensile index of 52 ± 2.6 Nm/g at the same freeness as the 80 μm ultrasonication treatment.

In summary, ultrasonication and enzymatic pre-treatment were successful in modifying the softwood fibres. Ultrasonication at 80 μm seemed to show the most promise, but when comparing the results to that of the untreated and enzymatically treated, mechanically refined fibres, the tensile strength was not developed without negatively affecting the tear strength. It also seemed that a high tensile strength came at the cost of freeness when using ultrasonication and enzymatic pre-treatment. Once again ultrasonication proved to be more effective in modifying fibres at a low energy.

5.3 Ultrasonication and refining of high-dosage enzymatically treated softwood

In an attempt to solve the problem of the high freeness reduction, a higher enzymatic dosage was investigated. Therefore, an experiment was done to determine the efficacy of treating the pulp with an enzyme dosage of 200 g/t before introducing ultrasonication.

5.3.1 Freeness of high-dosage enzymatically treated softwood

The same treatment procedure as with the 50 g/t enzymatic pre-treatment was followed for the 200 g/t dosage enzymatic pre-treatment, and the freeness results can be seen in Figure 5.14.

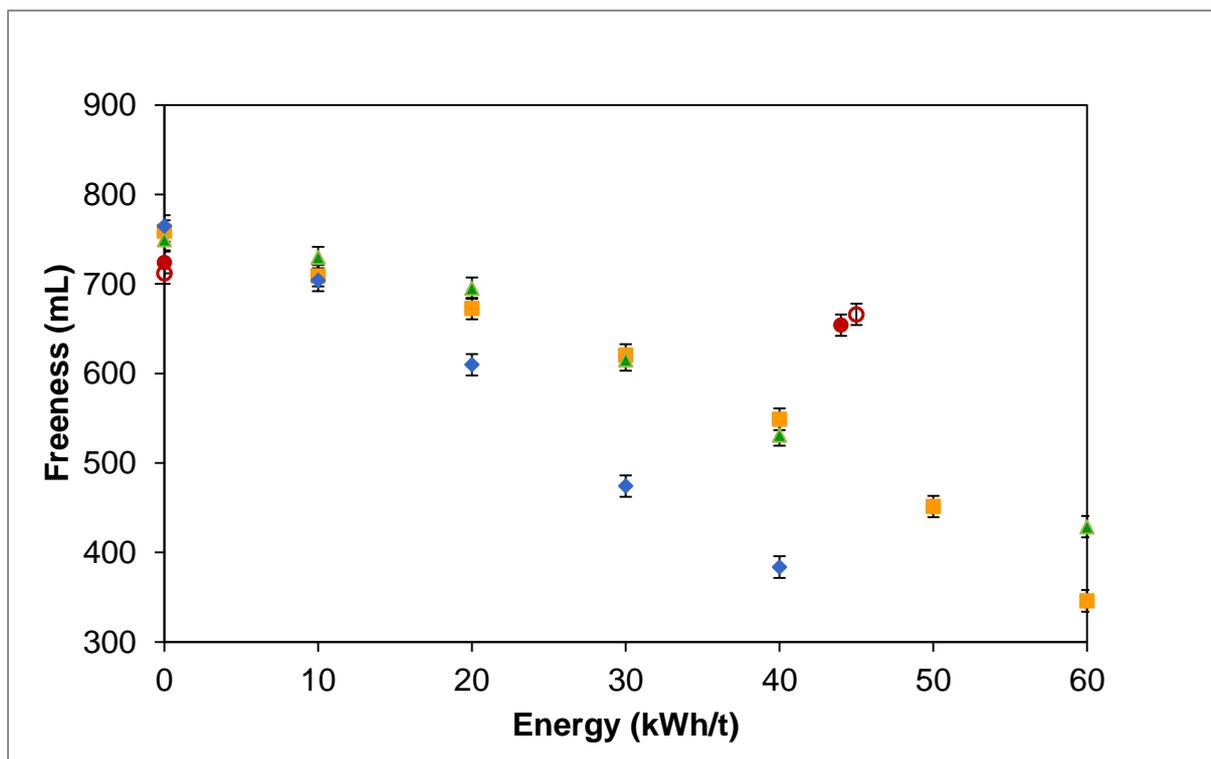


Figure 5.14: Softwood pulp freeness after 200 g/t enzymatic pre-treatment and mechanical refining or ultrasonication (● Untreated mechanically refined, ○ Enzymatically treated, mechanically refined, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The enzymatically treated, sonicated pulp freeness decreased significantly when compared to the mechanically refined pulp. Ultrasonication at high amplitudes (80 μm and 106 μm) seemed to result in comparable pulp freeness. The low-amplitude ultrasonication (53 μm), however, resulted in significantly lower freeness at energies above 20 kWh/t. This lower freeness may indicate that fibre modification was more effective at low amplitudes when using an excessive enzyme dosage. Previous studies have found that a prolonged enzymatic pre-treatment time may increase the fibre modification effect (Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002); Sun *et al.* (2002)). The effect of the higher enzymatic dosage and the notably longer treatment time associated with ultrasonication at low amplitude may have resulted in more pronounced fibre modification. The more apparent freeness decrease may also be because the fibres were damaged by the higher enzymatic dosage and prolonged treatment time.

The freeness comparison of sonicated untreated, 50 g/t and 200 g/t enzymatic pre-treatment is presented in Figure 5.15.

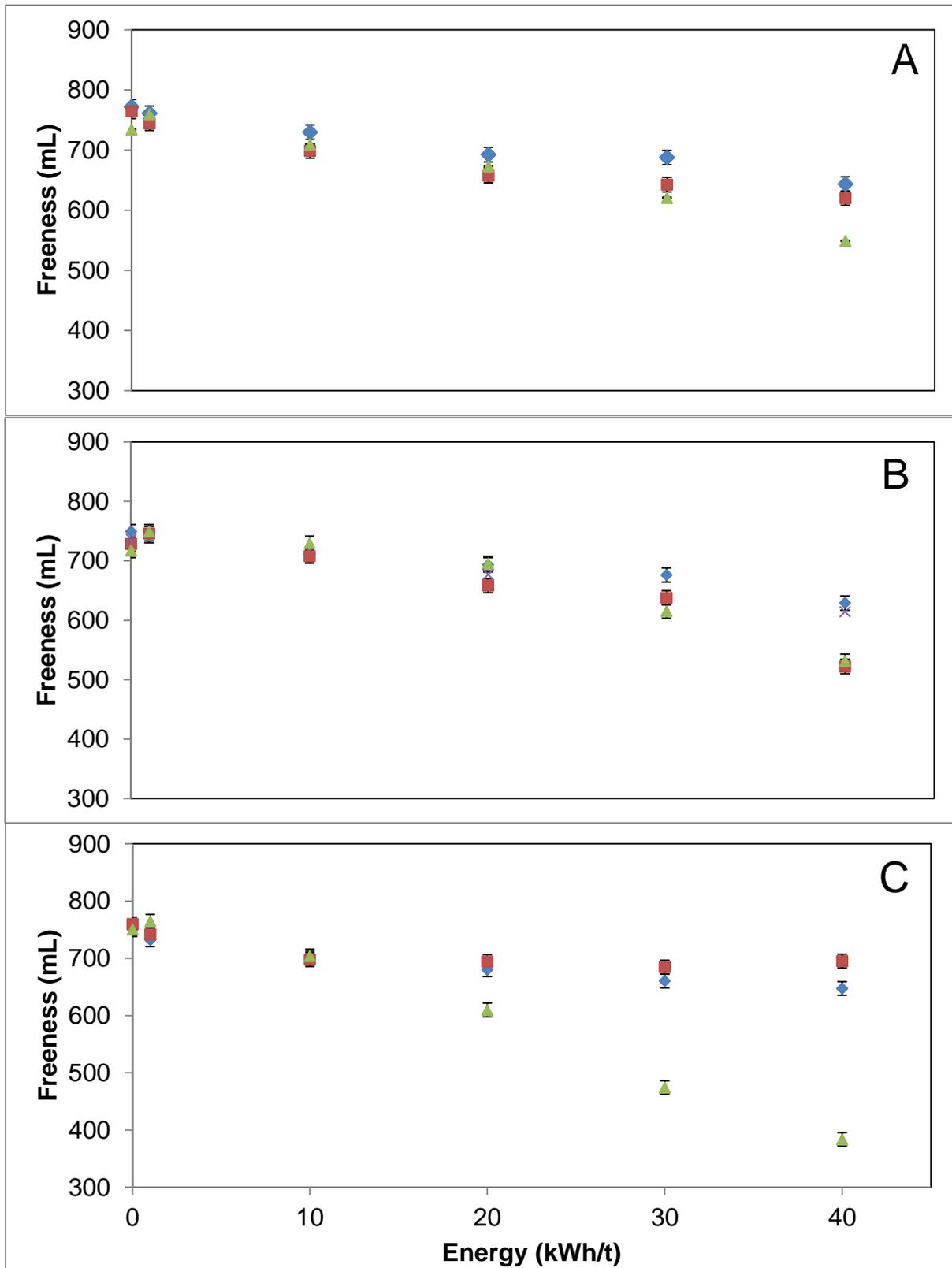


Figure 5.15: Freeness comparison of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; \blacklozenge Untreated, \blacksquare Enzymatically treated [50 g/t], \blacktriangle Enzymatically treated [200g/t])

When comparing the freeness of the ultrasonication control, 50 g/t enzymatic pre-treatment and 200 g/t enzymatic pre-treatment, the results were very similar, except at the level of amplitude 53 μm . It seemed that the combination of the enzymatic and ultrasonication treatment had no significant effect on the freeness of the fibres. The 53 μm sonicated pulp that was treated with the higher dosage enzyme (200 g/t) resulted in notably lower freeness. An explanation may be that the modification effect was greater due to a higher enzyme dosage and longer treatment time. The morphology results indicated elevated fines content, which may explain the decrease in freeness (Appendix A2: Tables A2.3, A2.6 and A2.9). This was supported by Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lombay *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002), who found that prolonged treatment times may result in achieving high levels of modification faster.

5.3.2 Tensile strength of high-dosage enzymatically treated softwood

The tensile strength results of the 200 g/t enzymatic pre-treatment on the softwood can be seen in Figure 5.16.

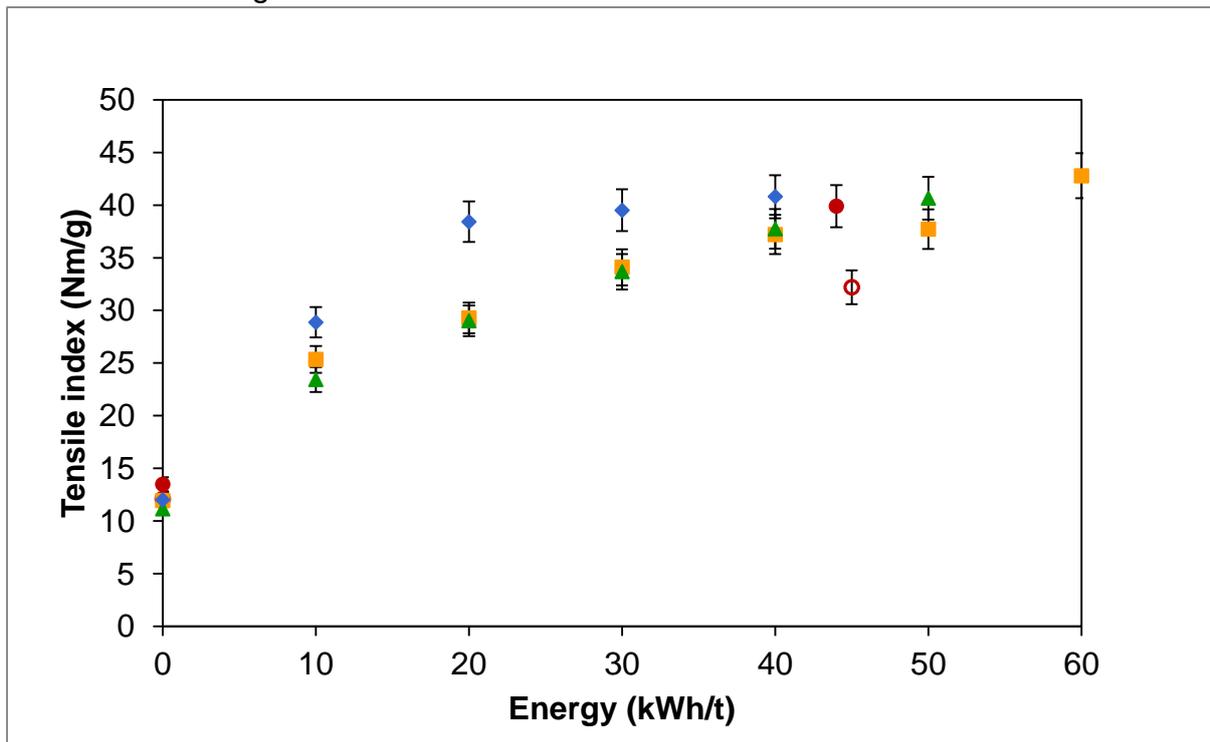


Figure 5.16: Tensile strength results for 200 g/t enzymatically treated softwood fibres after different levels of energy treatment with mechanical refining and ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated, mechanically refined, ◆ Enzymatically treated ultrasonication at 50 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The 200 g/t enzymatic/ultrasonication treatment increased the tensile strength of the fibres. The tensile strength results supported the freeness findings of the 53 μm ultrasonication treatment. The higher tensile strength results induced by low-amplitude ultrasonication, in comparison to the high-amplitude ultrasonication, indicated that the fibres were effectively modified, not merely damaged. The high-amplitude ultrasonication (80 μm and 106 μm) produced similar results, where the highest tensile strength of $43 \pm 2 \text{ Nm/g}$ was recorded at an energy level of 60 kWh/t and amplitude 106 μm . Ultrasonication produced similar results compared to mechanical refining, which may indicate that the higher enzymatic pre-treatment was more effective in refining the fibres.

A comparison of the tensile strength of sonicated fibres at different enzymatic dosage treatments can be seen in Figure 5.17.

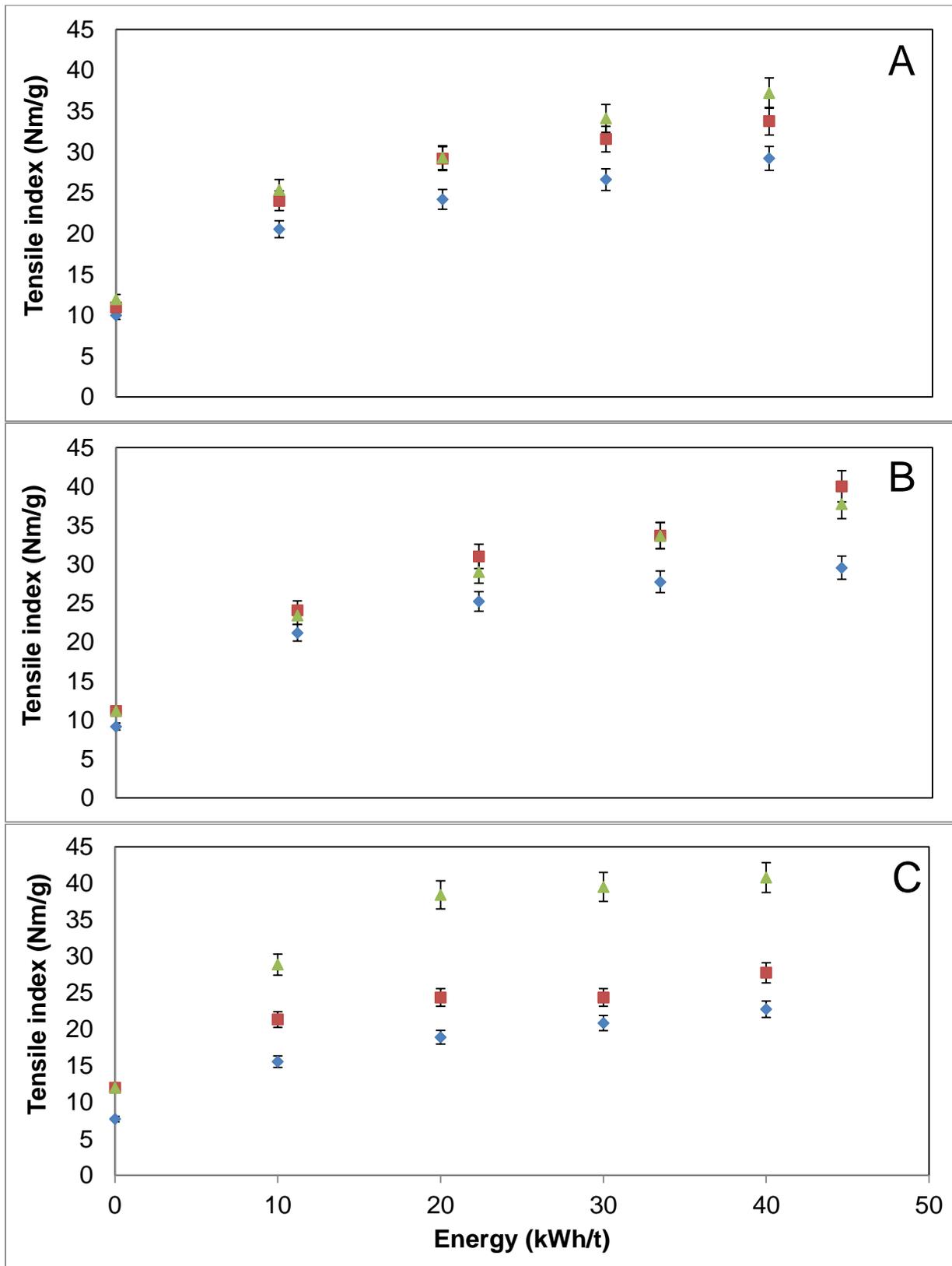


Figure 5.17: Tensile strength comparison of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; ♦ Untreated, ■ 50 g/t Enzymatically treated, ▲ 200 g/t Enzymatically treated).

There was very little change when comparing the tensile strength of the different enzyme dosages in ultrasonication, but the tensile strength of the enzymatically treated fibres was constantly higher than that of the control. It must be noted that the enzymatically treated, sonicated (at 53 μm) fibres displayed the highest tensile strength results. The morphology results indicated that a higher level of fibrillation was achieved at 53 μm , compared to the other amplitudes (Appendix A2: Tables A2.3, A2.7 and A2.9).

5.3.3 Tear strength of high-dosage enzymatically treated softwood

The tear strength results for the 200 g/t enzymatically treated softwood pulp can be seen in Figure 5.18.

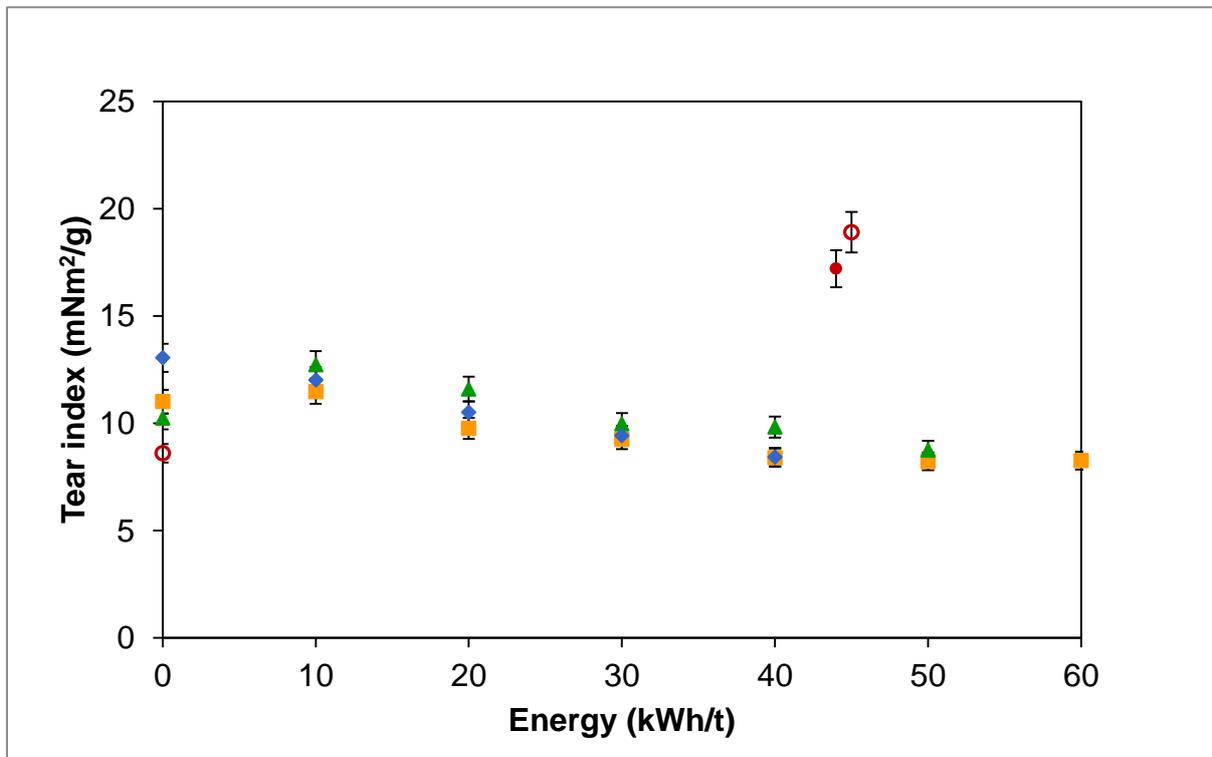


Figure 5.18: Tear strength results for 200 g/t enzymatically treated softwood fibres after mechanical refining or ultrasonication. (○ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

Initially the tear strength seemed to increase for the 200 g/t enzymatically treated sonicated pulp, but a significant decrease can be noted from energies above 10 kWh/t. The sonicated pulp displayed similar tear strength results, regardless of the amplitude applied. The mechanically refined pulp resulted in consistently higher tear strength

values when compared to ultrasonication. The higher enzyme dosage may have caused the pulp to be modified to a maximum point, where after the tear strength started decreasing, supporting the findings of Oksanen *et al.* (1997) and Josefsson (2006), who also noted that a maximum point of modification can be reached, but that the treatment may be detrimental to the fibres.

In Figure 5.19, the comparison of tear strengths for different enzymatic dosages can be seen.

