The Influence of Mechanical Pulping Treatment on the Physical Properties of Wood Fibre Plastic Composites

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Medium density fibreboard (MDF) fibres produced by a mechanical pulping process have shown potential for reinforcement in natural fibre composites (NFCs). In this work, the effect of process options, available in a pilot-scale fibre processing facility, on NFC properties were investigated. These were: a) refining energy; b) pre-treatment by sulphonation (*i.e.* chemi-thermo-mechanical pulping (CTMP)) and c) whether the extractives stream (*i.e*. the plug screw pressate) was discarded or included with the fibre. There were improvements in composite performance with refining energy, although these were not strong or consistent across composite properties. The CTMP fibres gave a substantial improvement over conventional MDF fibres in flexural, tensile, and impact properties, which may be due to improved fibre-matrix interfacial properties because of better mechanical interlocking and the removal of extractives.

Keywords: Wood fibre plastic composites; Fibre modification; Mechanical pulp refining; Composite properties; Pilot-scale; SEM

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INTRODUCTION

Natural fibres have been modified for use in natural fibre composites (NFCs). An overview of fibre modification for composite materials aimed at improving their performance has been prepared by Belgacem and Gandini (2008). Typically, most of the modifications are applied after the fibre has been separated. Chemical modifications include acetylation, grafting with siloxanes, and isocyanates (Belgacem and Gandini 2008). Physical modifications include the level of refining energy (mechanical energy used to separate fibres and enhance their properties), temperature, and plasma exposure (Mukhopadhyay and Fangueiro 2009; Gibeop *et al*. 2013).

Another opportunity for physical and chemical modifications of fibres is during the process of converting them from wood chips, *i.e*. during pulping. This conversion process can be mechanical or chemical, and the nature of this determines the chemistry and performance of the resultant fibres (Sorieul *et al*. 2016). For example, removing hemicelluloses, lignin, or both, from the fibre cell wall (Ou *et al*. 2014) shows significant changes in the properties of the resultant composite (high density polyethylene). The removal of hemicelluloses results in improvements in properties, which can be attributed to increased hydrophobicity and interfacial bonding (Hosseinaei *et al*. 2012; Ou *et al*. 2014). The influence of lignin is more complex. Although lignin removal can improve composite properties (Ou *et al*. 2014), the presence of lignin can also have the effect of improving properties due to chemical interactions with coupling agents (Arbelaiz *et al*.

2005; Peltola 2010; Graupner *et al*. 2014; Peltola *et al*. 2019).

Chemi-thermo-mechanical pulping (CTMP) is a process that allows for chemical pre-treatment prior to mechanical pulping. Such a pre-treatment of wood chips with an aqueous solution of sodium sulphite is commonly employed in the pulp and paper industry. The wood chips are heated in a solution of sodium sulphite prior to pressurised refining. Sulphonation of wood reduces both the lignin softening temperature and the elastic shear modulus (Atack and Heitner 1979). It has been proposed that this phenomenon is due to the replacement of lignin's hydroxyl and ether functionalities by sulphonate groups. As sulphonate groups cannot form interchain links (Atack and Heitner 1979), the lignin is weakened. This type of CTMP treatment also results in a small loss of fibre material, mostly lignin and fines (small cell fragments) (Börås and Gatenholm 1999).

A medium density fibreboard (MDF) process is a mechanical pulping process in which wood chips are pre-heated (172 °C) to soften the lignin, which enables a gentle separation of fibres with a disc refiner. This high temperature results in the redistribution of wood components soluble in hot water, predominantly hemicelluloses with a minor amount of lignin.

Industrial process settings, in a pilot-scale biorefinery, have been used previously to evaluate MDF fibres in polypropylene (PP) composites (Dickson *et al*. 2014). In this current work, a more extreme range of the available fibre process options within the same pilot biorefinery were used to evaluate their effect on composite properties. The process options evaluated were:

- Pre-treatment (*i.e.*, sulphonation)
- Refining energy
- Retaining or discarding hot water (steam) extractives.

The hypothesis was that the extremes of the available processing conditions will generate a range of modifications to the MDF fibre wall. These differences in cell wall chemistry, fibre flexibility (longitudinal and transverse), and extractives levels will then be reflected in composite performance.

EXPERIMENTAL

Materials

MDF fibre production

The MDF fibres were produced at the Scion pilot-scale biorefinery (Rotorua, New Zealand) from radiata pine (*Pinus radiata* D. Don) wood chips. The treatments applied as part of the MDF fibre production are described in Table 1 and Fig. 1. Fibres were made with non-typical (high/low) refiner energy inputs as well as a more industrially common level, termed medium. The plug-screw pressate after the 172 °C pre-heater stage (containing hot water extractives) was either fed-forward (*i.e.* redeposited on the fibre) or discarded (*i.e.* removed from the fibre). Feeding forward is the standard commercial practice. During the sulphite pre-treatment, wood chips were impregnated with 13.3% sodium sulphite solution at pH 7.5 in a separate stage prior to MDF fibre pulping. This sulphite addition level is higher than typically used in the pulp and paper industry and was selected to maximise the effects of sulphonation. After refining, the fibres were dried in a tube drier to a moisture content of 10 to 20% and packed in air-tight bags before composites production (Fig. 1).