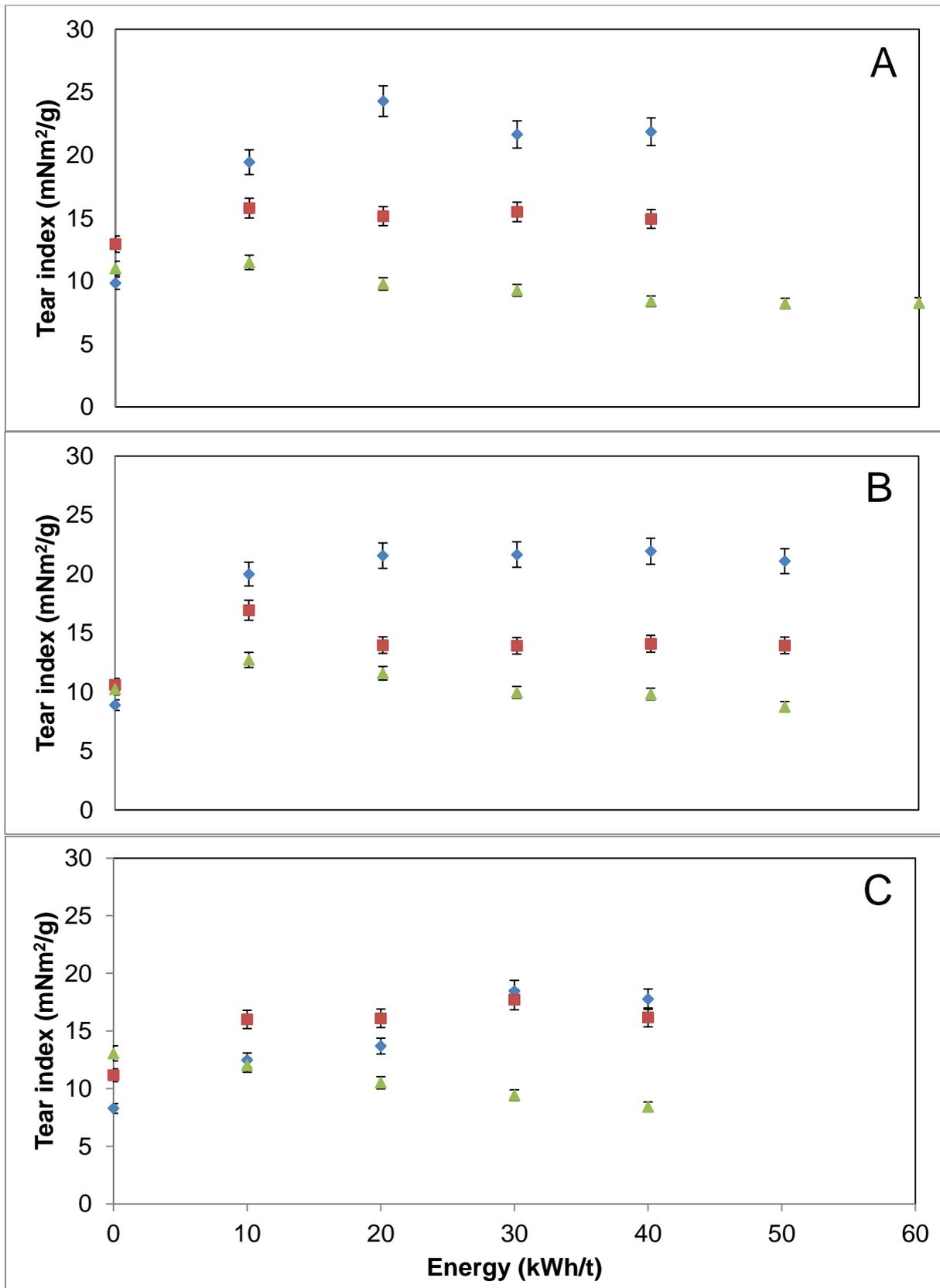


Figure 5.19: Tear strength of untreated and enzymatically treated sonicated softwood fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm [C]; ♦ Untreated, ■ Enzymatically treated [50 g/t], ▲ Enzymatically treated [200g/t]).

When comparing the different enzyme dosages and ultrasonication, the results were similar except for the 0 kWh/t treatment, where the 200 g/t enzymatic dosage was significantly higher. These tear strength results support the findings of Peter Josefsson (2006). What it may have proven, additionally, was that the higher enzymatic dosages caused enhanced fibre modification. The tear strength results also seemed to indicate that the enhanced fibre modification effect was only for a finite period of time. Once a certain time has passed, there was no added benefit from the higher dosage, which supports the findings of Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lomboy *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002).

5.3.4 Tear/tensile strength relationship of high-dosage enzymatically treated softwood

The tear and tensile strength relationship of the 200 g/t enzymatically treated pulp can be seen in Figure 5.20.

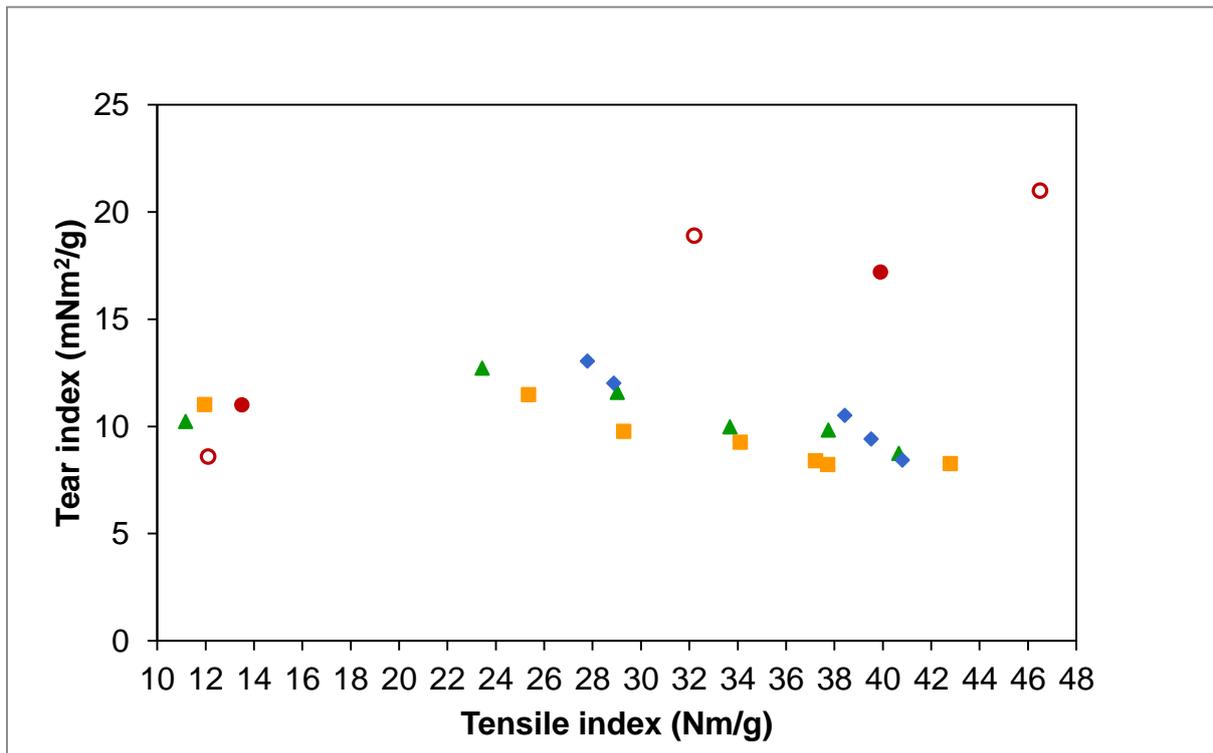


Figure 5.20: Tear and tensile strength relationship of 200 g/t enzymatically treated softwood fibres after different levels of energy treatment with mechanical refining and ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 50 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

The tear-tensile strength relationship of the mechanically refined experiment was the highest. Ultrasonication was effective in modifying the tensile strength of the fibres, but it was not effective in doing so without negatively affecting the tear strength. The reason for this may be that the OCC fibres were shortened by the treatment, thereby affecting the tear strength. The shorter fibres, however, do not have an effect on the tensile strength. Ultrasonication produced a maximum tear strength of 12 ± 0.5 mNm²/g at a tensile strength of 28 ± 1.4 Nm/g, which was significantly lower than the mechanically refined tear strength of 21 ± 0.9 mNm²/g at a tensile strength of 46 ± 2.8 Nm/g.

5.3.5 Freeness and tensile strength relationship of high-dosage enzymatically treated softwood

The freeness and tensile strength relationship is presented in Figure 5.21.

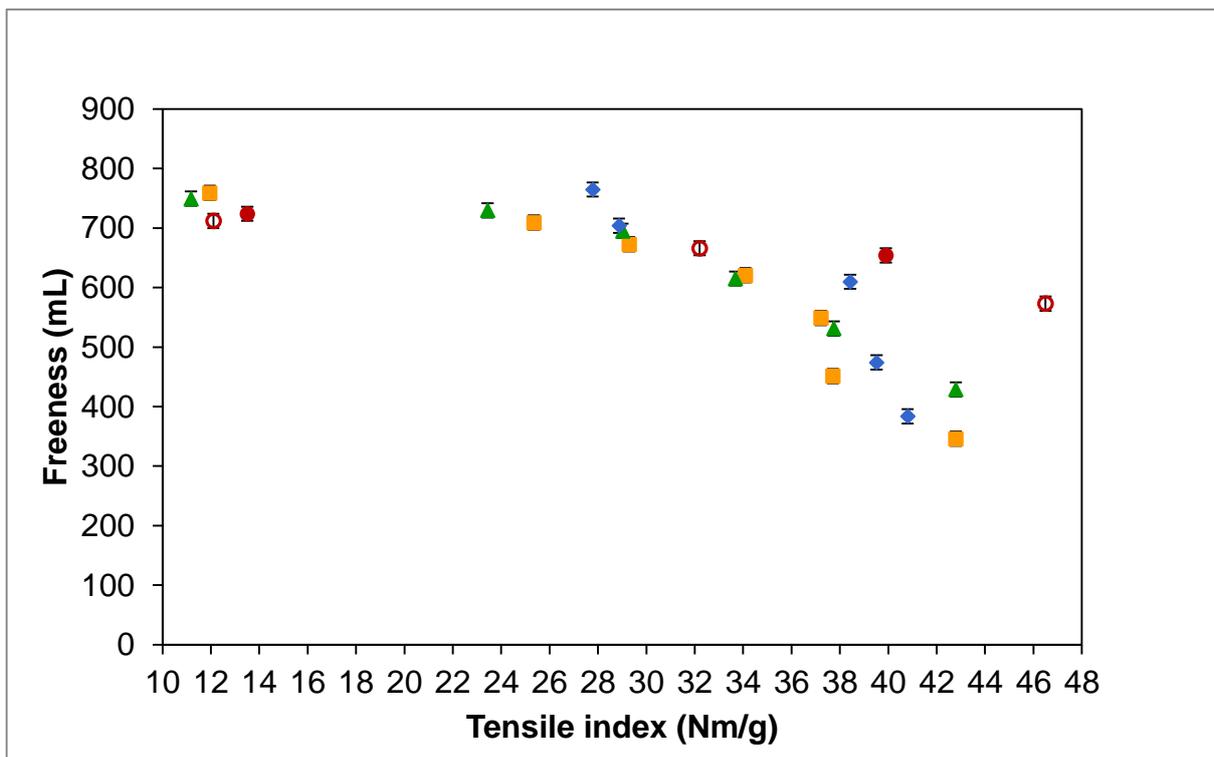


Figure 5.21: Softwood pulp freeness and tensile strength relationship of 200 g/t enzymatically treated softwood fibres after mechanical refining or ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 50 μm, ▲ Enzymatically treated ultrasonication at 80 μm, ■ Enzymatically treated ultrasonication at 106 μm).

The 200 g/t enzymatically treated ultrasonication at 80 and 106 μm displayed the optimum relationship between freeness and tensile strength when compared to the mechanical refining treatments. However, once the tensile strength was developed beyond 33 Nm/g, the freeness also decreased significantly compared to mechanical refining.

In summary, there seemed to be a relationship between enzymatic dosage, ultrasonication intensity and treatment times. When using an enzymatic dosage of 50 g/t, a slightly longer treatment time and less ultrasonication intensity, the result was higher tensile strength. When using the 200g/t enzymatic dosage, the longest treatment time and lowest ultrasonication intensity (53 μm), the tensile strength of the fibres increased. In both instances the tensile strength improved at the cost of losing more freeness and tear strength than mechanical refining.

5.4 Ultrasonication and refining of softwood followed by 100 g/t enzymatic treatment

The 100 g/t enzymatic post-treatment was done in the way described in Chapter 3, followed by the same pulp and strength tests as with the other softwood experiments. A ultrasonication amplitude of 80 μm was selected, based on the more consistently good results obtained throughout the control and 50 g/t enzymatic pre-treatments.

5.4.1 Freeness of softwood followed by 100g/t enzymatic treatment

The freeness of the 100 g/t enzymatically post-treated pulp can be seen in Figure 5.22.

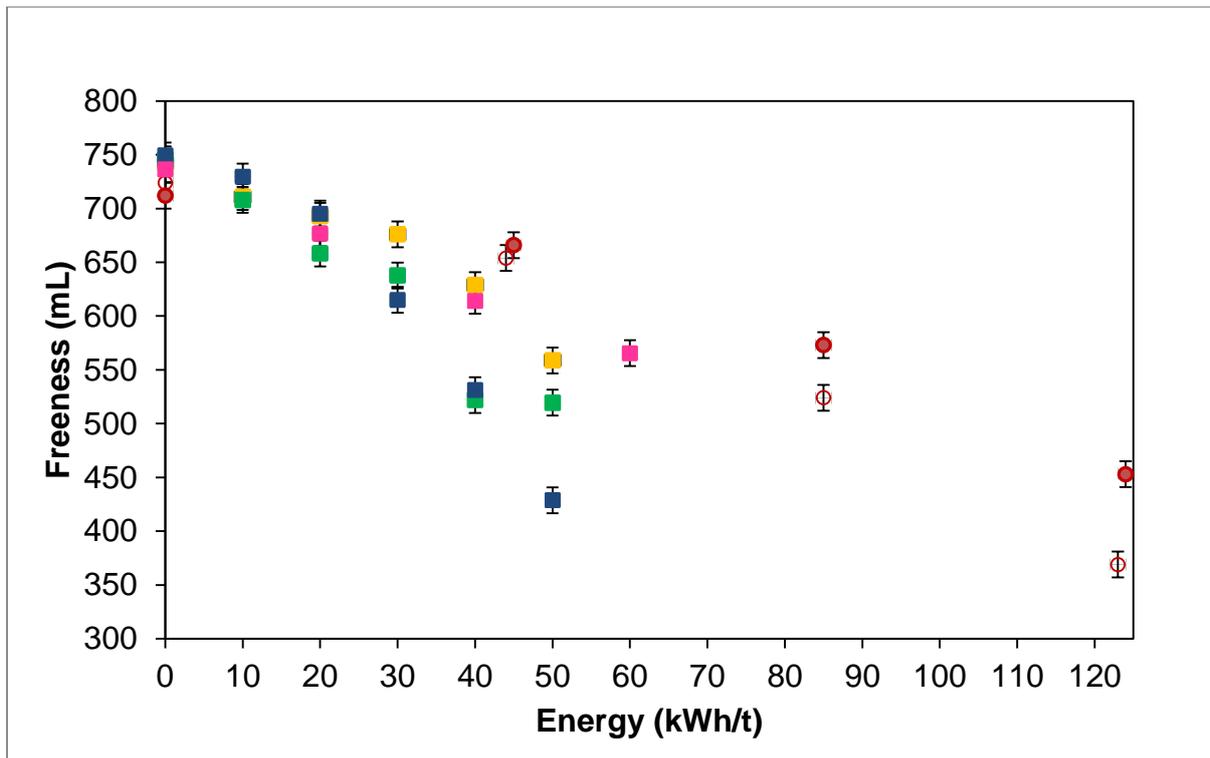


Figure 5.22: Softwood freeness comparison of all ultrasonication experiments at 80 μm (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ○ Enzymatically treated, mechanically refined [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The freeness of the sonicated sample that was enzymatically post-treated at a 100 g/t dosage was similar to that of the other ultrasonication experiments at 80 μm , and slightly lower than the mechanically refined pulp. As explained in Chapter 4.4.1, the enzyme contact time was believed to be longer for the enzymatic pre-treatment experiments, as it was suspected that the enzyme was not successfully deactivated by ultrasonication. Therefore, based on previous studies by Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lombay *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002), it was expected that the results from the enzymatic post-treatment wouldn't be as significant as for the enzymatic pre-treatment experiments.

5.4.2 Tensile strength of softwood followed by 100 g/t enzymatic treatment

The tensile strength of the 100 g/t enzymatically post-treated softwood pulp can be seen in Figure 5.23.

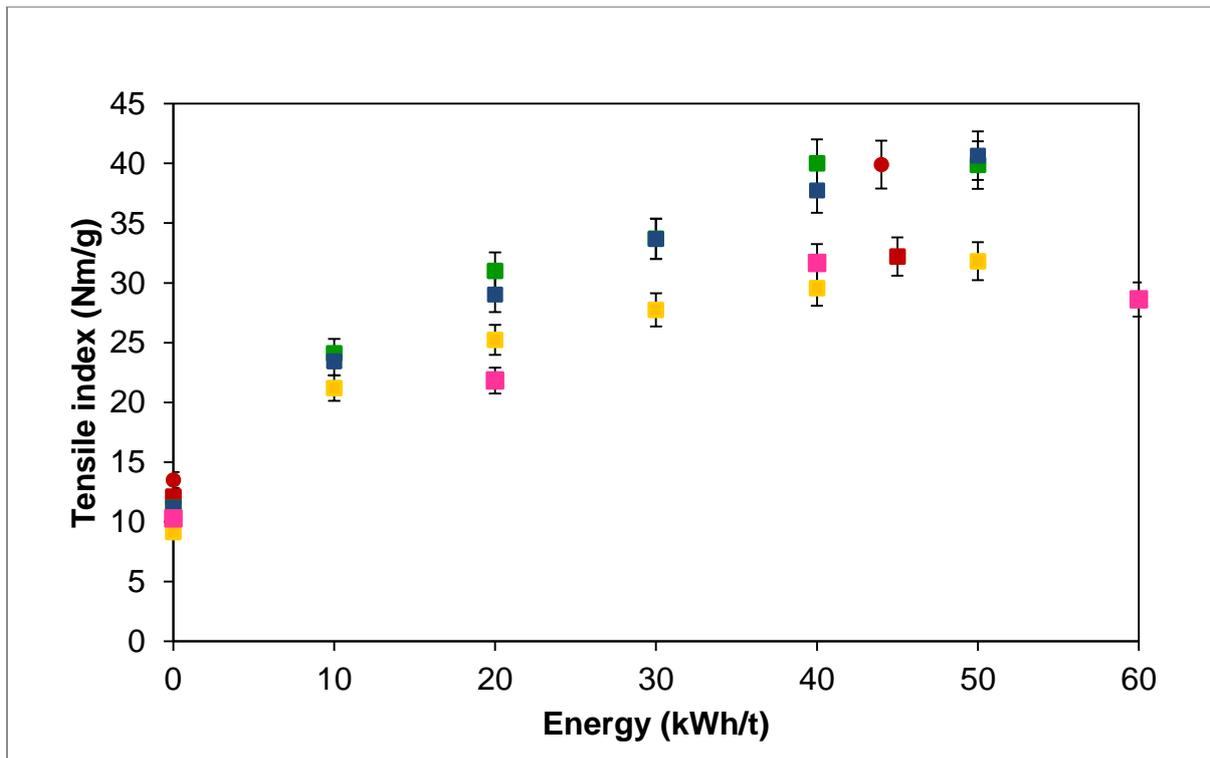


Figure 5:23. Tensile strength of all softwood ultrasonication experiments at 80 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

Though the enzymatically post-treated sample had the overall lowest tensile strength, it was substantially lower. The lower tensile strength could mean that the freeness indicated a lower level of fibre modification, rather than a more effective method of removing colloidal cellulose. At low energies (0-20 kWh/t) the tensile strength of the 100 g/t enzymatic post-treatment was similar to the ultrasonication control. Once again, the shorter enzymatic post-treatment time, compared to the enzymatic pre-treatment, may have played a role in effectively modifying the fibres. This supports Anna Joseffson's (2006) findings, that ultrasonication on its own cannot equal the results of mechanical refining.

5.4.3 Tear strength of softwood followed by 100 g/t enzymatic treatment

The tear strength of the 100 g/t enzymatic post-treatment is presented in Figure 5.24.

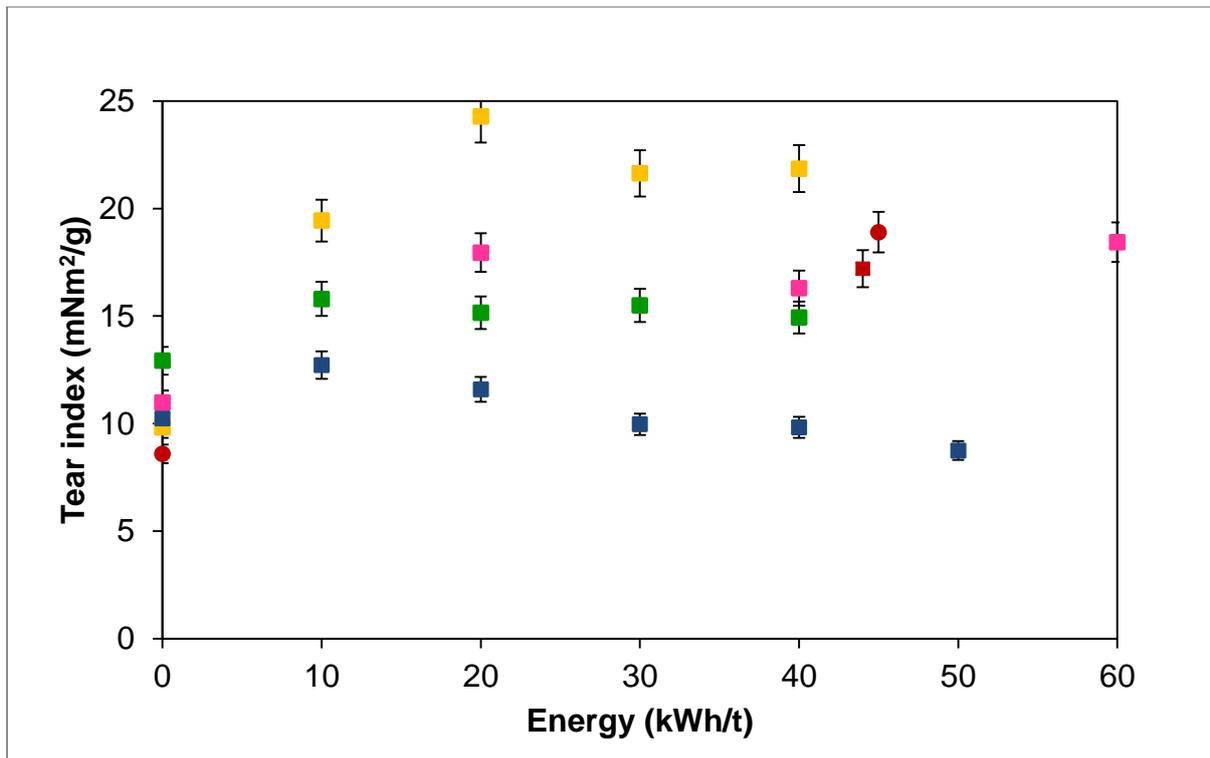


Figure 5.24: Tear strength of all softwood ultrasonication experiments at 80 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined, enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The tear strength of the enzymatic post-treatment was similar to the 50 g/t enzymatically treated ultrasonication experiment. It appeared that the shorter enzymatic post-treatment time, compared to the enzymatic pre-treatment, had positive results on the tear strength of the softwood. This might have been due to the enzyme making the fibre less susceptible to the refining effects, resulting in less fibre damage. The untreated sonicated softwood fibre also displayed positive tear strength results. Combining ultrasonication and enzymatic post-treatment seemed to be effective in developing the tensile strength of the fibres, but it was not effective in developing the tear strength. Ultrasonication without enzymatic post-treatment, however, seemed to improve the tear strength significantly.

5.4.4 Tear, tensile and freeness strength relationship of sonicated softwood followed by 100 g/t enzymatic treatment

The tear strength, tensile strength and freeness relationships can be seen in Figure 5.25.

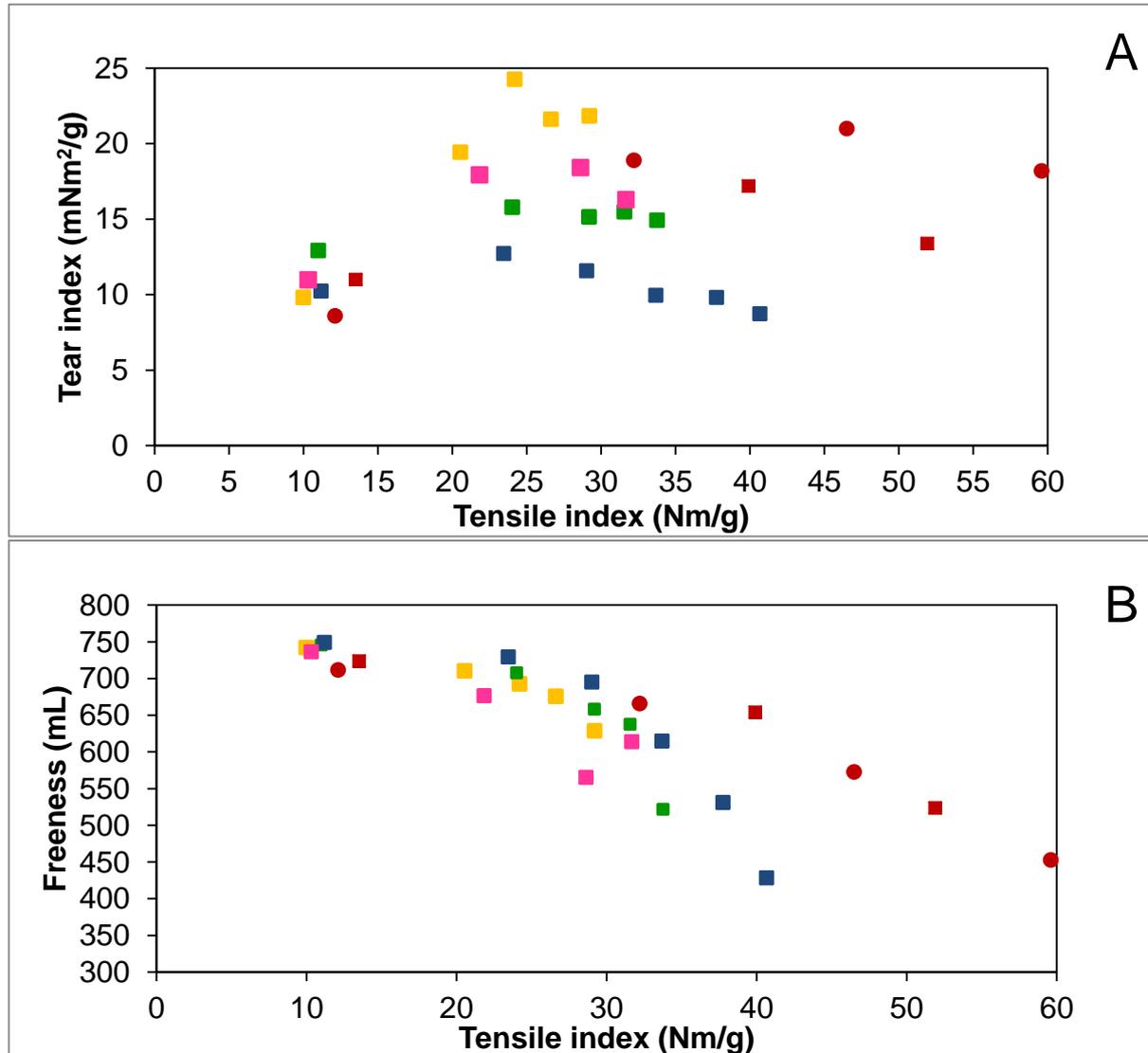


Figure 5.25: Tear and tensile strength relationship (A) and freeness and tear strength relationship (B) of all softwood ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining (■ Ultrasonication with enzymatic post-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined and enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic pre-treatment (100 g/t), ■ Ultrasonication with enzymatic post-treatment [50 g/t], ■ Ultrasonication control).

The enzymatic post-treatment tensile strength results looked similar to the enzymatic pre-treatment results at tensile strengths between 30 ± 1.5 and 34 ± 1.7 Nm/g. The

difference was that the enzymatic post-treatment could not modify the fibres beyond a tensile strength of 34 ± 1.7 Nm/g and a tear strength of 6.51 ± 0.3 mNm²/g. Compared to the ultrasonication and enzymatic pre-treatments, which reached values of 44 ± 2.2 Nm/g and 7.49 ± 0.3 mNm²/g, the enzymatic post-treatment was not effective.

In summary, the enzymatic post-treatment had a positive result on the strength properties of the hand-sheets, although it was lower than the enzymatic pre-treatments, and it caused a smaller decrease in freeness, which was positive for the paper machines. The post-treatment results were, however, not comparable to the strength results of mechanical refining or the previous enzymatic and ultrasonication experiments. A possible explanation could be that the shorter enzymatic post-treatment time caused a smaller fibre modification effect when compared to the enzymatic pre-treatment experiments. Compared to the enzymatic pre-treatments, enzymatic post-treatment was not effective at fibre modification .

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CHAPTER 6: Ultrasonication of old corrugated containers (OCC) pulp

The influence of ultrasonication and enzymatic treatments on old corrugated containers pulp (referred to as OCC pulp throughout the rest of the chapter) was investigated. For this chapter the mechanical refining was done because the mixture of different recycled containers created a unique pulp, meaning existing data could not be used. The pulps were sonicated and the results compared to mechanical refining to determine if ultrasonication and enzymatic treatment may be a viable alternative.

6.1 Measurement of the development of untreated OCC pulp

In the first set of treatments no enzyme was added and the pulp was developed by means of ultrasonication. The resulting pulp was tested for the degree of freeness, and the hand-sheets, made from the sonicated pulp, were tested for tensile strength and tear strength and compared to the mechanically refined experiment results.

6.1.1 Freeness of untreated OCC pulp

The freeness of the pulp was tested as described in Chapter 3, by taking a sample and rapidly cooling it to 20°C before the test was done. The freeness results can be seen in Figure 6.1.

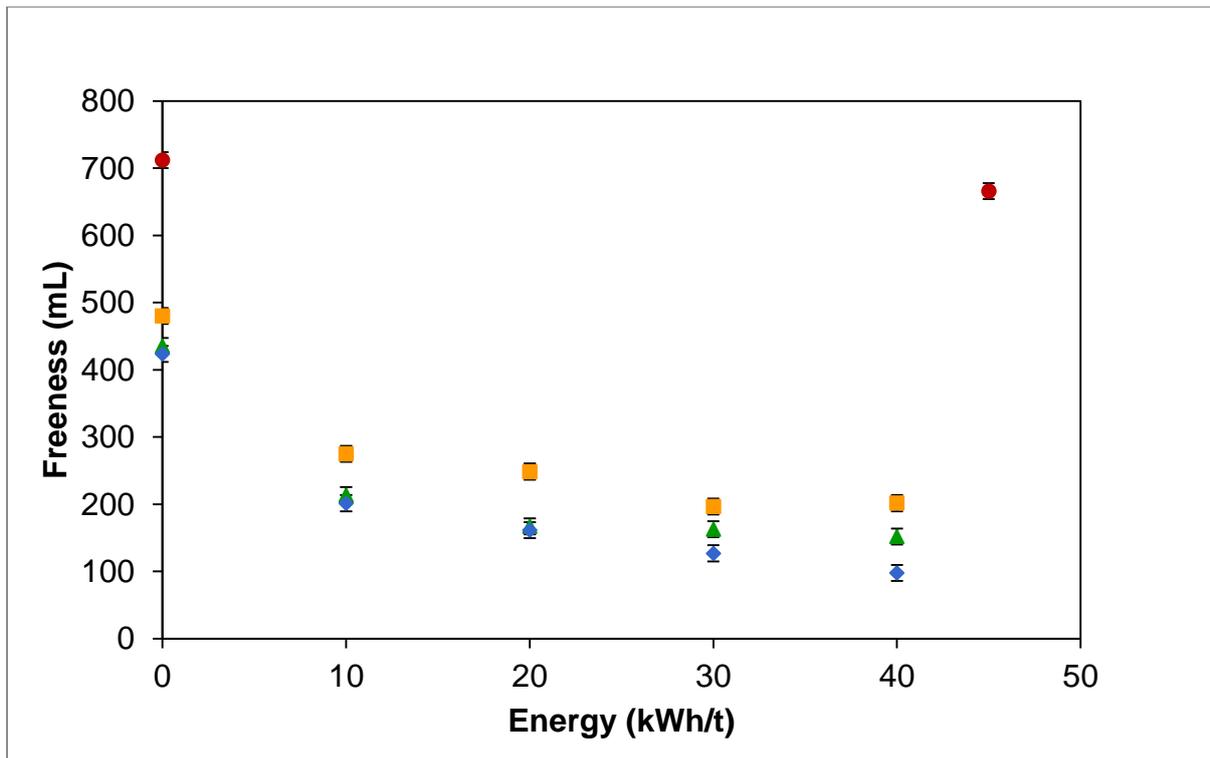


Figure 6.1: OCC pulp freeness after treatment with mechanical refining and ultrasonication respectively at different energy levels (● Mechanical refining, ◆ Ultrasonication at 53 μm, ▲ Ultrasonication at 80 μm, ■ Ultrasonication at 106 μm).

The freeness decreased for both mechanical refining and ultrasonication treatments, which was explained by Rehman's (2013) and Suslick's (1989) findings: Fibre development in ultrasonication and mechanical refining were similar, and both result in increased fibre contact area, which causes the freeness to decrease.

The uniqueness of the pulp can be observed when comparing the difference in freeness for mechanically refined pulp and sonicated pulp at 0 kWh/t. This difference may be explained by the composition of the OCC pulp. Although the samples were similar, the slightest irregularity could cause an unpredictable result. The difference in freeness at various energies was therefore monitored and reported on. Ultrasonication caused a significant decrease in freeness between 0 kWh/t and 10 kWh/t, which seemed to be the same as for the hardwood and softwood experiments. After the initial decreases, the freeness followed an almost linear decrease from 10 kWh/t to 40 kWh/t. The total decrease in freeness between 0 and 40 kWh/t was between 279 ± 7 mL and 325 ± 7 mL (between 42 ± 1 % and 24 ± 2 %). Ultrasonication at 53 μm resulted in the lowest freeness, and can be explained by the higher broken

fibre and fine material content (Appendix A3, Tables A3.1, 3.4, 3.7). Mechanical refining also resulted in a decreased freeness, but it was significantly less than with ultrasonication. Between 0 and 45 kWh/t, the freeness decreased by 46 ± 12 mL (7 ± 2 %). The morphology results on the OCC fibres indicated a shorter average fibre length (Chapter 3, Table 3.1). The shorter fibres may indicate that the OCC pulp consisted mainly of hardwood fibres and recycled softwood fibres, which were shortened by the refining and recycling processes. The shorter OCC fibres reflect the freeness results of the hardwood tests reported in Chapter 4. As seen with the hardwood results, the low-amplitude ultrasonication resulted in consistently lower freeness results when compared to the higher amplitudes. This lower freeness suggests that the resulting fibre development effect was more apparent. Previous studies stated that an increase in ultrasonication treatment time increased the modification effect on the medium (Huang *et al.* 2007; Haung *et al.*, 2011; Montalbo-Lomboy *et al.*, 2010; Nikolic *et al.*, 2010; Sun & Tomkinson, 2002; Sun *et al.*, 2002), and the treatment time for the lower amplitude ultrasonication was 1.8 times longer than the high-amplitude treatment time (Table 3.2).

6.1.2 Tensile strength of untreated OCC pulp

Following the freeness tests, hand-sheets were made and the average tensile strength was tested. The effect of ultrasonication and mechanical refining is presented in Figure 6.2.

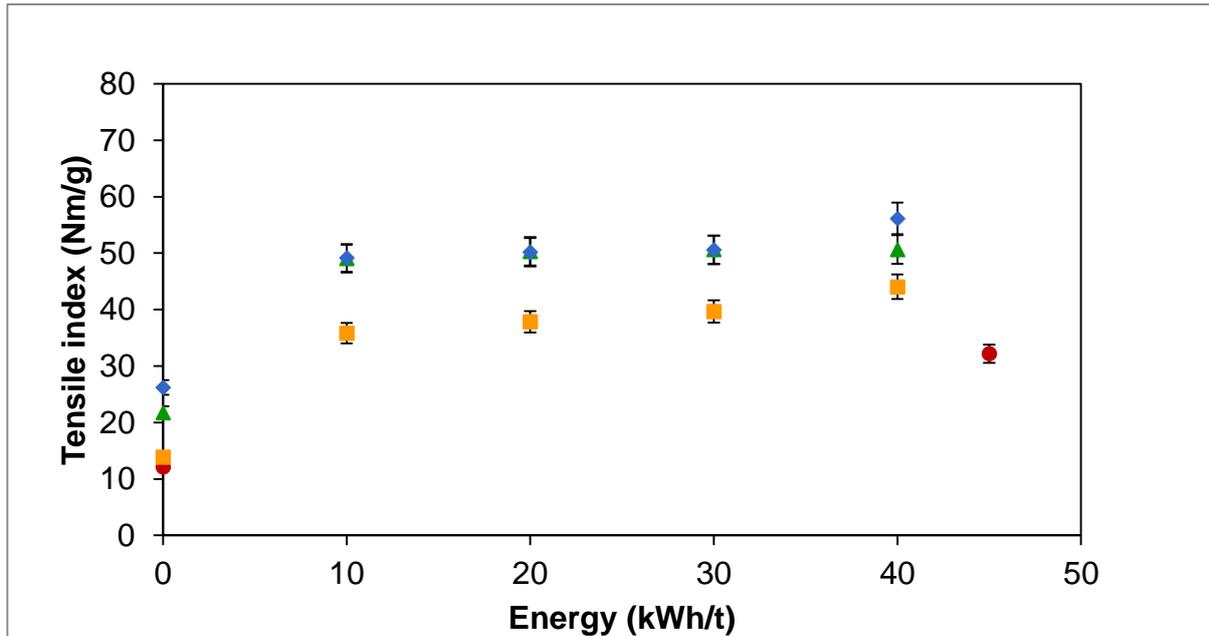


Figure 6.2: Tensile strength results of OCC fibres after different levels of energy treatment (● Mechanical refining, ◆ Ultrasonication at 53 μm, ▲ Ultrasonication at 80 μm, ■ Ultrasonication at 106 μm).

Tensile strength increased in line with treatment energy input, which compares with the hardwood results reported in Chapter 4. The tensile strength increases indicate that the decrease in freeness supported the successful modification of fibres. There was a large initial increase in the sonicated pulp's tensile strength, but once the energy input exceeded 10 kWh/t, the change in tensile strength was less. The 53 μm and 80 μm treatments had similar tensile strength results, but the tensile strength of 53 μm treated pulp was consistently higher. The morphology results indicated that there were higher fibrillation with the 53 μm and 80 μm treatments, with the 106 μm resulting in the lowest fibrillation, which explained the tensile strength results (Appendix A3, Tables A3.1, A3.4 and A3.7). The higher tensile strength results support the findings of Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002) and Sun *et al.* (2002) that an increased ultrasonication time is effective in modifying the medium. They also noted, however, that treatment efficiency decreased after a certain maximum time, which may explain the lower increase in tensile strength after 10 kWh/t. The highest tensile strength of 56 ± 2.8 Nm/g was recorded at 40 kWh/t using ultrasonication at 53 μm. Mechanical refining resulted in a maximum of 32.2 Nm/g, which was recorded at 45 kWh/t. High-amplitude (106 μm) ultrasonication did not seem as effective in modifying the fibres.

6.1.3 Tear strength of untreated OCC pulp

The third and final strength property that was tested, was tear strength. The results are shown in Figure 6.3.

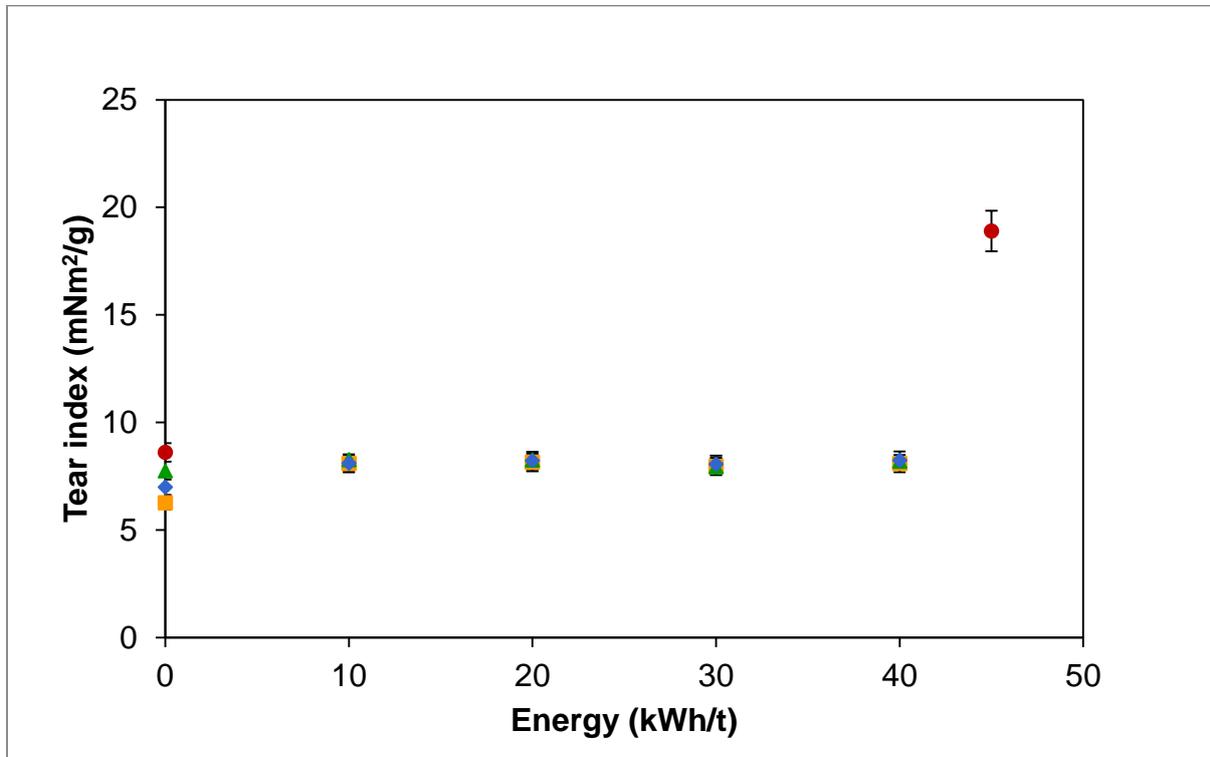


Figure 6.3: Tear strength of OCC fibres at different treatment-energy levels (● Mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

There was an increase in tear strength for mechanical refining and ultrasonication. Ultrasonication, however, resulted in a very small tear strength increase compared to mechanical refining. All three amplitudes had similar results, and there was no clear indication that different amplitudes had any unique effects on the tear strength. The comparable results may prove that the longer treatment time at amplitude 53 µm increased the tensile strength at the cost of the tear strength. The same can be said for the 80 µm treatment, which would explain why the tear strength results look similar for all amplitudes. Ultrasonication caused the OCC fibres to collapse, but the treatment may have been too harsh on the OCC fibres, resulting in the further shortening of fibres and causing the tear strength to remain constant. This result could be explained by Chen *et al.* (2010:7041), who found that the tear strength decreases with increased treatment times.

Mechanical refining, however, significantly increased the tear strength and the maximum tear strength of $18.9 \pm 0.8 \text{ mNm}^2/\text{g}$ was recorded at 45 kWh/t. Ultrasonication reached a maximum tear strength of $8.23 \pm 0.3 \text{ mNm}^2/\text{g}$ at 40 kWh/t.

6.1.4 Tear/tensile strength relationship of untreated OCC pulp

The relationship between tear and tensile strength is presented in Figure 6.4 and provides a basis for comparing the overall strength of the paper after it was mechanically refined or sonicated.

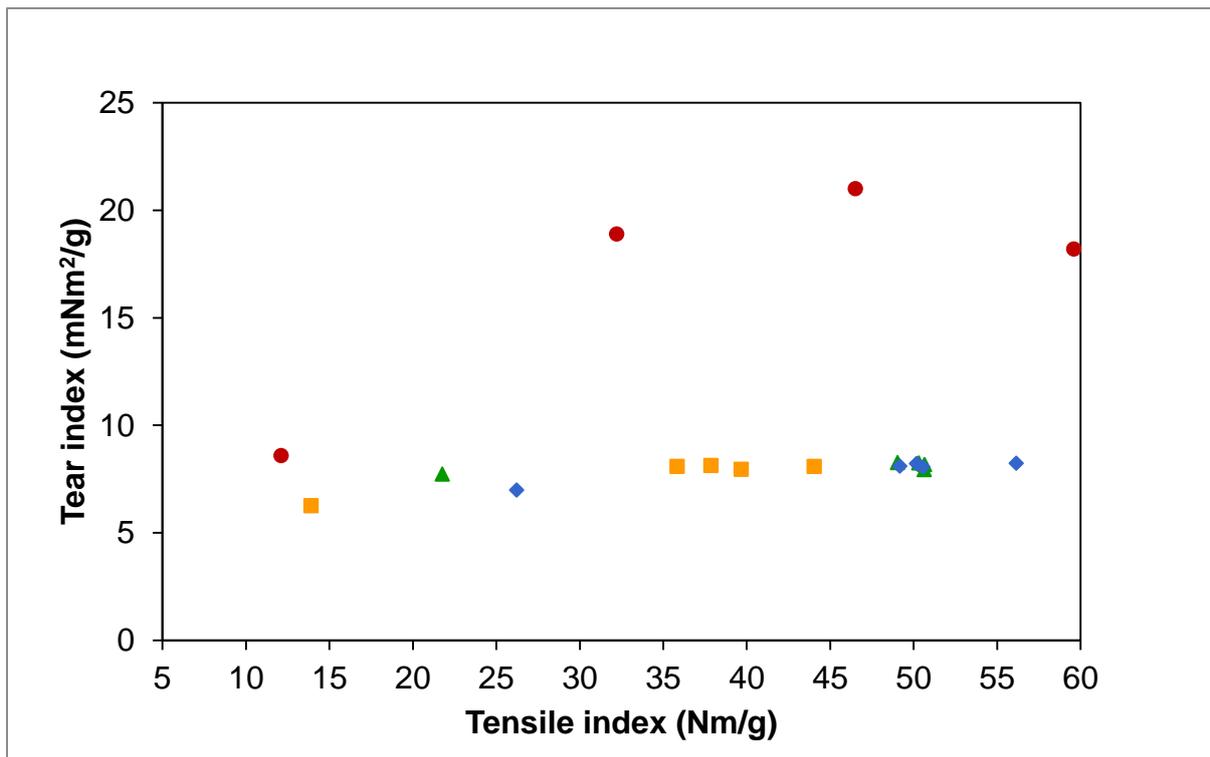


Figure 6.4: Tear and tensile strength relationship of treated OCC fibres (● Mechanical refining, ◆ Ultrasonication at 53 μm , ▲ Ultrasonication at 80 μm , ■ Ultrasonication at 106 μm).

The overall tear and tensile strength relationship of the mechanically refined pulp was significantly higher than that of the sonicated pulps. Ultrasonication resulted in a high tensile strength, but the tear strength was underdeveloped compared to mechanical refining.

Ultrasonication at amplitude 53 μm showed potential when compared to mechanical refining, with the highest tear strength of $8.3 \pm 0.32 \text{ mNm}^2/\text{g}$ achieved at a tensile strength of $56 \pm 2.8 \text{ Nm/g}$.

6.1.5 Freeness-tensile strength relationship of untreated OCC pulp

The relationship between freeness and tensile strength was important, because it showed the interaction between the apparent fibre modification (freeness) and ideal fibre modification (tensile strength). This interaction can be seen in Figure 6.5.

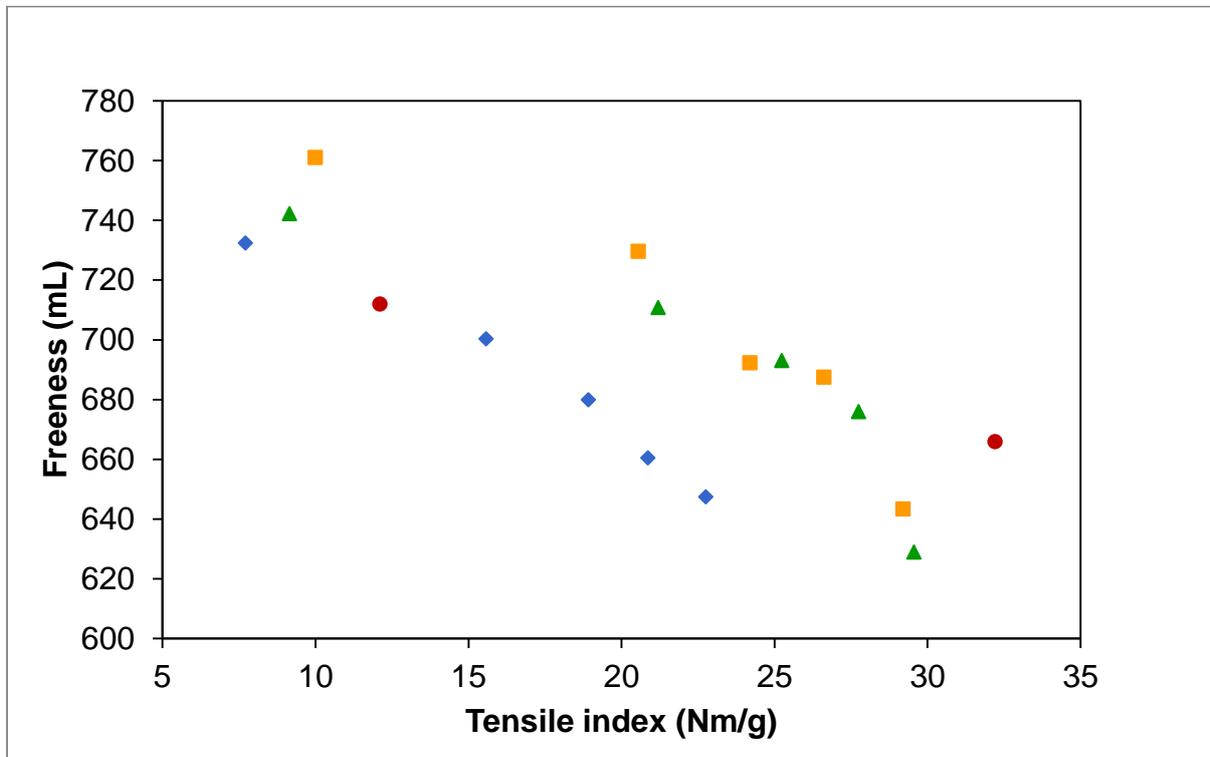


Figure 6.5: OCC freeness and tensile strength relationship (● Mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Ultrasonication at 80 µm, ■ Ultrasonication at 106 µm).

A high freeness will facilitate good drainage in the paper machine and result in minimal blockages, while a high tensile strength will confirm that the fibres were ideally modified and not just severely damaged (Miao *et al.*, 2013:1432). The low freeness of the sonicated pulps was a large drawback. Mechanical refining was effective in increasing the tear and tensile strengths of the fibres without decreasing the freeness at the same rate as ultrasonication.

In summary, at low energy inputs ultrasonication was more effective at developing the tensile strength of fibres. Ultrasonication at amplitude 53 µm had the potential to induce the desired fibre modification effects by using less energy than mechanical refining. The main drawbacks in using ultrasonication were the considerable decrease in pulp freeness, the small effect on tear strength and the inefficiency in modifying the fibres at higher energy inputs. Joseffson (2010) came to the conclusion that

ultrasonication certainly displayed the fibre modification potential, but that it was not as effective as mechanical refining when used on its own.

6.2 Ultrasonication and refining of low-dosage enzymatically treated OCC

In order to address the shortcomings of ultrasonication with regard to freeness and tear strength, an enzyme was added to the pulp and the tests were repeated. Previous studies (Steel & Wolfaardt, 2010:2) found the enzyme, endoglucanase, increased the freeness of the fibres. For the next set of treatments, the recommended dosage of 50 g/t was used to treat the OCC fibres in an attempt to reduce the rate of freeness decline and monitor the tear strength.

6.2.1 Freeness of low-dosage enzymatically treated OCC

The result of the enzymatic pre-treatment on freeness can be seen in Figure 6.6.

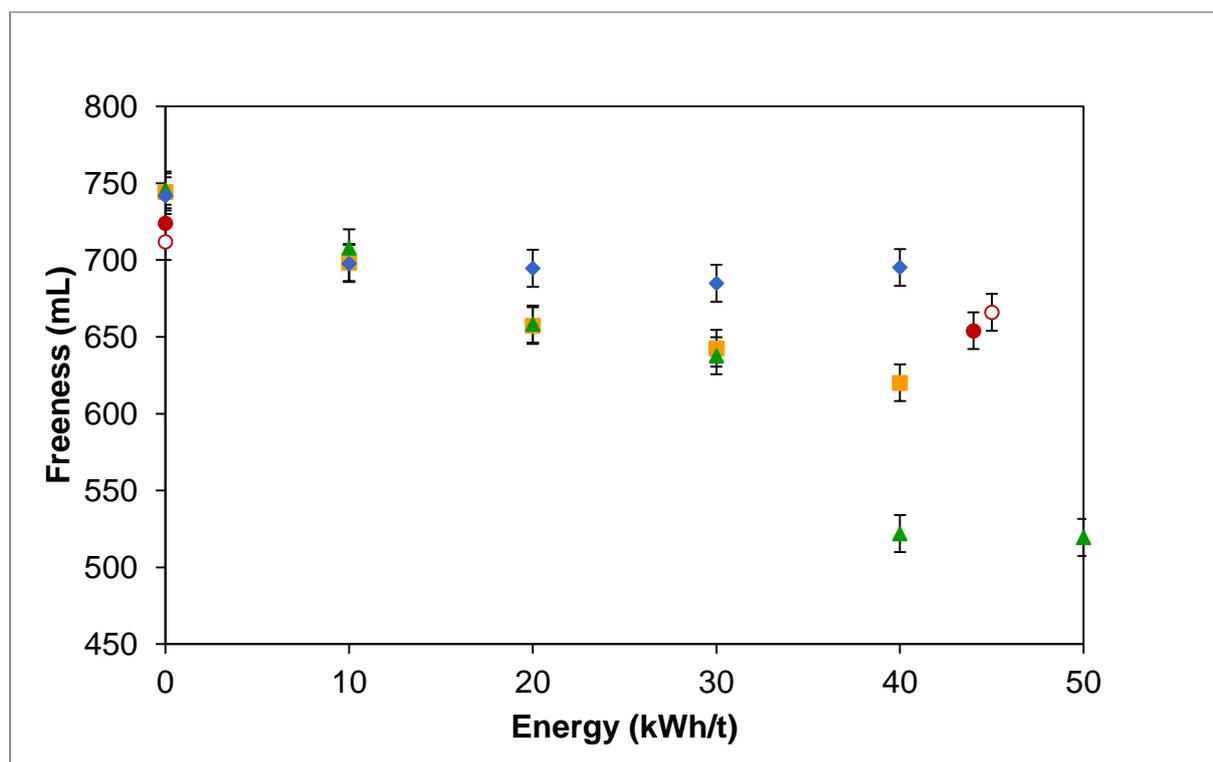


Figure 6.6: OCC pulp freeness after 50 g/t enzymatic pre-treatment and mechanical refining or ultrasonication (○ Untreated mechanically refined, ● Enzymatically treated, mechanically refined, ◆ Enzymatically treated with ultrasonication at 53 μm, ▲ Enzymatically treated with ultrasonication at 80 μm, ■ Enzymatically treated with ultrasonication at 106 μm).

The freeness of the enzymatically treated pulps was significantly higher than that of the untreated pulps in Section 6.1. The freeness of the enzymatically treated sonicated pulp decreased at a considerably lower rate when compared to the untreated sonicated pulp in Section 6.1. The three amplitudes had similar results up to 40 kWh/t, where after a clear difference in freeness could be observed. The 80 μm treatment resulted in the lowest freeness of 522 ± 12 mL at 40 kWh/t, which was explained by the higher broken fibre content (Appendix A3, Tables A3.2, A3.5, A3.8). The reason for this low freeness may be that the combination of a longer treatment time (compared to the 106 μm treatment) and the higher treatment intensity (compared to the 53 μm treatment) resulted in an increased fibre modification effect. The highest freeness of 695 ± 12 mL and lowest rate of freeness decrease were recorded at 53 μm . The total decrease in freeness for OCC pulp between 0 and 40kWh/t was 46 ± 7 mL (6 ± 1 %), recorded at 53 μm . Though the higher amplitude ultrasonication treatments resulted in lower freeness results, the rate of decrease was still lower than for the untreated sonicated pulp (Section 6.1). The slower rate of decrease may be explained by previous studies done by Wolfaardt and Steele (2010) on endoglucanase. They observed a removal of fines and, possibly, colloidal cellulose when applying the recommended dosage of 50 g/t endoglucanase to the pulp. The results for the untreated and enzymatically treated mechanical refining were similar, and no added benefit from the enzymatic pre-treatment was noted.

A comparison of untreated and enzymatically treated sonicated fibres can be seen in Figure 6.7.

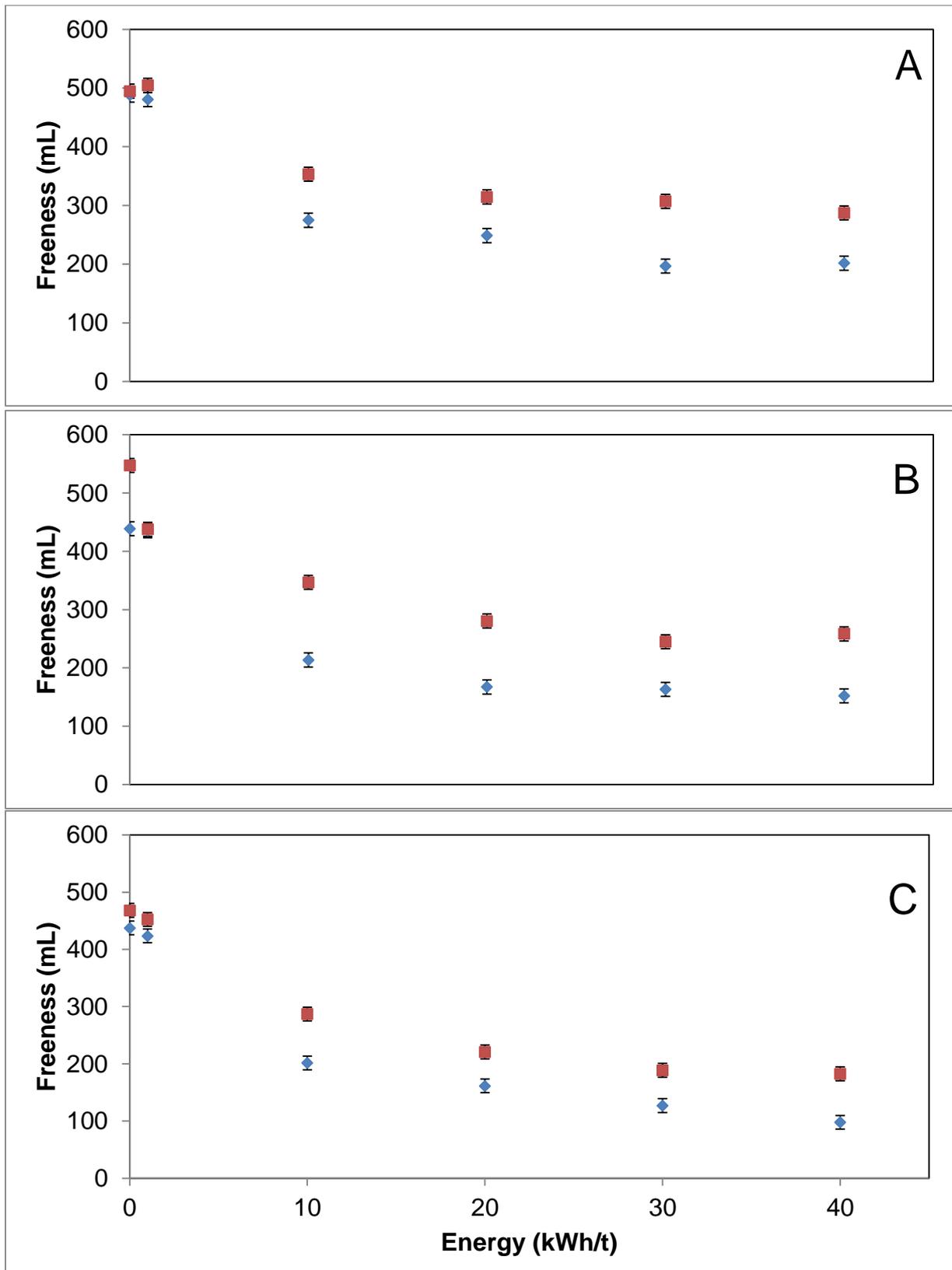


Figure 6.7: Freeness of untreated and enzymatically treated sonicated OCC fibres (106 µm [A], 80 µm [B], 53 µm [C]; ♦- Untreated, ■ 50 g/t Enzymatically treated,).

The enzymatically treated sonicated pulp had a consistently higher freeness value compared to the control experiments. The higher freeness supports the findings of Wolfaardt & Steele (2012) that endoglucanase treatment resulted in slightly higher freeness values due to the removal of fines.

6.2.2 Tensile strength of low-dosage enzymatically treated OCC

Following the freeness tests, the pulp was made into hand-sheets and the first strength tests were conducted. The tensile strength results for the enzymatically treated sonicated pulp can be seen in Figure 6.8.

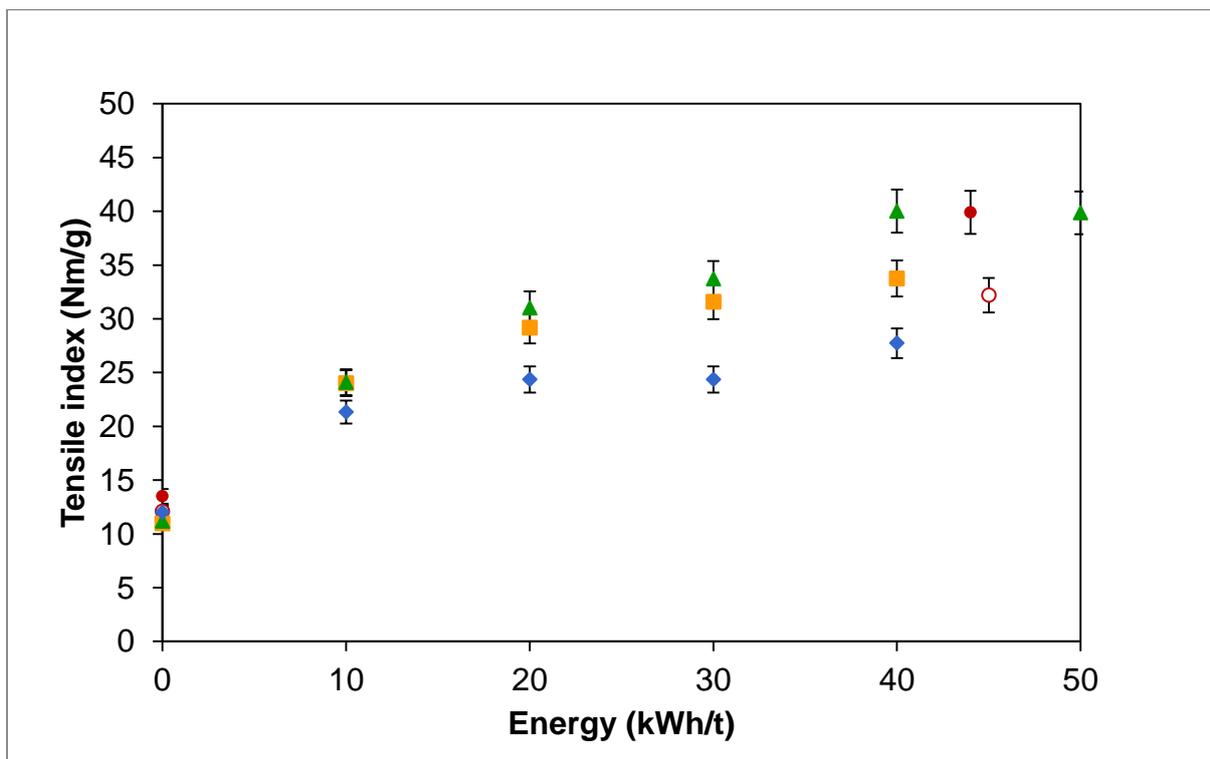


Figure 6.8: Tensile strength results for enzymatically treated OCC fibres after mechanical refining or ultrasonication (○ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

There was a significant increase in tensile strength for all treatments. The enzymatically treated pulp that was sonicated at 80 µm resulted in the highest tensile strength (40.2 ± 2 Nm/g). The initial increases for sonicated pulps were large, but not as significant as with the untreated sonicated pulp in Section 6.1. It seems that the 80 µm ultrasonication treatment resulted in consistently higher tensile strength results

when compared to the other amplitudes. These tensile strength results support the freeness findings in Figure 6.6 and show that the lower freeness indicated a larger fibre modification effect and not necessarily increased fibre damage. The 80 μm result may indicate that the balance between treatment intensity and treatment time was reached as described by Oksanen *et al.* (1997) and Pere *et al.* (1995).

The tensile strength of the enzymatically treated mechanically refined fibres was slightly higher than that of the untreated mechanically refined fibres and similar to the enzymatically treated sonicated fibres. The highest tensile strength achieved by the enzymatically treated and mechanically refined fibres was 39.9 ± 2 Nm/g.

Figure 6.9 compares the tensile strength of the untreated sonicated fibres to the enzymatically treated sonicated fibres.

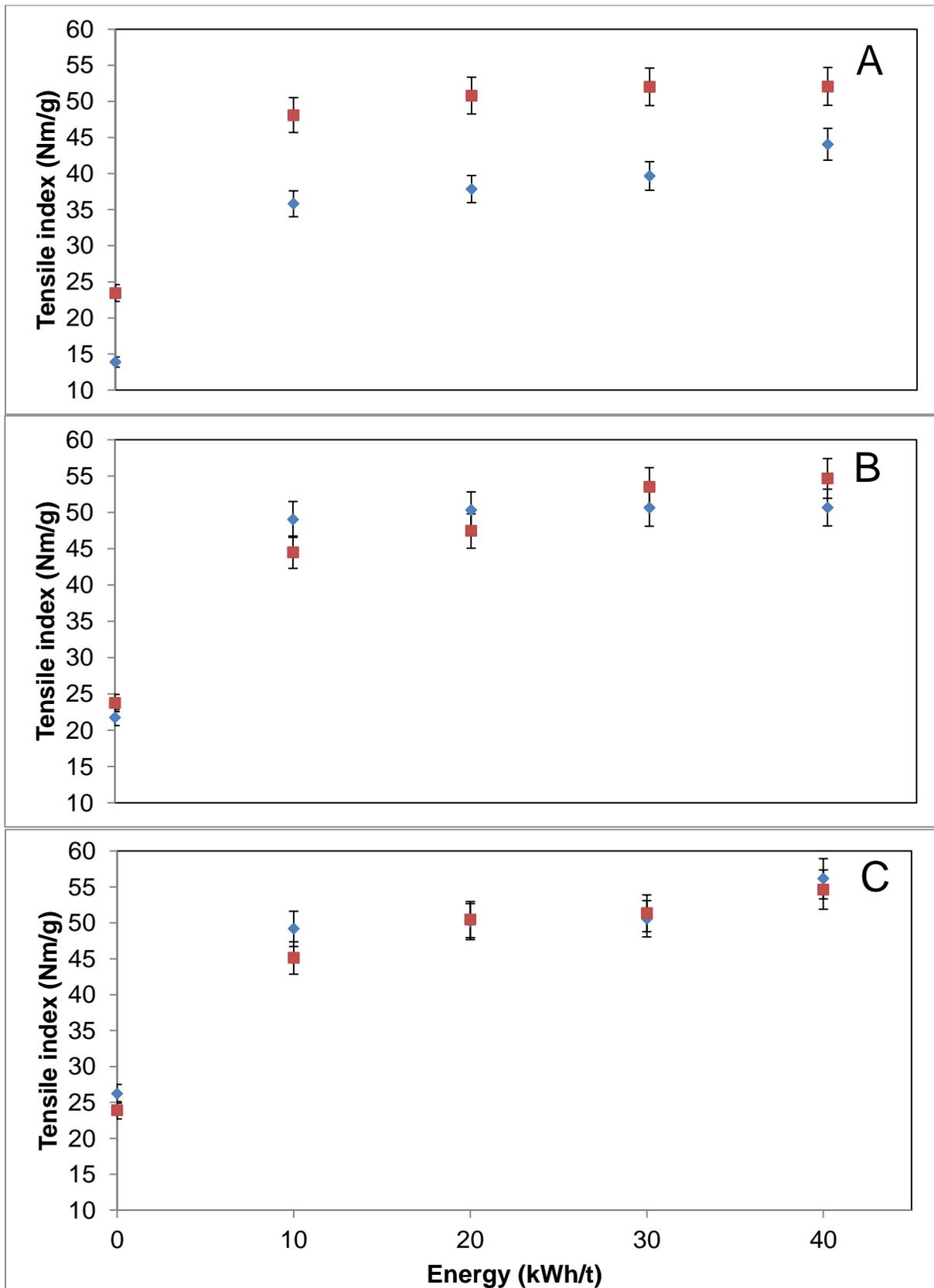


Figure 6.9: Tensile strength of untreated and enzymatically treated sonicated OCC fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; \blacklozenge Untreated, \blacksquare Enzymatically treated at 50 g/t).

The tensile strength of the enzymatically treated fibres was similar to the untreated sonicated fibres at low and medium amplitudes (53 μm and 80 μm), but the enzymatically treated fibres at 106 μm resulted in consistently higher tensile strength values. The higher tensile strength results at 106 μm may be explained by the treatment times: the higher amplitude used 56 % less time (Table 3.2) to reach the same energy levels as the 80 μm treatment, meaning that the enzyme was in contact with the pulp for a shorter time. The effectiveness of the shorter treatment time may be explained by Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lomboy *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002) and Sun *et al.* (2002), who found that it might be detrimental to fibres to be subjected to prolonged ultrasonication treatment times.

6.2.3 Tear strength of low-dosage enzymatically treated OCC

The tear strength of the enzymatically treated fibres can be seen in Figure 6.10.

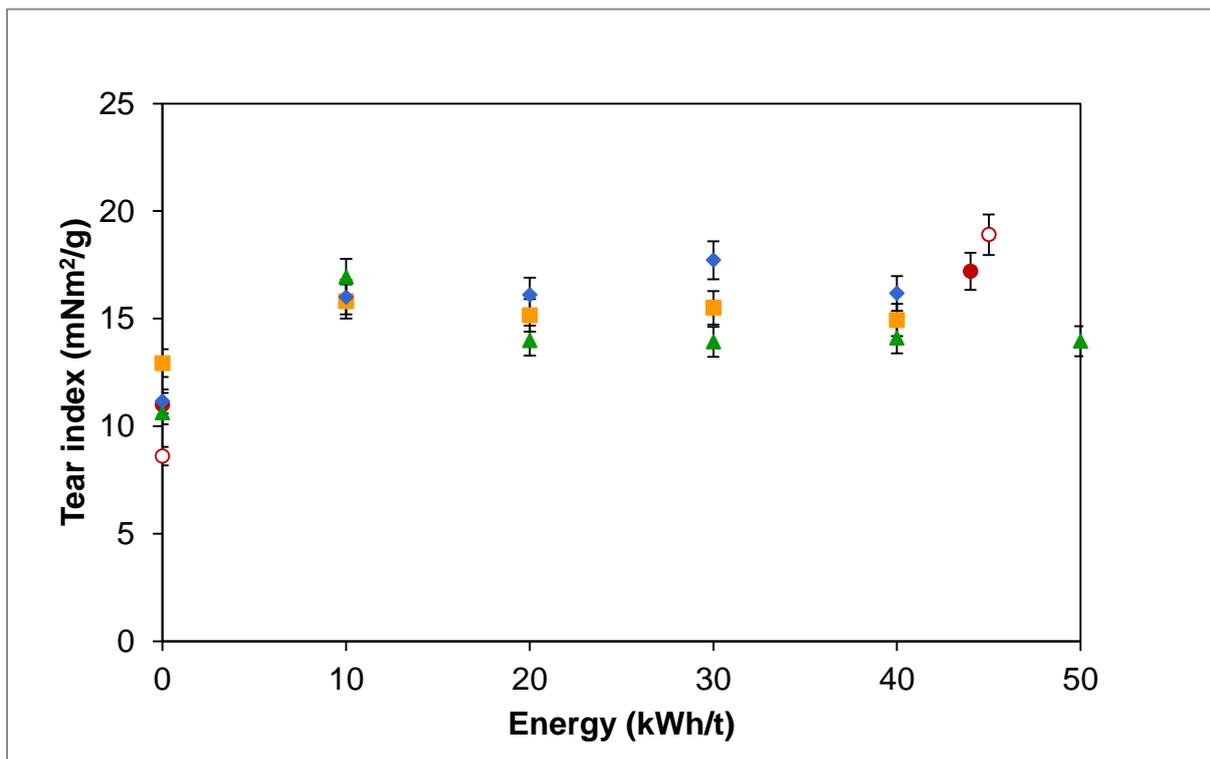


Figure 6.10: Tear strength results for enzymatically treated OCC fibres after mechanical refining or ultrasonication (○ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The tear strength of the enzymatically treated experiments increased more than the untreated experiments in Section 6.1. There was a large initial increase for the sonicated fibres, where after the tear strength remained relatively constant around the 15 mNm²/g mark. The morphology results indicated that the fibre length was similar between the different amplitude treatments (Appendix A3, Tables A3.2, A3.5, A3.8). It seemed that the mechanically refined fibres and sonicated fibres presented similar results, with the enzymatically treated and mechanically refined fibres resulting in slightly higher tear strength values at 45 kWh/t. It appeared that ultrasonication at 80 µm could develop the tensile strength of the fibres, but only at the cost of not developing the tear strength. This result was the same as the tear strength results cited in Section 6.1 and may indicate that ultrasonication was efficient in collapsing and fibrillating the fibres, but it was too harsh on the shorter fibres, and may have shortened them further. The shortened fibres result in decreased tear strength.

A comparison between the tear strength of untreated sonicated fibres and the enzymatically treated sonicated fibres can be seen in Figure 6.11.

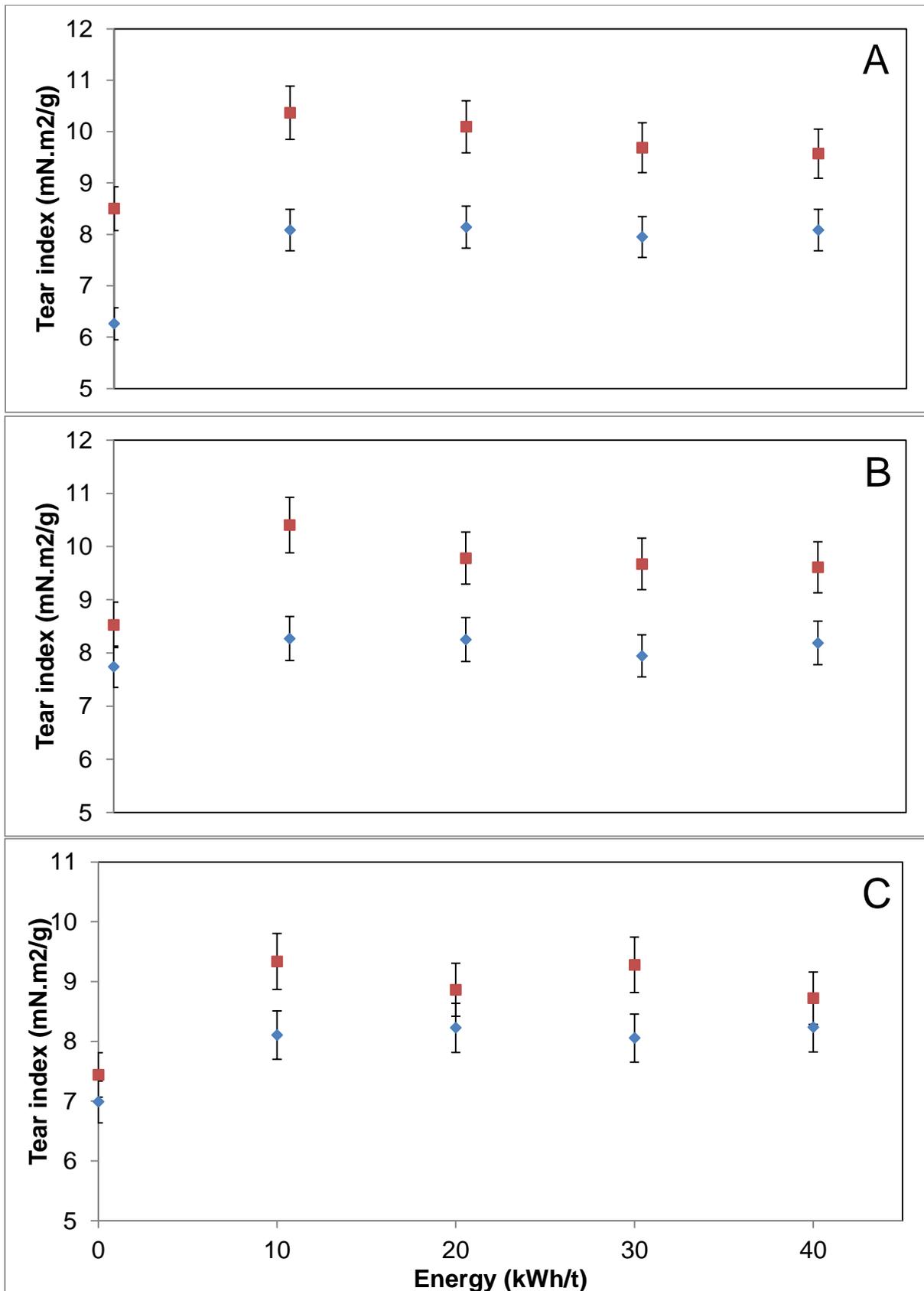


Figure 6.11: Tear strength of untreated and enzymatically treated sonicated OCC fibres. (106 µm [A], 80 µm [B], 53 µm [C]; ♦ Untreated, ■ Enzymatically treated at 50 g/t).

When comparing the tear strength of the untreated sonicated fibres to that of the 50 g/t enzymatically treated fibres, one can see that the enzymatic pre-treatment seems to result in consistently higher tear strength values. The difference between tear strength for the enzymatically treated fibres and untreated fibres was more apparent at higher amplitudes, which may support the tensile strength findings – that a longer treatment time may have a degrading effect on the fibres.

6.2.4 Tear strength versus tensile strength relationship of low-dosage enzymatically treated OCC

In Figure 6.12 the tear and tensile strength relationship can be seen.

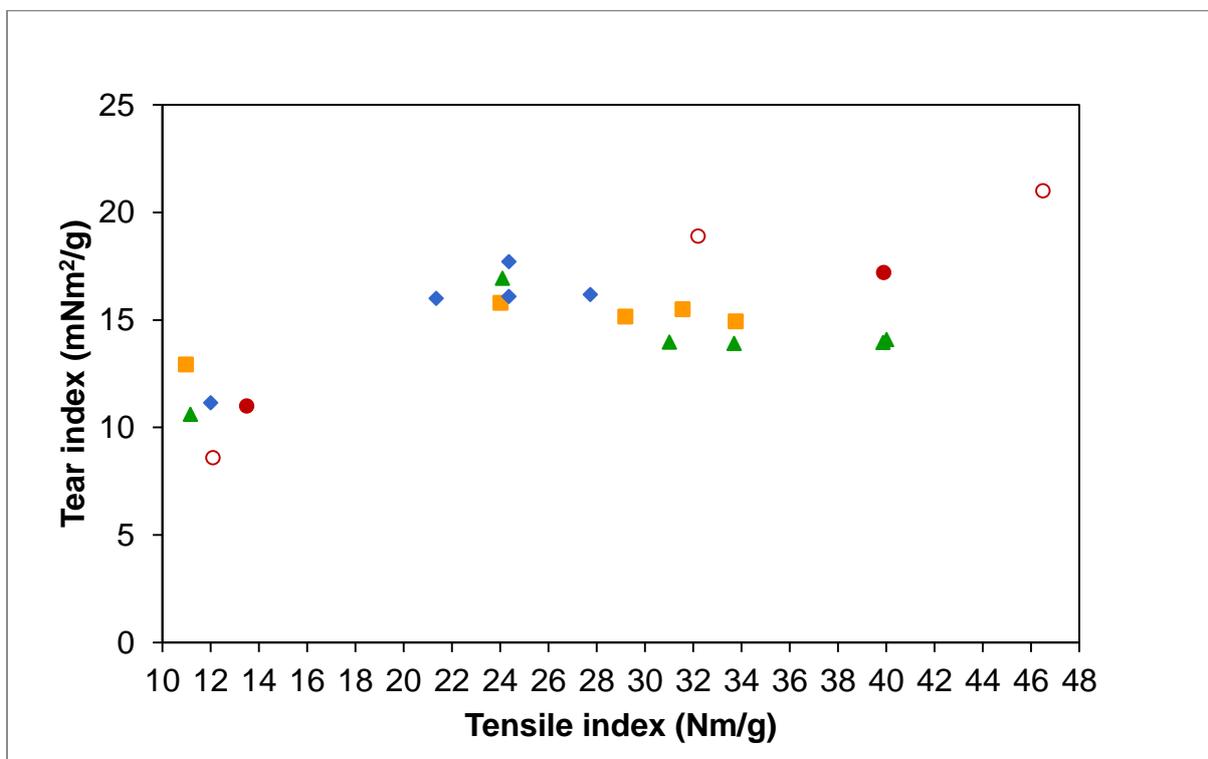


Figure 6.12: Tear and tensile strength relationship of 50 g/t enzymatically treated fibres (○ Enzymatically treated and mechanically refined, ● Mechanical refining, ◆ Enzymatically treated ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

In all ultrasonication cases there was an increase in the tear index, with a comparable increase in the tensile index. However, when compared to mechanical refining, the tear and tensile strength relationship could not be improved to the same extent as by ultrasonication. Mechanical refining had a seemingly linear effect on the relationship at lower tensile strengths, before it reached an equilibrium point. The enzymatically

treated, mechanically refined fibres showed a constant increase in the relationship, but it was lower than the untreated mechanically refined fibres. Ultrasonication at 106 μm displayed positive results at tensile indices of $20 \pm 1 \text{ Nm/g}$ and $36 \pm 1.8 \text{ Nm/g}$, with corresponding tear indices of $4 \pm 0.2 \text{ mNm}^2/\text{g}$ and $8.1 \pm 0.3 \text{ mNm}^2/\text{g}$ respectively. The relationship of ultrasonication at 53 μm was similar to the mechanically refined samples, but reached a maximum at a tensile strength of $35 \pm 1.5 \text{ Nm/g}$.

6.2.5 Freeness and tensile strength relationship of low-dosage enzymatically treated OCC

The tensile strength and freeness relationship of the enzymatically treated fibres can be seen in Figure 6.13.

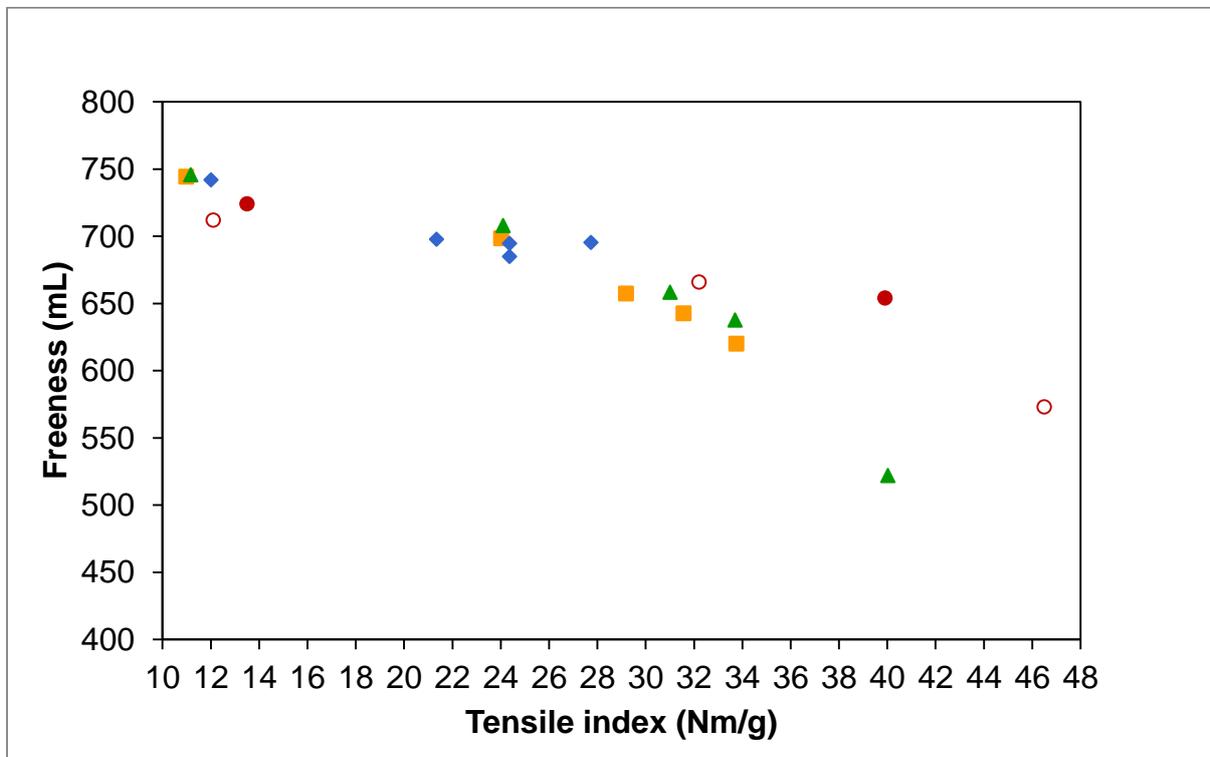


Figure 6.13: Freeness and tensile strength relationship of 50 g/t enzymatically treated OCC fibres (○ Enzymatically treated and mechanically refined, ● Mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

In all cases the tensile strength of the fibres could not be increased without losing freeness. There was a higher loss of freeness during ultrasonication than during mechanical refining. This graph shows that ultrasonication and enzymatic pre-

treatment combined could not develop the tensile strength of the fibres without negatively impacting the freeness.

In summary, the combination of ultrasonication and enzymatic pre-treatment was successful in increasing the freeness of the pulp (regardless of ultrasonication amplitude) and also showed promise in the development of the strength properties. It seemed that the combination of high-amplitude ultrasonication and enzymatic pre-treatment was the most effective in developing the strength properties.

6.3 Ultrasonication and refining of high-dosage enzymatically treated OCC

Due to the better strength and freeness results achieved by the low enzymatic dosage, it was decided to investigate the effect of high enzymatic dosage on the freeness and strength properties of the sonicated pulp. An endoglucanase dosage of 200 g/t was added to the pulp as a pre-treatment.

6.3.1 Freeness of high-dosage enzymatically treated OCC

The same treatment procedure as with the 50 g/t enzymatic pre-treatment was followed for the 200 g/t dosage enzymatic pre-treatment, and the freeness results can be seen in Figure 6.14.

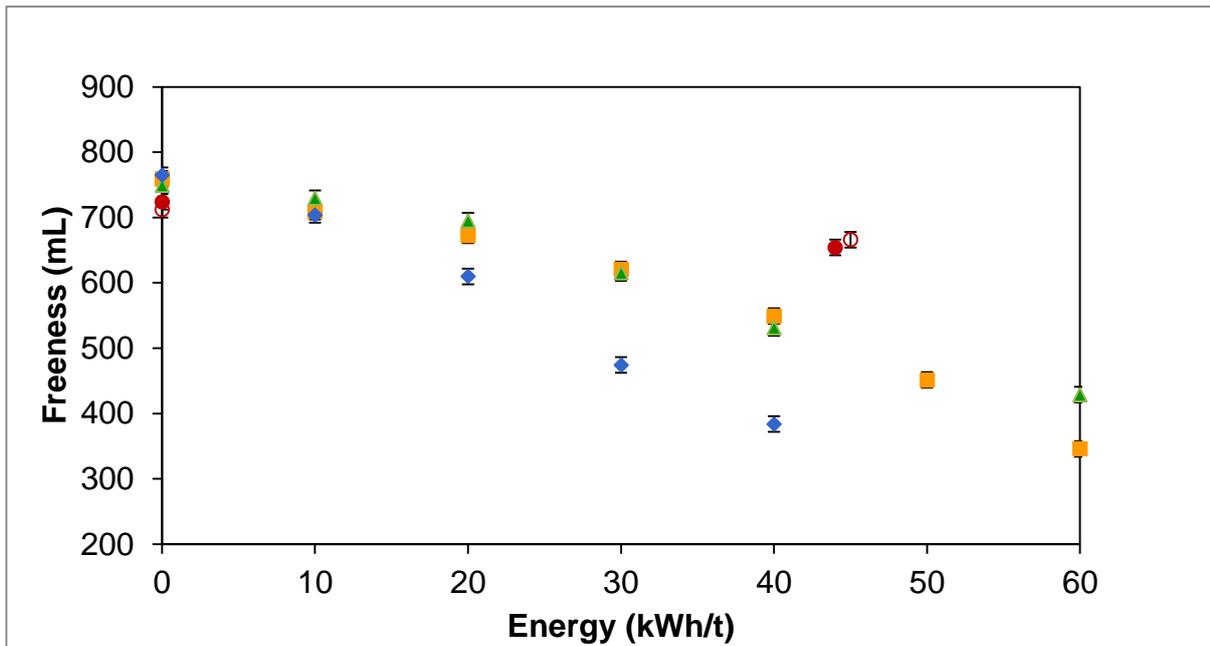


Figure 6.14: OCC pulp freeness after 200 g/t enzymatic pre-treatment at different energy levels with mechanical refining and ultrasonication respectively (○ Untreated mechanically refined, ● Enzymatically treated and mechanically refined, ◆ Enzymatically treated ultrasonication at 53 μm, ▲ Enzymatically treated ultrasonication at 80 μm, ■ Enzymatically treated ultrasonication at 106 μm).

An almost linear decrease can be observed for all ultrasonication treatments, and compared to the low enzymatic dosage samples, the decrease was more substantial. The reason for this significant decrease may be because the higher enzyme dosage resulted in a harsher treatment than the low dosage. It was apparent that the high-amplitude ultrasonication caused the lowest rate of freeness decline, while the low amplitudes resulted in a faster rate of freeness decline. It seemed that the fines content was slightly higher with the low amplitude ultrasonication when compared to the higher amplitude ultrasonication treatments (Appendix A3, Tables A3.3, A3.6, A3.9). The difference the various amplitudes made to the freeness results can be explained by the treatment times: the longer treatment times required by the low-amplitude ultrasonication seemed to have a detrimental effect on the pulp due to the prolonged enzymatic pre-treatment time. This result supports the findings of Huang *et al.* 2007; Haung *et al.*, 2011; Montalbo-Lomboy *et al.*, 2010; Nikolic *et al.*, 2010; Sun & Tomkinson, 2002; and Sun *et al.*, 2002.

The freeness comparison of sonicated untreated, 50 g/t and 200 g/t enzymatic pre-treatment is presented in Figure 6.15.

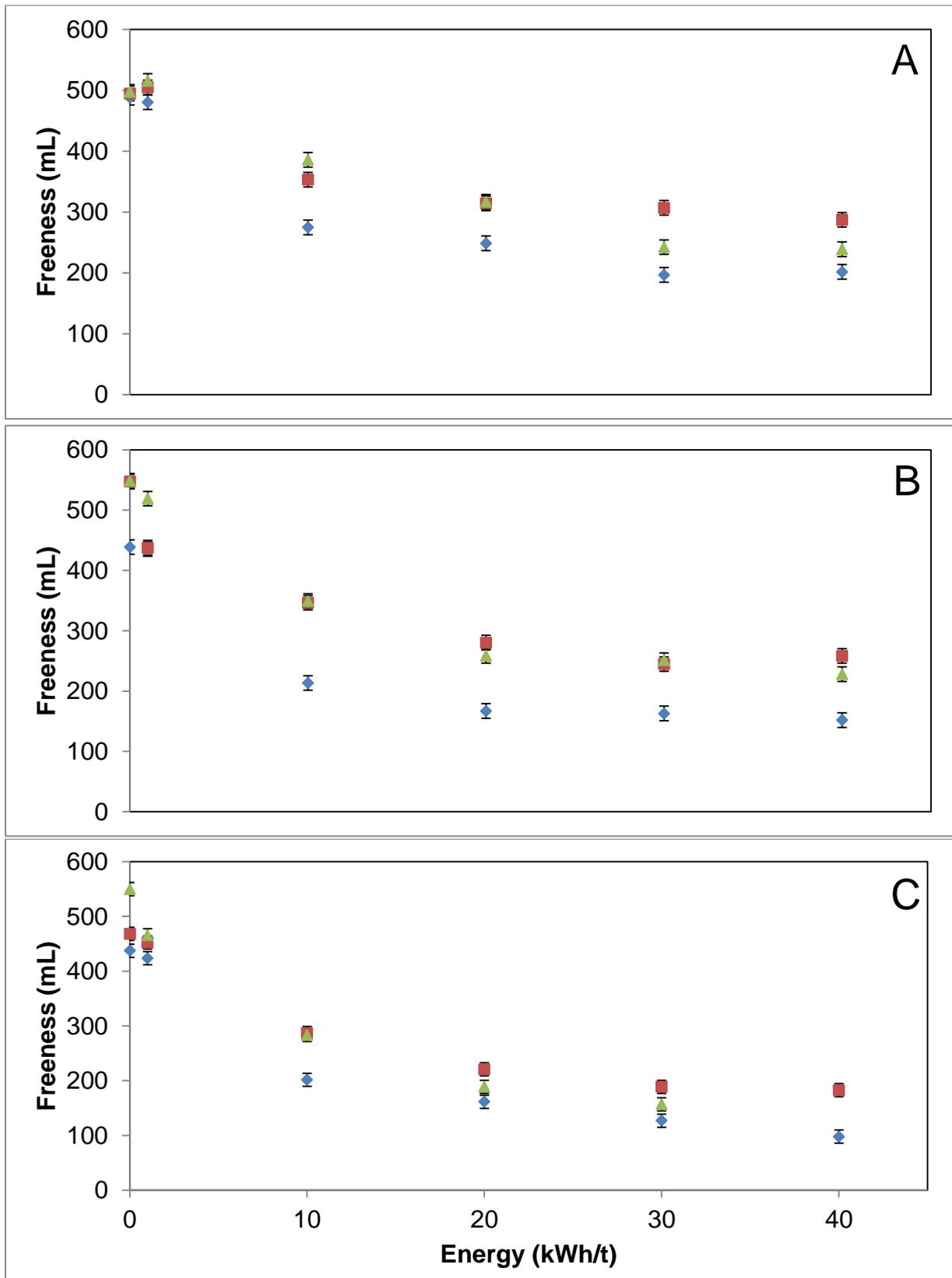


Figure 6.15: Freeness comparison of untreated and enzymatically treated sonicated OCC fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; (♦ Untreated, ■ Enzymatically treated at 50 g/t, ▲ Enzymatically treated at 200 g/t).

When comparing the freeness of the ultrasonication control, 50 g/t enzymatic pre-treatment and 200 g/t enzymatic pre-treatment experiments, the results were very similar. The exception was the 80 μm amplitude experiments, where the untreated pulp resulted in notably lower freeness values. It seemed that enzymatic dosage had very little effect on the freeness of the pulp, but that enzymatically treated pulp generally resulted in higher freeness values. It also seemed that the enzymatic pre-treatment time was the variable that resulted in the most significant freeness values, again supporting Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lombay *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002). This also explained why the different enzymatic dosages had little effect on the freeness.

6.3.2 Tensile strength of high-dosage enzymatically treated OCC

The tensile strength results of the 200 g/t enzymatic pre-treatment can be seen in Figure 6.16.

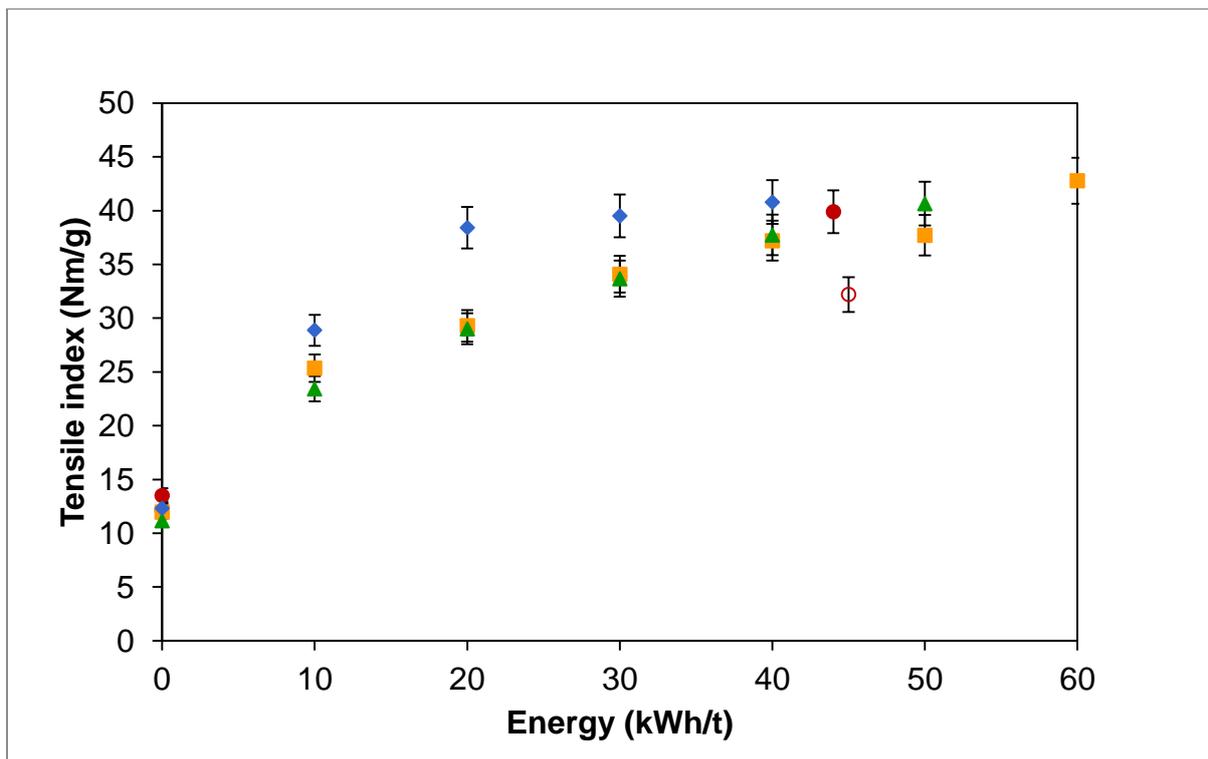


Figure 6.16: Tensile strength results of 200 g/t enzymatically treated OCC fibres after mechanical refining and ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm).

The 200 g/t enzymatic-ultrasonication treatment increased the tensile strength of the fibres rapidly at lower energy inputs (0 to 20 kWh/t), where after the tensile strength reached a plateau. It was also noted that the tensile strength of the enzymatically treated fibres was higher than the untreated mechanically refined fibres. The 53 μm 200 g/t enzymatic ultrasonication resulted in the highest tensile strength of 40.8 ± 2 Nm/g. Ultrasonication at higher amplitudes resulted in very similar tensile strength results and was constantly lower than the tensile strength of the 53 μm treatment. The fibre morphology indicated similar fibrillation between the amplitudes with slightly higher fines content in the 53 μm treatment (Appendix A3, Tables A3.3, A3.6, A3.9). The reason may be that the longer, lower-intensity treatment combined with the higher enzymatic pre-treatment reached the balance of treatment time and intensity as described by Oksanen *et al.* (1997) and Pere *et al.* (1995).

A comparison of the tensile strength of sonicated fibres at different enzymatic dosage treatments can be seen in Figure 6.17.

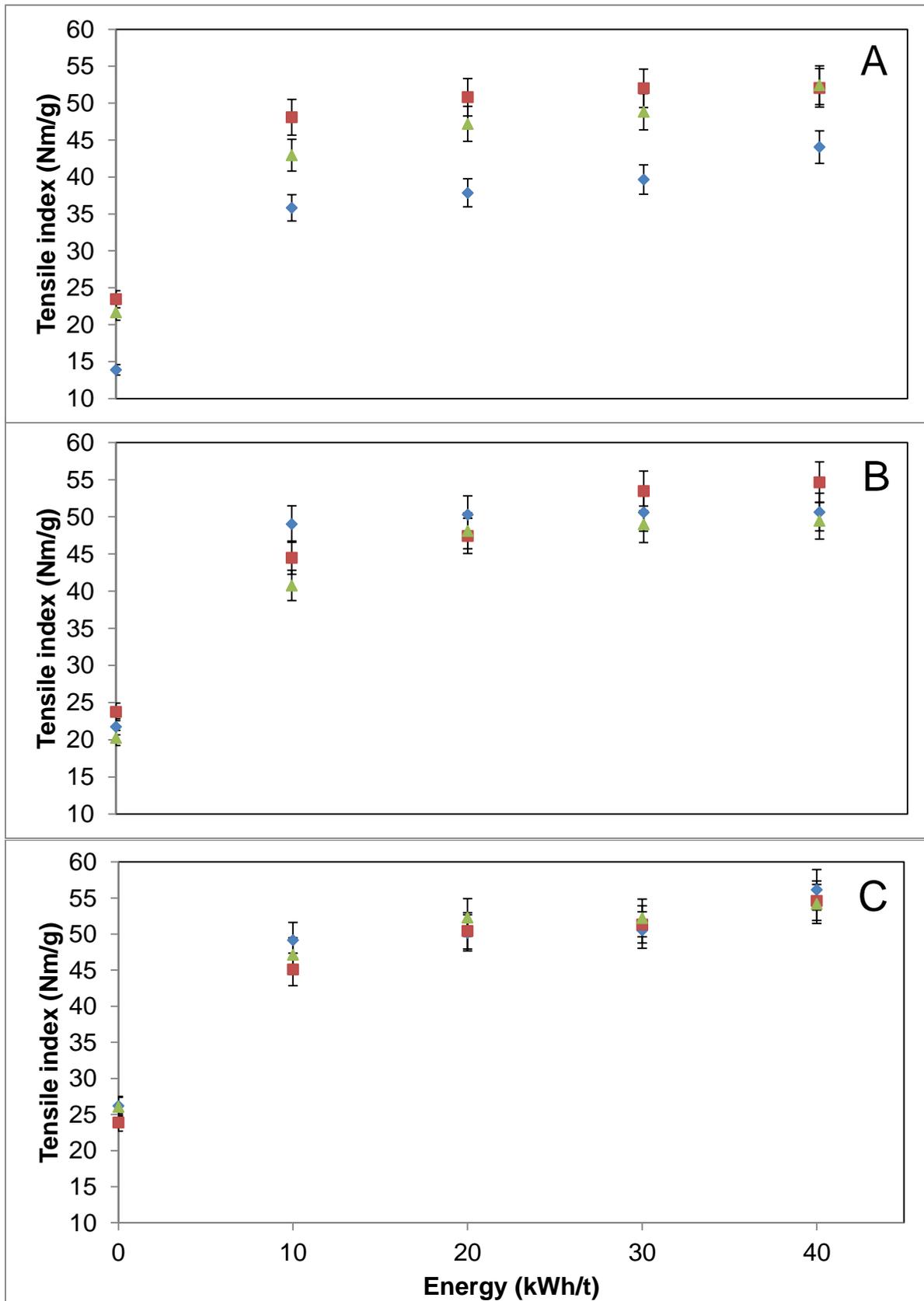


Figure 6.17: Tensile strength comparison of untreated and enzymatically treated sonicated OCC fibres at different amplitudes (106 μm [A], 80 μm [B], 53 μm [C]; ♦ Untreated, ■ Enzymatically treated at 50 g/t, ▲ Enzymatically treated at 200 g/t).

There was very little change when comparing the tensile strength of the different sonicated enzymatic dosages, but the tensile strength of the enzymatically treated fibres was generally higher than that of the control. It did seem, however, that the enzymatic dosages had very little effect on the tensile strength. It also seemed that the treatment time was the variable with the largest effect, which supports Oksanen *et al.* (1997) and Pere *et al.* (1995), who stated that ultrasonication and enzymatic pre-treatment had a positive modification effect on the fibres for a finite period of time.

6.3.3 Tear strength of high-dosage enzymatically treated OCC

The tear strength results for the 200 g/t enzymatically treated pulp can be seen in Figure 6.18.

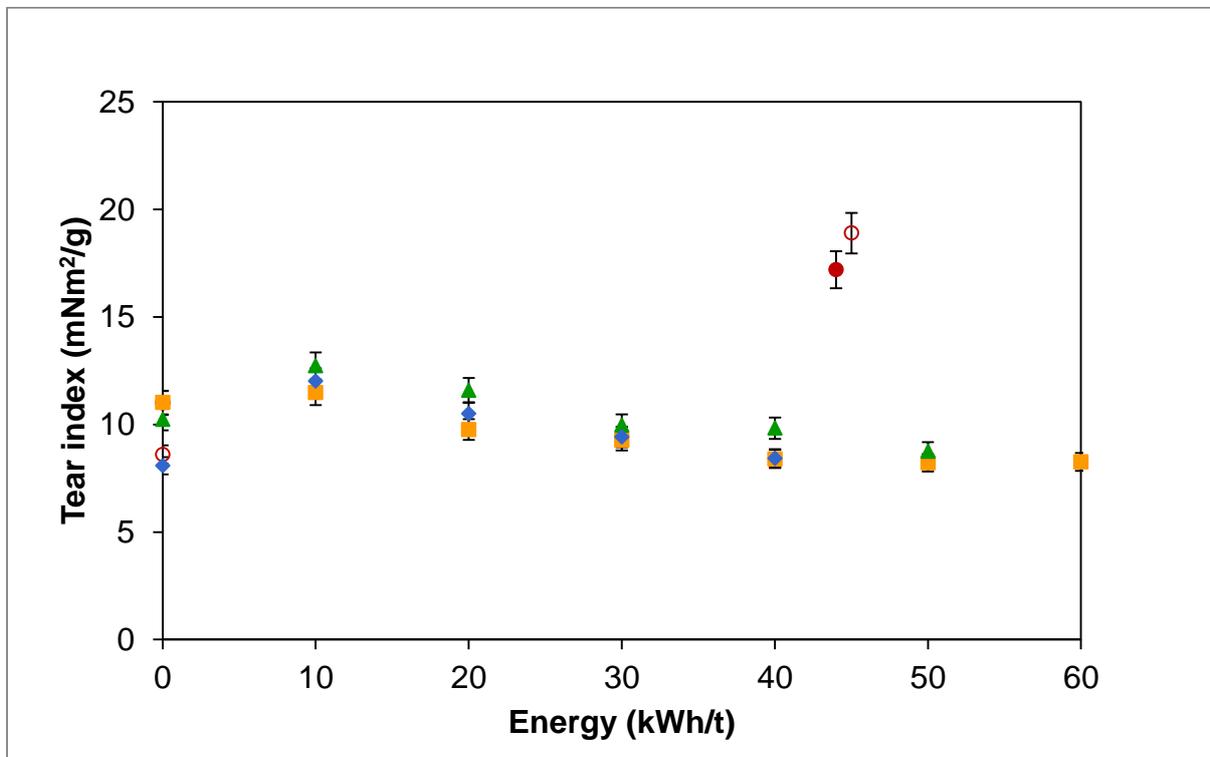


Figure 6.18: Tear strength results for 200 g/t enzymatically treated OCC fibres after mechanical refining and ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated with mechanical refining, ◆ Enzymatically treated ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

The tear strength seemed to be affected negatively by ultrasonication and high enzymatic dosage. There was a clear initial increase in tear strength, where after the decline was almost linear. The highest tear strength was achieved at 10 kWh/t by the

80 μm ultrasonication treatment, but it was significantly lower than the mechanically refined treatments. This supports what can be seen in Chapter 4, where the hardwood fibres displayed similar results. The explanation for the low tear strength may be that the higher enzymatic dosage causes the sonicated pulp to reach its maximum point of modification faster, which could support the findings of Oksanen *et al.* (1997) and Josefsson (2006). Ultrasonication at higher amplitudes (80 μm and 106 μm) produced higher tear strength results compared to ultrasonication at a low amplitude.

In Figure 6.19, the comparison of tear strengths for different enzymatic dosages can be seen.

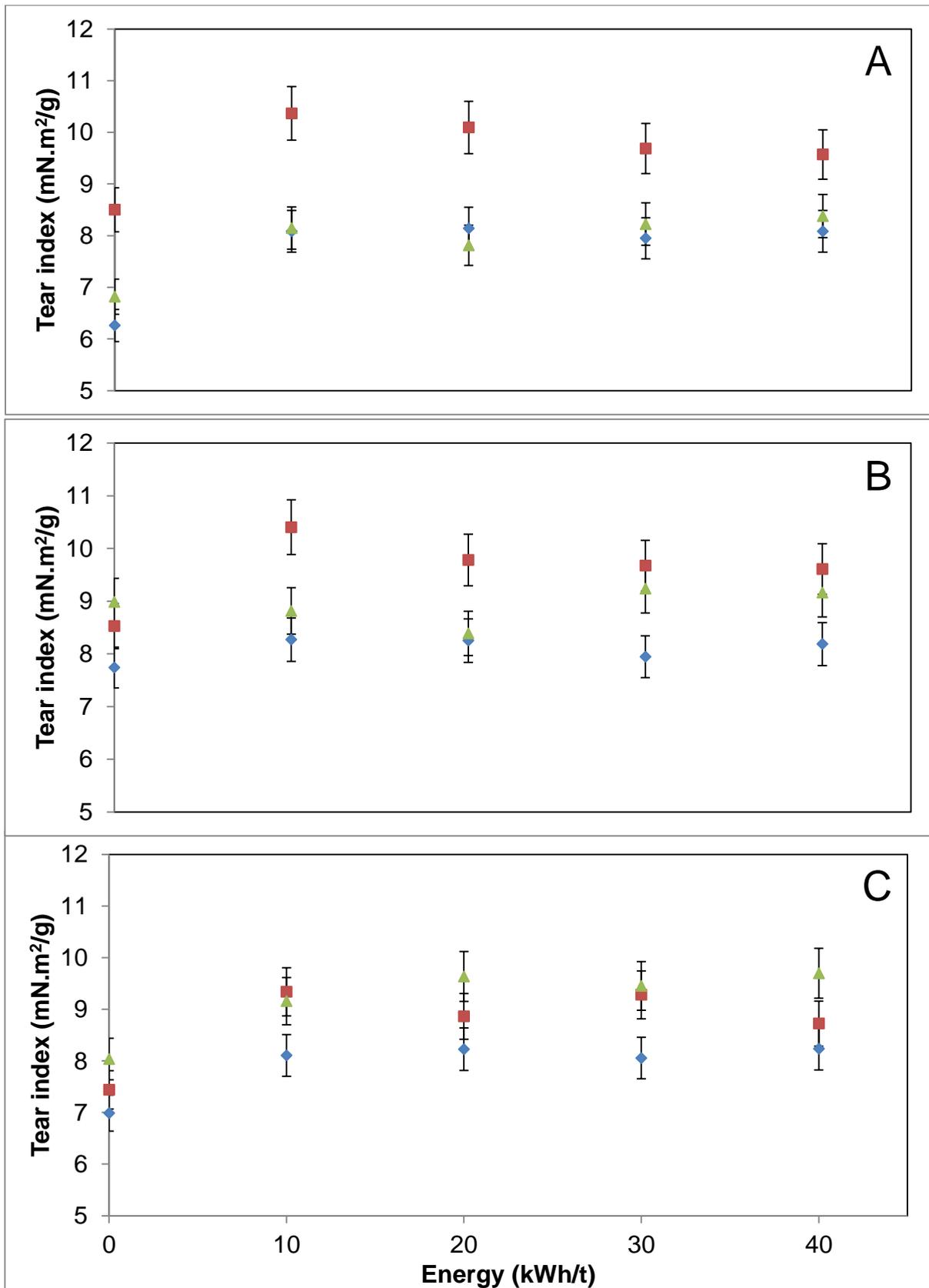


Figure 6.19: Tear strength of untreated and enzymatically treated and sonicated OCC fibres at different amplitudes (106 µm [A], 80 µm [B], 53 µm [C]; ♦ Untreated, ■ Enzymatically treated [50 g/t], ▲ Enzymatically treated [200 g/t]).

When comparing the different enzymatic dosages and ultrasonication, the results were similar at the 80 μm and 53 μm treatments. The fibre morphology indicated similar fibre lengths at the different enzyme dosages, which explained the similar tear strength results (Appendix A3, Tables A3.1-A3.9). It seemed that enzymatic dosage had very little effect on the tear strength, but that different amplitudes seemed to cause different results. The higher amplitudes resulted in higher tear strengths, meaning that a shorter time was needed to get the optimum tear strength results through ultrasonication. This may support the findings of Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lomboy *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002).

6.3.4 Tear and tensile strength relationship of high-dosage enzymatically treated OCC

The tear and tensile strength relationship of the 200 g/t enzymatically treated pulp can be seen in Figure 6.20.

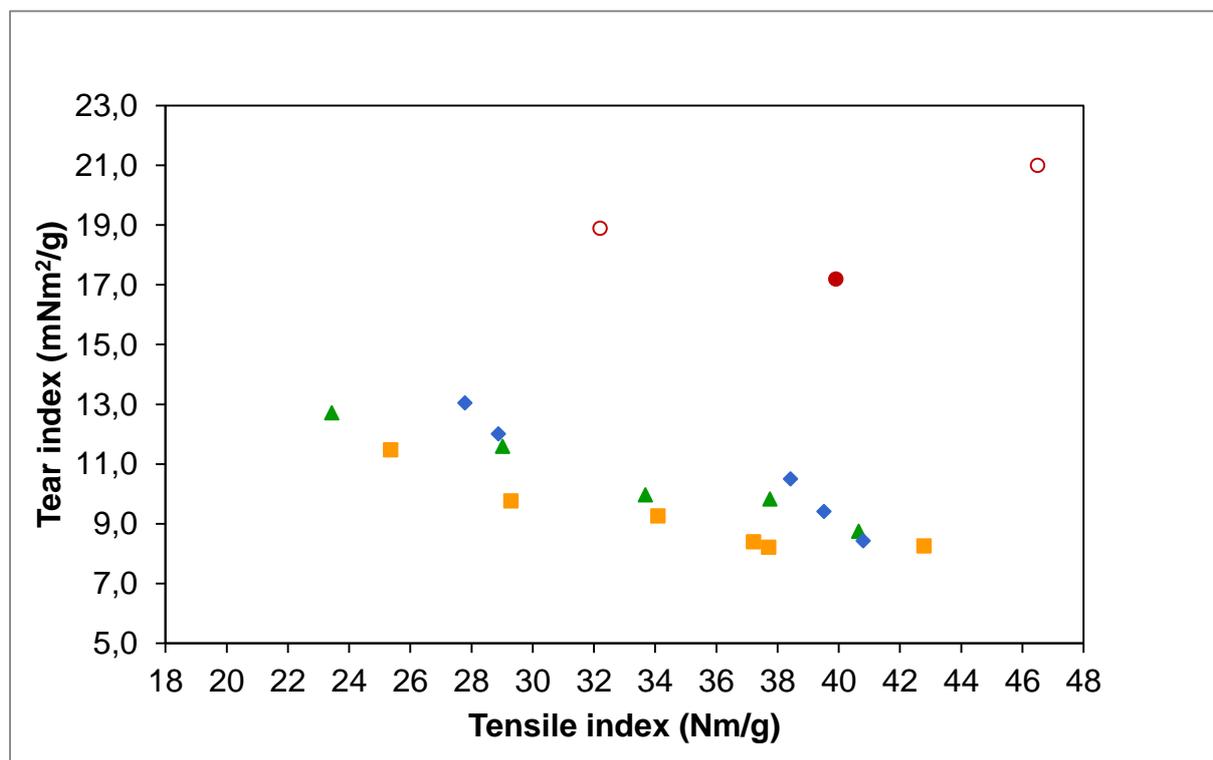


Figure 6.20: Tear and tensile strength relationship of 200 g/t enzymatically treated OCC fibres after mechanical refining or ultrasonication (● Untreated mechanical refining, ○ Enzymatically treated with mechanical refining, ◆ Enzymatically treated ultrasonication at 53 μm , ▲ Enzymatically treated ultrasonication at 80 μm , ■ Enzymatically treated ultrasonication at 106 μm .)

The mechanically refined experiment resulted in the highest tear-tensile strength relationship, and it seemed that the tensile strength of the sonicated paper could not be developed without negatively affecting the tear strength. The same trend could be noted for all amplitudes, but it seemed that the high-amplitude treatment resulted in the highest tensile results. The highest tear strength results were achieved by low-amplitude ultrasonication.

6.3.5 Freeness and tensile strength relationship of high-dosage enzymatically treated OCC

The freeness and tensile strength relationship is presented in Figure 6.21.

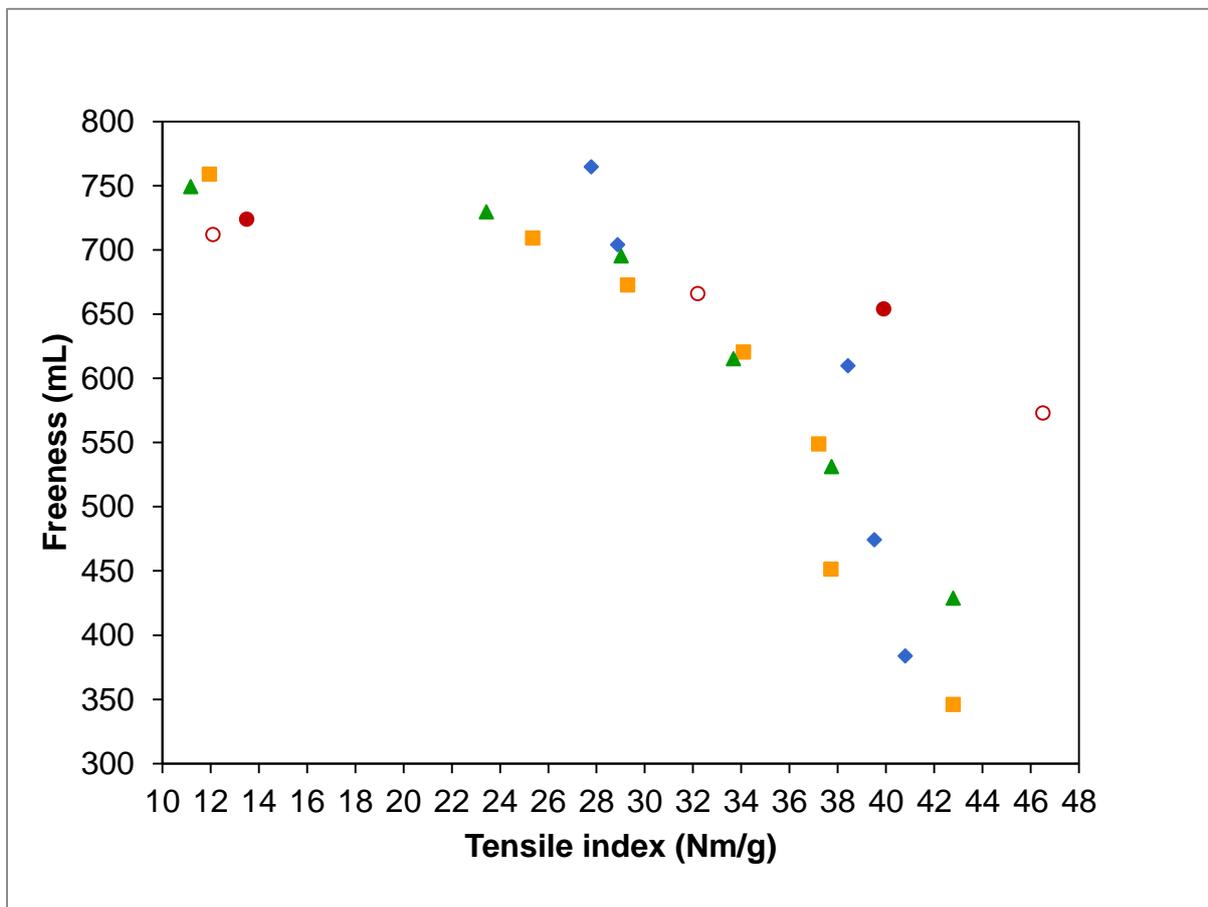


Figure 6.21: OCC pulp freeness and tensile strength relationship of 200 g/t enzymatically treated fibres after mechanical refining or ultrasonication (■ Untreated mechanical refining, ● Enzymatically treated mechanical refining, ◆ Ultrasonication at 53 µm, ▲ Enzymatically treated ultrasonication at 80 µm, ■ Enzymatically treated ultrasonication at 106 µm).

The freeness and tensile strength relationship was similar for the mechanically refined and sonicated fibres, but the mechanically refined pulp resulted in the highest tensile strength without significant reduction of freeness.

In summary, the increased enzymatic dosage did not result in any added strength benefit, and there seemed to be little difference in the freeness of the low-dosage and high-dosage experiments.

6.4 Ultrasonication and refining of OCC followed by 100 g/t enzymatic treatment

The 100 g/t enzymatic post-treatment was done as described in Chapter 3, followed by the same pulp and strength tests as with the other hardwood experiments. The selected ultrasonication amplitude was 53 μm , based on the more consistently good results obtained throughout the control, 50 g/t and 200 g/t experiments.

6.4.1 Freeness of OCC followed by 100 g/t enzymatic treatment

The freeness of the 100 g/t enzymatically post-treated pulp can be seen in Figure 6.22.

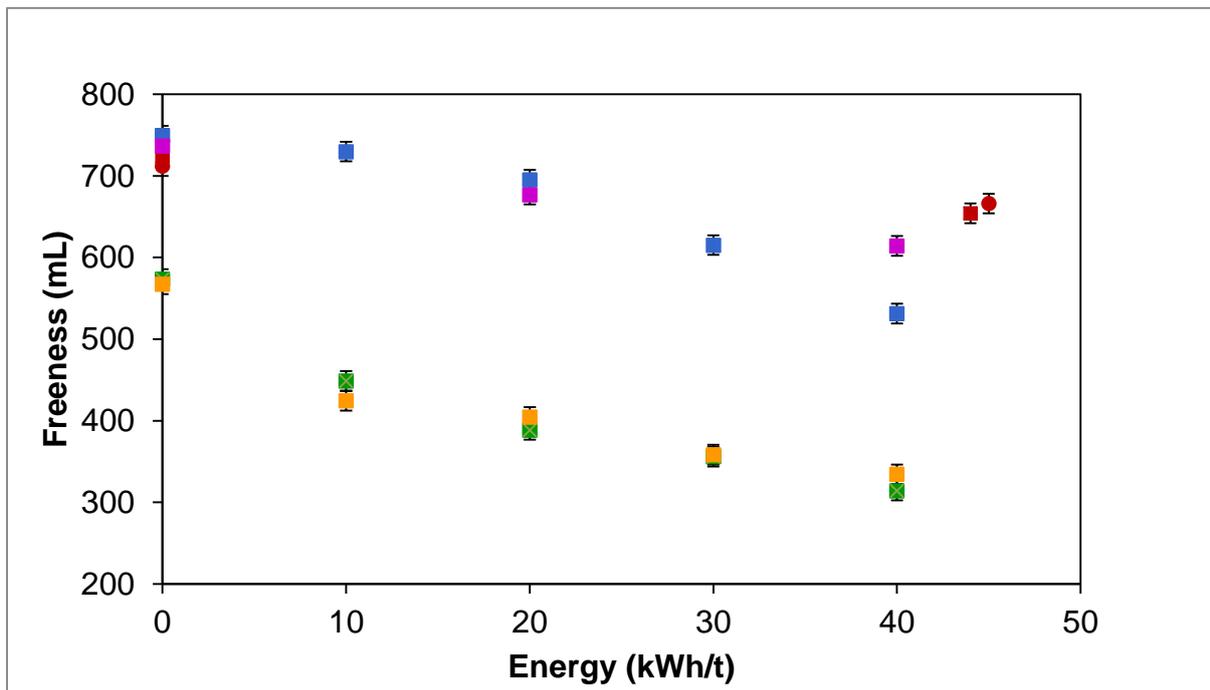


Figure 6.22: OCC freeness comparison of all ultrasonication experiments at 53 μm (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Enzymatically treated and mechanically refined [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The freeness of the sonicated pulp that was post-treated with 100 g/t of enzymes was similar to both mechanically refined pulps (enzymatically treated and untreated) and the sonicated pulp that was treated with a high dosage of enzymes (200 g/t). As explained in Chapter 4.4.1 and Chapter 5.5.1, it was suspected that the enzyme was not successfully deactivated by ultrasonication, as previously believed, leading to a longer enzymatic pre-treatment time. Therefore, based on previous studies by Huang *et al.* (2007), Haung *et al.* (2011), Montalbo-Lomboy *et al.* (2010), Nikolic *et al.* (2010), Sun & Tomkinson (2002) and Sun *et al.* (2002), it was expected that the freeness results from the enzymatic post-treatment would be significantly higher than those of the enzymatic pre-treatments. The higher freeness could mean that the effect of the enzymatic post-treatment was less than the control, 50 g/t and 200 g/t enzymatic pre-treatments. The higher freeness could also mean that the combination of the shorter enzymatic contact time and enzymatic post-treatment were effective in removing colloidal cellulose.

6.4.2 Tensile strength of OCC followed by 100 g/t enzymatic treatment

The tensile strength of the 100 g/t enzymatically post-treated pulp can be seen in Figure 6.3.

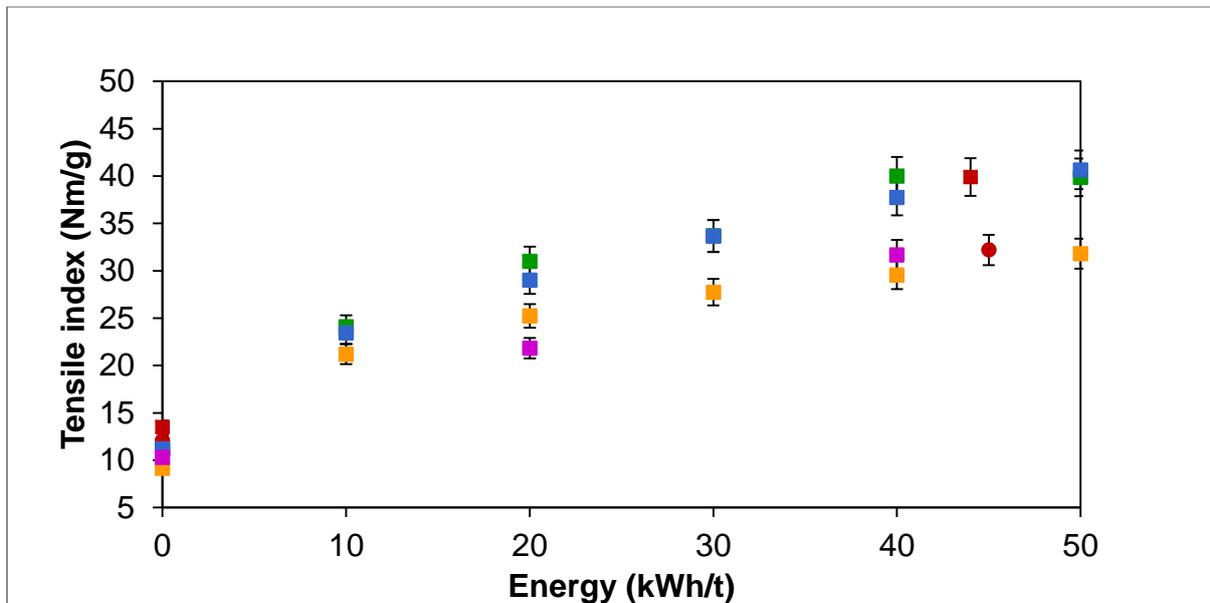


Figure 6:23 OCC tensile strength of all ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining. (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined and enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control.)

The enzymatically post-treated sample had the overall lowest tensile strength, but it was similar to the ultrasonication control treatment, which was expected – seeing that the enzymes were in contact with the pulp for a shorter period of time compared to the enzymatic pre-treatments. The shorter contact time could mean that the effect of the enzymes was so small, it was physically immeasurable. The low tensile strength values also proved that the higher freeness indicated a lower level of fibre modification, and not a more effective method of removing colloidal cellulose.

6.4.3 Tear strength of OCC followed by 100 g/t enzymatic treatment

The tear strength of the 100 g/t enzymatic post-treatment is presented in Figure 6.24.

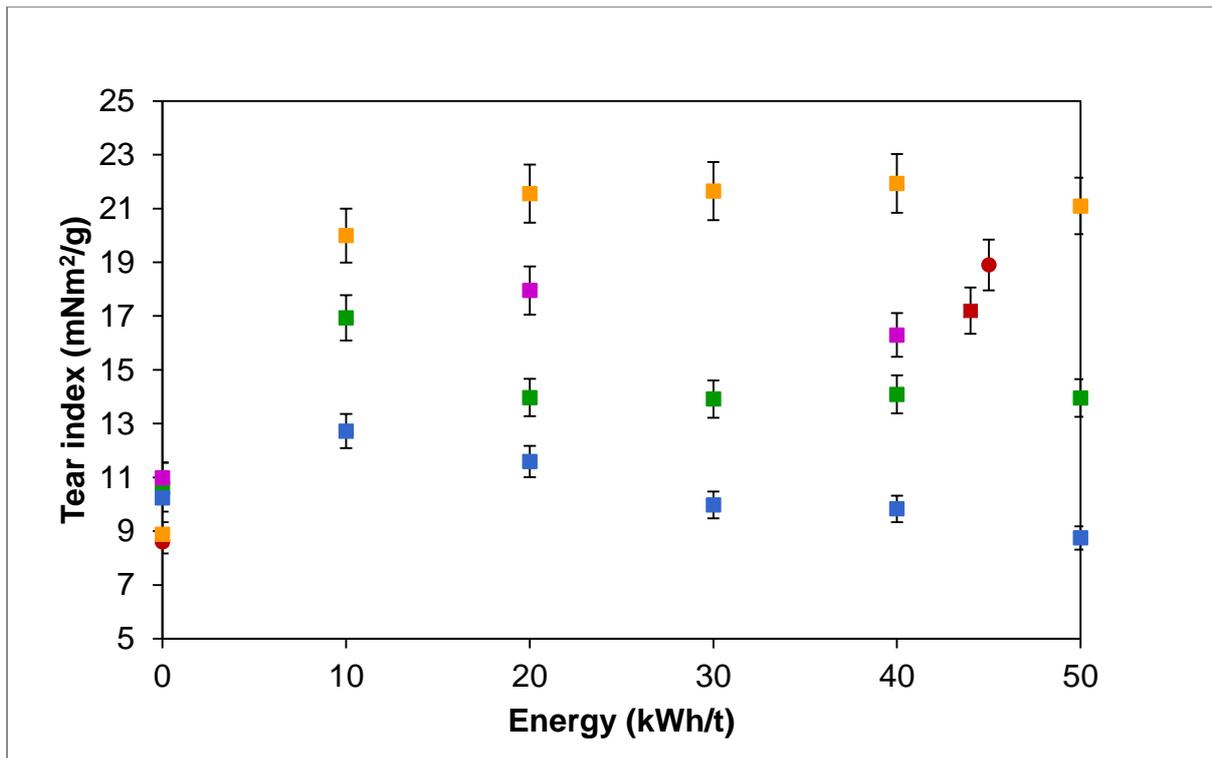


Figure 6.24: OCC tear strength of all ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined and enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The tear strength of the enzymatic post-treatment was very high, second only to the ultrasonication control treatment. The high tear strength and low tensile strength results together with the higher freeness results supported the findings of Oksanen *et al.* (1997) and Pere *et al.* (1995), who supported the notion that enzymatic pre-treatment time is a major factor in fibre modification. The shorter the enzymatic pre-treatment time, the less apparent the fibre modification effects become.

6.4.4 Tear, tensile and freeness strength relationships of OCC followed by 100 g/t enzymatic pre-treatment

The tear strength, tensile strength and freeness relationships can be seen in Figure 6.25.

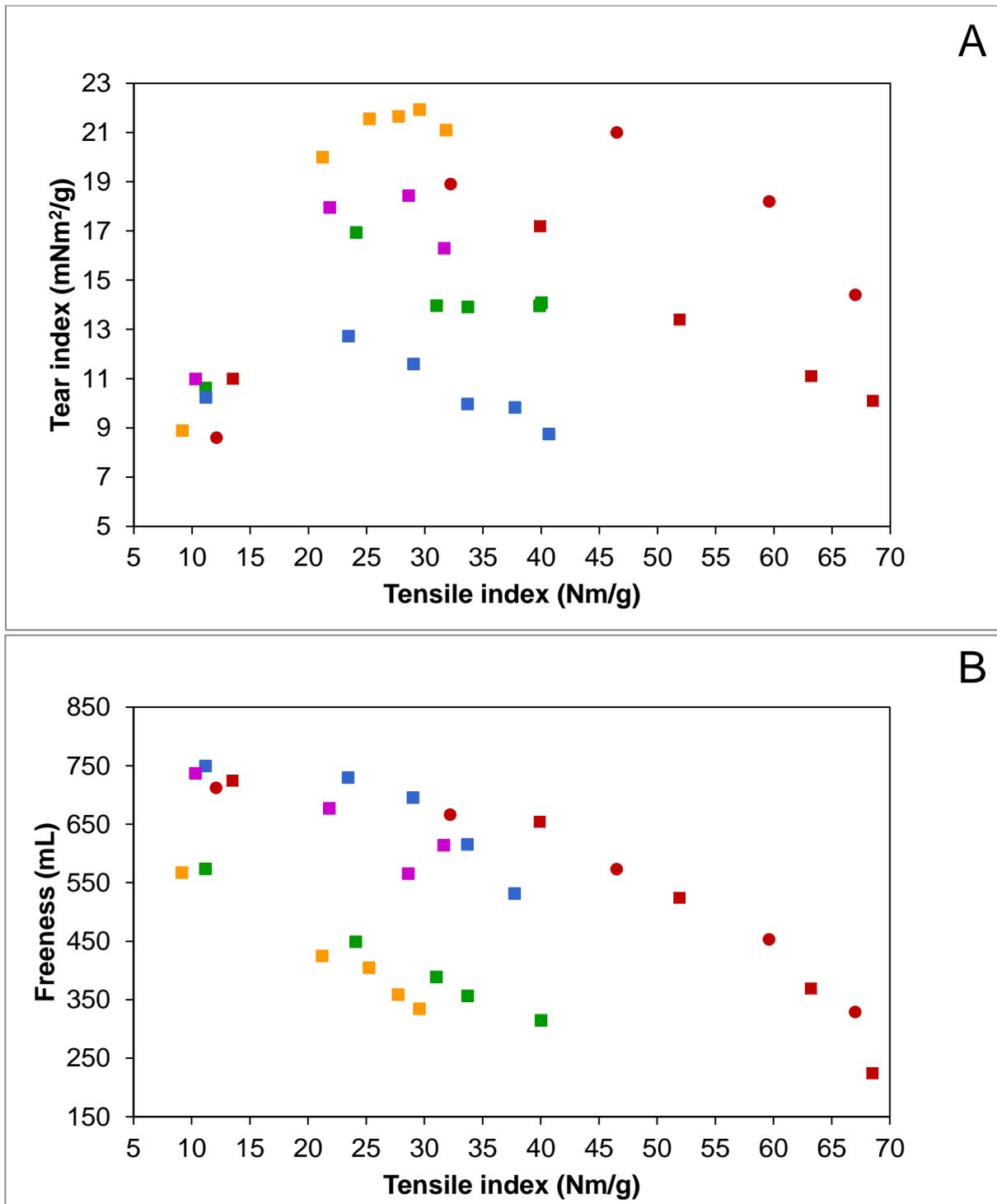


Figure 6.25: Tear and tensile strength relationship (A) and freeness and tensile strength relationship (B) of all OCC ultrasonication experiments at 53 μm compared to untreated mechanical refining and 50 g/t enzymatically treated mechanical refining. (■ Ultrasonication with enzymatic pre-treatment [200 g/t], ● Mechanically refined control, ■ Mechanically refined and enzymatically treated [50 g/t], ■ Ultrasonication with enzymatic post-treatment [100 g/t], ■ Ultrasonication with enzymatic pre-treatment [50 g/t], ■ Ultrasonication control).

The enzymatically post-treated pulp displayed a small decrease in freeness compared to the other enzymatic pre-treatments, which was seen as positive. It did seem, however, that the tensile strength of the fibres was not sufficiently developed by the enzymatic post-treatment. In fact, the sonicated control fibres and enzymatically post-treated fibres displayed similar tensile strength results, in theory meaning that the effects of the enzymatic post-treatment were very small. The same can be noted with the tear and tensile strength relationship, where the tear strength results were similar, especially if the experimental error is taken into account. The consistently lower tear strength results of the enzymatic post-treatment, compared to the ultrasonication treatment, indicate possible fibre modification. When the enzymatic post-treatment was compared to the other enzymatic pre-treatments, the difference between it and the ultrasonication treatment was small in comparison.

In summary the enzymatic post-treatment had a positive effect on the tear strength of the hand-sheets and caused a smaller decrease in freeness compared to the other enzymatic pre-treatments, which was positive for the paper machines. The post-treatment results were, however, not comparable to the tensile strength results of mechanically refined fibres or the previous enzymatic and ultrasonication treatments. A possible explanation could be that the shorter enzymatic post-treatment time caused a smaller fibre modification effect compared to the enzymatic pre-treatment experiments. This supports the findings of Huang *et al.* (2007); Haung *et al.* (2011); Montalbo-Lombay *et al.* (2010); Nikolic *et al.* (2010); Sun & Tomkinson (2002); Sun *et al.* (2002), who observed that treatment times were a factor when using enzymatic treatment and ultrasonication.

6.5 References

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Chapter 7: Conclusion and recommendations

In this study, the effect of ultrasonication and enzymatic treatment on paper pulps was investigated. The strength and freeness results of the treated pulps were compared to mechanical refining to investigate the validity of ultrasonication and enzymatic treatment replacing mechanical refining.

7.1 Ultrasonication

Ultrasonication required significantly more time to reach energies comparable to mechanical refining. Due to the longer treatment times, process heat built up and the ultrasonication treatments had to be stopped due to safety concerns. In the energy range of 0 to 50 kWh/t, ultrasonication seemed effective in modifying all pulps. In some cases, ultrasonication could not produce higher strength results than mechanical refining, but the low freeness values were problematic due to constrictions in pipe flow, which resulted in lower pump speeds.

Ultrasonication intensity, which was controlled by varying the amplitude, seemed to affect strength and freeness results. It must be noted, however, that the longer treatment times required for low-amplitude ultrasonication may have led to the strength and freeness differences. For softwood, the higher intensity ultrasonication (80 μm and 106 μm) produced the best results, while low intensity ultrasonication resulted in the best strength and freeness values for hardwood and OCC.

In the OCC and hardwood experiments, while the strength results of ultrasonication were consistently lower than those of mechanical refining, they were comparable. The low freeness results, however, indicated that mechanical refining was still a better option compared to ultrasonication.

The softwood pulp strength results were similar for mechanical refining and ultrasonication, with ultrasonication producing significantly higher tear strength values. The freeness values of ultrasonication also closely followed those of mechanical refining and did not result in a significant freeness decrease, as was observed with hardwood and OCC.

Overall it appeared that ultrasonication on its own was not a viable alternative to mechanical refining due to:

- Significantly longer treatment times.
- Heat build-up in the system, which may lead to system failure and health concerns.
- The large initial decrease in freeness (except with softwood fibres).
- Lower strength results when compared to mechanical refining (except with softwood fibres).

7.2 Enzymatic treatment

Strength results for all pulps appeared to improve when enzymatic treatment was introduced. The enzymatic treatment could not counter the decrease of freeness, as expected, but in all pulps a clear difference in strength results could be noted after the enzymatic treatment (at 0 kWh/t). The combination of enzymatic treatment and ultrasonication consistently resulted in improved strength results when compared to ultrasonication alone, regardless of the pulp used. The high enzyme dosage treatments had little effect on the pulp at higher energies, and produced similar results when compared to the low-dosage enzymatic treatments. It seems that a specific treatment time exists, beyond which enzymatic treatment has little additional effect on the pulp. It was therefore concluded that enzymatic treatment resulted in higher strength results and that enzymatic dosage amounts had little effect.

7.3 Treatment order

A clear difference in strength and freeness results was observed when the enzyme was added before ultrasonication compared to after ultrasonication. Where the enzyme was added before ultrasonication, it spent considerably more time in contact with the pulp at ideal temperatures. Where the enzymatic treatment followed ultrasonication, the enzyme was in contact with the pulp for a third of the time. It was concluded that the duration of the enzymatic treatment had the most effect on the pulp properties, meaning that the enzymatic pre-treatment resulted in the best results. The process time (re-pulping, ultrasonication, enzymatic treatment, incubation) for the enzymatic treatment following ultrasonication was not viable, due to the longer time

needed to incubate the pulp after ultrasonication. For the enzymatic pre-treatment, the re-pulping and incubation period were combined, resulting in a shorter process time.

7.4 Recommendations

Further work in this field is encouraged. An investigation on increasing the ultrasonication treatment time by regulating the temperature better, would add value and understanding to the field of biomass ultrasonication. A focussed study on ultrasonication is also recommended – where the paper properties are investigated closely and the use of electron microscopy is used to determine the change in fibre structure. The cross section of the handsheets can be studied closely, and the energy increments of ultrasonication can be decreased, as to provide a detailed view of how ultrasonication interacts with the fibres. A pulp sample, that resembles the true composition of paper, should be created and set through the same experiments, to understand how the properties are influenced.

A focussed study on softwood pulp should be initialized, as this was the pulp that indicated the most potential. Further understanding on the effect of ultrasonication amplitudes on the pulp would be valuable. A very valuable study into how ultrasonication can be done in a continues process should be investigated, this success of this study will change the way pulp refining is done.

Appendix A: Morfi results

Appendix A1: *Eucalyptus globulus* (hardwood) results.

Table A1.1: Ultrasonication of hardwood at 106 μm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	28.88	25.05	26.54	26.60	25.34
Fibre length, μm	785.33	789.67	793.00	790.67	792.67
Mean fibre width, μm	17.90	17.97	17.93	18.03	17.93
Mean fibre coarseness, mg/m	0.05	0.06	0.05	0.05	0.06
Kinked fibre content, %	34.16	26.43	24.50	24.73	23.28
Mean fibre curl index, %	9.43	7.40	7.23	7.18	6.86
Macro fibrillation index, %	0.69	0.63	0.65	0.66	0.64
Broken fibre content, %	20.63	20.86	20.40	20.24	20.24
Fines content, millions/g of pulp	105.26	108.73	110.00	105.72	98.17
Fines content, % in area	2.83	4.11	3.99	4.00	4.09

Table A1.2 Ultrasonication of hardwood at 106 μm , combined with low-dosage enzymatic treatment (50 g/t) morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	26.13	26.53	25.79	25.98	26.23
Fibre length, μm	788.00	787.33	790.33	790.67	796.00
Mean fibre width, μm	17.77	17.90	17.97	17.93	17.87
Mean fibre coarseness, mg/m	0.06	0.05	0.06	0.06	0.05
Kinked fibre content, %	33.47	27.36	26.06	25.31	24.84
Mean fibre curl index, %	9.11	7.73	7.46	7.25	7.11
Macro fibrillation index, %	0.67	0.64	0.64	0.65	0.64
Broken fibre content, %	20.06	20.19	20.12	20.37	20.07
Fines content, millions/g of pulp	87.07	91.87	90.87	91.94	91.40
Fines content, % in area	3.94	4.08	4.07	3.99	3.97

Appendix A1: Morfi results: *Eucalyptus globulus*

Table A1.3 Ultrasonication of hardwood at 106 µm, combined with high-dosage enzymatic treatment (200 g/t) morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	21.35	24.12	21.26	23.26	22.43
Fibre length, µm	781.33	787.33	783.00	792.67	790.67
Fibre width, µm	16.63	16.73	16.60	16.63	16.60
Fibre coarseness, mg/m	0.07	0.06	0.07	0.06	0.06
Kinked fibre content, %	31.98	27.28	25.74	24.44	23.89
Mean fibre curl index, %	8.28	7.41	6.92	6.96	6.86
Macro fibrillation index, %	0.56	0.61	0.55	0.58	0.56
Broken fibre content, %	15.37	15.10	15.41	14.41	14.77
Fines content, millions/g of pulp	79.92	85.72	78.39	80.17	78.84
Fines content, % in area	6.13	5.30	6.38	5.74	5.78

Table A1.4: Ultrasonication of hardwood at 80 µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	28.22	27.35	25.40	26.23	25.21
Fibre length, µm	792.00	792.67	790.67	793.33	793.33
Mean fibre width, µm	18.00	18.10	17.93	17.93	17.93
Mean fibre coarseness, mg/m	0.05	0.05	0.06	0.05	0.06
Kinked fibre content, %	33.86	25.16	23.97	22.45	22.55
Mean fibre curl index, %	9.45	7.34	7.03	6.68	6.77
Macro fibrillation index, %	0.71	0.68	0.64	0.66	0.64
Broken fibre content, %	21.18	20.81	20.63	20.22	20.14
Fines content, millions/g of pulp	106.58	115.00	109.21	110.18	106.91
Fines content, % in area	3.45	3.61	4.30	4.23	4.21

Table A1.5 Ultrasonication of hardwood at 80 µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	28.38	25.28	24.70	25.04	24.55
Fibre length, µm	792.00	790.67	792.67	787.00	787.00
Mean fibre width, µm	17.87	17.87	17.83	17.90	17.77
Mean fibre coarseness, mg/m	0.05	0.06	0.06	0.06	0.06
Kinked fibre content, %	32.84	27.00	26.12	25.32	24.50
Mean fibre curl index, %	9.17	7.66	7.34	7.23	6.97
Macro fibrillation index, %	0.70	0.63	0.62	0.62	0.61
Broken fibre content, %	19.95	19.93	20.56	20.50	20.08
Fines content, millions/g of pulp	89.61	89.70	89.70	90.85	89.78
Fines content, % in area	3.04	3.77	4.07	4.05	4.37

Table A1.6 Ultrasonication of hardwood at 80 µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	22.58	22.70	22.79	23.65	23.01
Fibre length, µm	784.00	787.33	787.33	790.00	792.00
Fibre width, µm	16.50	16.60	16.60	16.63	16.57
Fibre coarseness, mg/m	0.06	0.06	0.06	0.06	0.06
Kinked fibre content, %	34.51	27.24	25.32	24.51	23.49
Mean fibre curl index, %	9.14	7.41	7.12	6.98	6.95
Macro fibrillation index, %	0.58	0.58	0.56	0.59	0.57
Broken fibre content, %	15.23	15.17	14.86	14.70	15.04
Fines content, millions/g of pulp	73.01	82.05	83.16	87.65	81.02
Fines content, % in area	5.56	5.78	5.66	5.73	5.54

Table A1.7: Ultrasonication of hardwood at 53 µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	28.89	25.48	26.18	25.62	26.29
Fibre length, µm	795.00	789.00	789.33	789.33	796.00
Mean fibre width, µm	17.90	17.93	17.90	17.90	17.90
Mean fibre coarseness, mg/m	0.05	0.06	0.06	0.06	0.05
Kinked fibre content, %	33.83	24.66	23.31	22.13	21.85
Mean fibre curl index, %	9.49	7.01	6.88	6.80	6.85
Macro fibrillation index, %	0.72	0.66	0.66	0.65	0.66
Broken fibre content, %	20.34	20.44	20.71	20.15	20.31
Fines content, millions/g of pulp	110.90	112.03	111.96	111.54	113.80
Fines content, % in area	3.57	4.40	4.34	4.44	4.09

Table A1.8 Ultrasonication of hardwood at 53µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	25.88	25.06	25.62	25.85	26.32
Fibre length, µm	792.33	795.00	796.67	801.67	795.00
Mean fibre width, µm	17.27	17.17	17.27	17.27	17.27
Mean fibre coarseness, mg/m	0.06	0.06	0.06	0.06	0.06
Kinked fibre content, %	38.45	36.08	34.04	34.41	33.08
Mean fibre curl index, %	9.70	9.17	8.93	8.84	8.75
Macro fibrillation index, %	0.61	0.62	0.63	0.61	0.61
Broken fibre content, %	19.07	18.75	19.32	19.41	19.40
Fines content, millions/g of pulp	84.05	83.46	84.18	84.03	86.07
Fines content, % in area	3.87	3.85	3.72	3.48	3.60

Table A1.9 Ultrasonication of hardwood at 53 µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	22.43	22.30	21.72	22.27	20.81
Fibre length, µm	785.00	786.33	787.33	787.33	783.00
Fibre width, µm	16.67	16.67	16.67	16.60	16.60
Fibre coarseness, mg/m	0.06	0.06	0.07	0.06	0.07
Kinked fibre content, %	33.82	26.04	32.46	24.18	22.27
Mean fibre curl index, %	9.00	7.15	8.43	6.79	6.35
Macro fibrillation index, %	0.59	0.56	0.56	0.57	0.54
Broken fibre content, %	15.45	15.02	15.19	15.39	14.60
Fines content, millions/g of pulp	80.61	81.37	70.59	80.56	76.55
Fines content, % in area	5.87	6.08	5.80	5.92	6.60

Table A1.10 Ultrasonication of hardwood at 53 µm, followed by enzymatic treatment at 100 g/t morphology (Morfi) results.

	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	24.733	26.49	29.228	26.191
Fibre length, µm	782.33	789.67	790	789.33
Mean fibre width, µm	17.9	17.867	17.867	17.9
Mean fibre coarseness, mg/m	0.059	0.0549	0.0506	0.0553
Kinked fibre content, %	28.091	26.554	25.159	25.235
Mean fibre curl index, %	7.8113	7.62	7.448	7.3447
Macro fibrillation index, %	0.623	0.648	0.6437	0.6653
Broken fibre content, %	20.146	20.273	20.197	20.12
Fines content, millions/g of pulp	88.143	92.514	103.52	94.112
Fines content, % in area	4.332	4.1167	4.0563	3.8833

Appendix A2: *Pinus radiata* (softwood) Morfi results.

Table A2.1: Ultrasonication of softwood at 106 μm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	4.21	3.89	3.74	4.63	4.12
Fibre length, μm	2146.67	2187.00	2201.67	2188.00	2180.83
Fibre width, μm	32.10	32.50	32.53	32.67	32.45
Fibre coarseness, mg/m	0.18	0.20	0.20	0.18	0.19
Kinked fibre content, %	65.87	56.46	54.66	51.69	57.17
Mean fibre curl index, %	16.93	14.13	13.69	13.19	14.49
Macro fibrillation index, %	0.38	0.37	0.36	0.38	0.37
Broken fibre content, %	38.39	37.63	37.21	37.49	37.68
Fines content, millions/g of pulp	38.45	33.69	32.57	42.03	36.68
Fines content, % in area	1.98	1.96	1.98	2.23	2.04

Table A2.2 Ultrasonication of softwood at 106 μm , combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	2.98	3.46	4.03	3.97	3.91
Fibre length, μm	2114.33	2187.67	2203.00	2200.33	2200.00
Fibre width, μm	32.07	32.57	32.80	32.97	32.67
Fibre coarseness, mg/m	0.26	0.22	0.19	0.19	0.19
Kinked fibre content, %	65.09	53.52	51.87	49.83	48.71
Mean fibre curl index, %	16.36	13.64	13.44	13.19	13.05
Macro fibrillation index, %	0.34	0.36	0.39	0.40	0.39
Broken fibre content, %	38.25	37.79	38.45	38.16	36.31
Fines content, millions/g of pulp	25.49	29.68	33.93	36.31	34.00
Fines content, % in area	2.46	2.07	1.84	1.87	1.96

Table A2.3 Ultrasonication of softwood at 106 µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	4.60	3.45	4.07	4.04	4.90
Fibre length, µm	2098.33	2176.67	2173.00	2160.00	2179.00
Fibre width, µm	31.87	32.43	32.47	32.33	32.60
Fibre coarseness, mg/m	0.18	0.22	0.19	0.19	0.16
Kinked fibre content, %	64.67	54.55	51.18	48.41	45.84
Mean fibre curl index, %	16.36	14.01	13.97	13.57	13.46
Macro fibrillation index, %	0.36	0.44	0.47	0.55	0.64
Broken fibre content, %	37.82	37.82	37.16	37.57	38.48
Fines content, millions/g of pulp	64.47	68.10	66.67	71.22	92.94
Fines content, % in area	2.52	2.87	2.19	2.35	2.16

Table A2.4: Ultrasonication of softwood at 80µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.57	3.77	3.91	4.20	3.63
Fibre length, µm	2115.00	2193.33	2210.33	2228.67	2220.33
Fibre width, µm	31.73	32.10	32.83	32.83	32.57
Fibre coarseness, mg/m	0.22	0.20	0.19	0.18	0.21
Kinked fibre content, %	64.53	53.26	49.91	47.86	45.08
Mean fibre curl index, %	16.07	13.22	12.97	12.58	12.21
Macro fibrillation index, %	0.34	0.35	0.38	0.41	0.41
Broken fibre content, %	37.43	36.69	37.91	37.36	38.16
Fines content, millions/g of pulp	25.07	30.35	31.99	34.63	35.78
Fines content, % in area	2.17	2.06	1.89	1.84	2.23

Table A2.5 Ultrasonication of softwood at 80µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.69	4.08	4.95	4.25	4.20
Fibre length, µm	2127.33	2185.00	2223.67	2215.33	2185.00
Fibre width, µm	31.90	32.60	33.00	32.77	32.67
Fibre coarseness, mg/m	0.21	0.19	0.15	0.18	0.18
Kinked fibre content, %	65.56	53.44	49.52	47.02	44.63
Mean fibre curl index, %	16.65	13.69	13.34	12.97	13.18
Macro fibrillation index, %	0.35	0.37	0.44	0.44	0.52
Broken fibre content, %	37.41	36.72	38.14	37.52	37.99
Fines content, millions/g of pulp	28.41	35.48	47.58	46.42	45.99
Fines content, % in area	2.14	1.76	1.48	1.94	2.04

Table A2.6 Ultrasonication of softwood at 80µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Repulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.83	3.59	4.32	4.64	3.98
Fibre length, µm	2132.67	2192.67	2213.67	2198.67	2165.67
Fibre width, µm	32.07	32.33	32.73	32.67	32.53
Fibre coarseness, mg/m	0.20	0.21	0.17	0.17	0.20
Kinked fibre content, %	65.10	54.71	50.50	47.44	44.73
Mean fibre curl index, %	16.44	13.91	13.47	13.20	12.99
Macro fibrillation index, %	0.35	0.38	0.44	0.53	0.59
Broken fibre content, %	37.90	36.47	36.84	37.58	38.18
Fines content, millions/g of pulp	27.72	40.70	56.37	63.55	68.14
Fines content, % in area	1.80	2.11	1.90	1.88	2.39

Table A2.7: Ultrasonication of softwood at 53µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.51	4.13	4.33	3.74	5.72
Fibre length, µm	2119.67	2175.33	2189.33	2173.67	2197.00
Fibre width, µm	31.53	32.13	32.47	32.27	32.70
Fibre coarseness, mg/m	0.22	0.18	0.17	0.20	0.15
Kinked fibre content, %	64.88	59.51	56.57	56.00	54.72
Mean fibre curl index, %	16.32	14.34	13.78	13.68	13.35
Macro fibrillation index, %	0.34	0.37	0.38	0.38	0.41
Broken fibre content, %	36.70	36.26	36.31	38.22	37.97
Fines content, millions/g of pulp	35.52	36.97	36.94	39.84	64.41
Fines content, % in area	2.46	1.93	1.64	2.20	1.81

Table A2.8 Ultrasonication of softwood at 53 µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.710	3.732	3.574	3.355	3.219
Fibre length, µm	2137.667	2170.000	2182.000	2183.667	2166.667
Fibre width, µm	32.167	32.600	32.767	32.667	32.400
Fibre coarseness, mg/m	0.206	0.203	0.210	0.227	0.240
Kinked fibre content, %	65.632	59.427	57.347	55.807	54.765
Mean fibre curl index, %	16.900	14.696	14.490	14.098	13.921
Macro fibrillation index, %	0.352	0.368	0.371	0.375	0.397
Broken fibre content, %	37.830	38.179	37.879	37.828	37.938
Fines content, millions/g of pulp	40.846	39.194	35.973	36.159	41.616
Fines content, % in area	2.050	2.059	2.030	2.227	2.529

Table A2.9 Ultrasonication of softwood at 53µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	3.41	4.38	4.32	4.64	3.98
Fibre length, µm	2132.67	2181.33	2213.67	2198.67	2165.67
Fibre width, µm	31.97	32.57	32.73	32.67	32.53
Fibre coarseness, mg/m	0.23	0.17	0.17	0.17	0.20
Kinked fibre content, %	63.45	52.77	50.50	47.44	44.73
Mean fibre curl index, %	16.29	13.98	13.47	13.20	12.99
Macro fibrillation index, %	0.33	0.43	0.44	0.53	0.59
Broken fibre content, %	36.47	36.78	36.84	37.58	38.18
Fines content, millions/g of pulp	30.56	50.58	56.37	63.55	68.14
Fines content, % in area	2.13	1.83	1.90	1.88	2.39

Table A2.10 Ultrasonication of softwood at 53 µm, followed by enzymatic treatment at 100 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	4.26	6.56	7.05	10.71
Fibre length, µm	1977.33	2085.00	2117.67	2058.67
Fibre width, µm	27.83	28.57	29.17	29.07
Fibre coarseness, mg/m	0.25	0.16	0.15	0.10
Kinked fibre content, %	43.66	34.98	32.37	29.11
Mean fibre curl index, %	11.93	10.27	9.71	9.37
Macro fibrillation index, %	0.37	0.41	0.48	0.60
Broken fibre content, %	35.59	35.49	36.20	36.55
Fines content, millions/g of pulp	36.76	40.94	41.82	54.16
Fines content, % in area	1.90	1.17	1.02	0.64

Appendix A3: Old corrugated containers (OCC) results.

Table A3.1: Ultrasonication of OCC at 106 μm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.03	9.12	10.78	9.76	9.81
Fibre length, μm	936.60	1042.20	1024.20	1058.40	1037.40
Fibre width, μm	20.07	20.46	20.61	20.61	20.61
Fibre coarseness, mg/m	0.14	0.11	0.10	0.11	0.11
Kinked fibre content, %	17.84	15.32	15.20	14.82	15.32
Mean fibre curl index, %	5.74	5.40	5.52	5.45	5.53
Macro fibrillation index, %	0.86	0.90	0.95	0.92	0.92
Broken fibre content, %	23.27	23.58	24.28	23.76	23.84
Fines content, millions/g of pulp	186.94	223.17	264.38	239.28	233.06
Fines content, % in area	7.94	7.18	5.81	6.30	6.33

Table A3.2 Ultrasonication of OCC at 106 μm , combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.92	10.13	11.98	10.85	10.90
Fibre length, μm	1040.67	1158.00	1138.00	1176.00	1152.67
Fibre width, μm	22.30	22.73	22.90	22.90	22.90
Fibre coarseness, mg/m	0.15	0.13	0.11	0.12	0.12
Kinked fibre content, %	19.82	17.02	16.89	16.46	17.02
Mean fibre curl index, %	6.38	6.00	6.13	6.05	6.15
Macro fibrillation index, %	0.96	1.00	1.06	1.02	1.02
Broken fibre content, %	25.86	26.20	26.98	26.40	26.49
Fines content, millions/g of pulp	207.71	247.97	293.76	265.87	258.96
Fines content, % in area	8.82	7.98	6.46	7.00	6.98

Table A3.3 Ultrasonication of OCC at 106 µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	7.00	9.09	9.52	10.93	10.01
Fibre length, µm	1067.00	1142.33	1127.00	1110.67	1136.00
Fibre width, µm	21.53	22.20	22.17	22.23	22.47
Fibre coarseness, mg/m	0.19	0.14	0.14	0.12	0.13
Kinked fibre content, %	21.38	17.79	17.08	16.56	16.28
Mean fibre curl index, %	6.45	6.03	5.87	5.89	5.92
Macro fibrillation index, %	0.83	0.90	0.89	0.94	0.91
Broken fibre content, %	24.31	25.63	24.85	25.51	25.88
Fines content, millions/g of pulp	164.26	220.92	221.00	243.26	218.18
Fines content, % in area	10.84	9.00	8.63	7.74	7.75

Table A3.4: Ultrasonication of OCC at 80µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.73	13.16	12.87	13.05	12.76
Fibre length, µm	1009.67	1017.67	994.33	1005.00	1016.00
Fibre width, µm	21.57	22.47	22.53	22.73	22.80
Fibre coarseness, mg/m	0.16	0.11	0.11	0.11	0.11
Kinked fibre content, %	19.27	16.00	16.02	15.16	15.33
Mean fibre curl index, %	6.16	6.02	6.00	5.97	6.02
Macro fibrillation index, %	0.86	0.99	0.99	1.02	1.02
Broken fibre content, %	24.42	25.70	27.38	26.70	26.21
Fines content, millions/g of pulp	177.83	270.06	258.70	251.69	240.79
Fines content, % in area	10.12	8.53	8.66	7.70	7.67

Table A3.5 Ultrasonication of OCC at 80 µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.09	10.92	10.28	10.90	10.19
Fibre length, µm	1080.00	1192.67	1192.00	1192.33	1175.67
Fibre width, µm	21.97	23.10	23.10	23.27	23.37
Fibre coarseness, mg/m	0.17	0.12	0.13	0.12	0.13
Kinked fibre content, %	21.27	18.27	17.73	17.47	16.95
Mean fibre curl index, %	6.53	6.24	6.22	6.24	6.19
Macro fibrillation index, %	0.92	1.02	0.97	1.04	1.02
Broken fibre content, %	25.00	26.73	26.45	26.85	27.38
Fines content, millions/g of pulp	170.15	246.91	241.29	248.70	237.50
Fines content, % in area	9.78	6.44	6.96	6.13	7.27

Table A3.6 Ultrasonication of OCC at 80 µm, combined with high-dosage enzymatic treatment at 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	7.58	9.97	11.25	10.65	10.01
Fibre length, µm	1119.67	1183.33	1157.67	1163.00	1136.00
Fibre width, µm	22.60	23.17	23.07	23.23	22.47
Fibre coarseness, mg/m	0.18	0.13	0.12	0.12	0.13
Kinked fibre content, %	18.70	16.18	14.90	14.83	16.28
Mean fibre curl index, %	6.22	5.87	5.75	5.76	5.92
Macro fibrillation index, %	0.93	1.00	1.02	1.02	0.91
Broken fibre content, %	26.23	27.15	26.97	27.00	25.88
Fines content, millions/g of pulp	169.70	244.02	261.40	239.16	218.18
Fines content, % in area	9.60	7.97	6.93	7.06	7.75

Table A3.7: Ultrasonication of OCC at 53µm morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	15.99	19.51	18.32	18.61	19.20
Fibre length, µm	923.00	937.00	913.00	920.67	896.00
Fibre width, µm	22.23	22.57	22.80	23.20	23.50
Fibre coarseness, mg/m	0.12	0.09	0.10	0.10	0.10
Kinked fibre content, %	12.99	11.35	10.66	10.31	10.06
Mean fibre curl index, %	5.36	4.98	5.02	5.00	5.08
Macro fibrillation index, %	0.96	1.03	1.04	1.08	1.13
Broken fibre content, %	31.09	30.27	30.07	30.47	30.56
Fines content, millions/g of pulp	216.24	252.67	236.91	230.08	229.62
Fines content, % in area	6.68	5.22	5.20	5.27	4.38

Table A3.8 Ultrasonication of OCC at 53µm, combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	9.732	10.732	11.475	11.100	10.912
Fibre length, µm	1018.333	1140.333	1118.333	1093.333	1062.667
Fibre width, µm	21.767	23.067	23.167	23.100	23.033
Fibre coarseness, mg/m	0.155	0.122	0.115	0.120	0.124
Kinked fibre content, %	17.617	15.546	15.068	14.838	14.921
Mean fibre curl index, %	5.781	5.796	5.916	5.866	5.866
Macro fibrillation index, %	0.894	1.034	1.065	1.072	1.075
Broken fibre content, %	24.637	26.651	26.864	27.106	26.755
Fines content, millions/g of pulp	225.793	248.295	261.301	244.327	236.656
Fines content, % in area	11.046	7.269	7.094	6.483	7.082

Table A3.9 Ultrasonication of OCC at 53 μ m, combined with high-dosage enzymatic treatment 200 g/t morphology (Morfi) results.

	Re-pulp	10 kWh/t	20 kWh/t	30 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.80	11.33	11.19	10.98	12.98
Fibre length, μ m	1094.00	1167.67	1161.33	1139.00	1087.88
Fibre width, μ m	21.93	22.87	23.07	23.40	22.33
Fibre coarseness, mg/m	0.15	0.11	0.12	0.12	0.10
Kinked fibre content, %	19.62	15.77	15.40	15.04	16.94
Mean fibre curl index, %	6.31	5.88	5.99	5.89	6.20
Macro fibrillation index, %	0.91	0.99	1.04	1.07	1.02
Broken fibre content, %	24.17	25.81	26.39	26.43	25.32
Fines content, millions/g of pulp	184.46	251.00	230.89	221.51	250.24
Fines content, % in area	8.82	6.74	5.83	5.68	6.24

Table A3.10 Mechanical refining of OCC pulp morphology (Morfi) results.

	Re-pulp	14 kWh/t	21 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.09	8.32	8.96	8.83
Fibre length, μ m	1148.00	1212.00	1168.00	1184.50
Fibre width, μ m	22.25	22.40	22.25	22.55
Fibre coarseness, mg/m	0.00	0.00	0.00	0.00
Kinked fibre content, %	19.00	18.43	16.90	16.80
Mean fibre curl index, %	6.14	6.18	5.93	6.00
Macro fibrillation index, %	0.00	0.00	0.00	0.00
Broken fibre content, %	22.41	22.46	22.85	22.83
Fines content, millions/g of pulp	248.57	252.67	270.06	223.17
Fines content, % in area	9.42	8.39	9.65	9.61

Table A3.11 Mechanical refining of OCC pulp combined with low-dosage enzymatic treatment at 50 g/t morphology (Morfi) results.

	Re-pulp	14 kWh/t	21 kWh/t	40 kWh/t
Fibre content, millions/g of pulp	8.41	8.87	9.34	9.70
Fibre length, μm	1151.50	1195.50	1133.00	1059.50
Fibre width, μm	22.45	21.90	22.10	22.30
Fibre coarseness, mg/m	0.00	0.00	0.00	0.00
Kinked fibre content, %	18.89	16.14	15.97	15.24
Mean fibre curl index, %	6.18	5.80	5.68	5.64
Macro fibrillation index, %	0.00	0.00	0.00	0.00
Broken fibre content, %	22.22	21.64	22.11	23.89
Fines content, millions/g of pulp	237.50	248.29	246.91	247.97
Fines content, % in area	8.31	10.18	10.46	11.08