Table 1. Refining Conditions and Treatments

Fibre Type	Extractives	Specific Energy for Sample (kWh/t)[a]	Energy Level	ID
Standard MDF	Forward	249	Low	07 ForLo
		392	Medium	08 ForMed
		523	High	09 ForHi
	Discarded	266	Low	03 DisLo
		418	Medium	06 DisMed
		587	High	05 DisHi
Sulphite Pre-treatment CTMP	Forward	211	Low	19 ForLo
		389	Medium	20 ForMed
		533	High	21 ForHi
	Discarded	201	Low	23 DisLo
		356	Medium	22 DisMed

Note: a: energy input is calculated on an oven dried basis and includes the refiner idle load

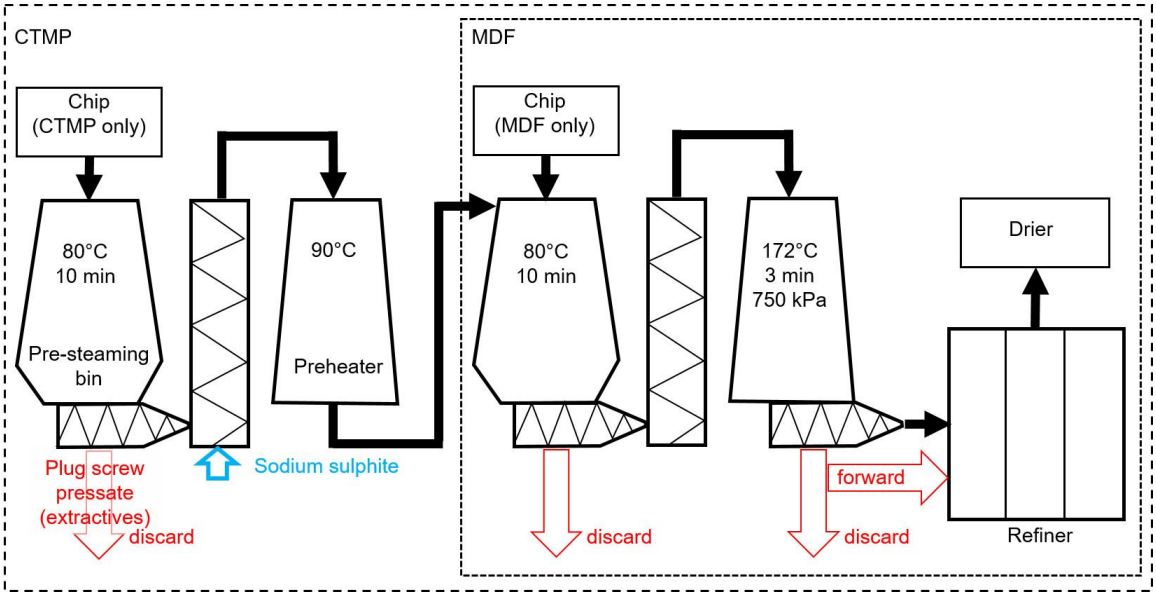

Fig. 1. Process diagram for CTMP and MDF fibres

Method

NFC production by extrusion compounding

The MDF fibre was converted into cubes by firstly hot-pressing fibres into thin sheets and subsequent cutting the sheets into small (4 × 4 mm) cubes (Warnes and Fernyhough 2010).

The MDF cubes were then compounded at 40 wt% loading into copolymer polypropylene (PP) (Sumitomo ar564, Rabigh Refining & Petrochemical Co., Rabigh, Saudi Arabia) with 3 wt% maleic anhydride grafted PP (MAPP) (Epolene G3015, Eastman, USA) as a coupling agent. The extruder (LTE26-40, LabTech Engineering Co. Ltd, Samutprakarn, Thailand) had a 26 mm screw diameter with co-rotating twin screws with a 40 L/D (length/diameter) ratio. The PP and MAPP were dry blended and fed into the main feed using a Weighbatch™ DS-20 (Weighbatch, Hamilton, New Zealand) gravimetric feeder. The MDF cubes, which had been oven dried overnight at 105 °C, were

side-fed into the extruder using a K-Tron K-ML-SFS-KT20 twin-screw (Coperion K-Tron, Sewell, NJ, USA) gravimetric feeder. Two atmospheric venting ports and one vacuum crammer (0.7 bar) degassing port were used to remove the entrapped air in the melt. The melt was extruded through a 2 strand die and pulled into a water bath before being granulated into 3 mm pellets. Each formulation was extruded at 200 rpm screw speed and 8 $kg \cdot h^{-1}$ total extrusion throughput to ensure proper fibre mixing with a gentle screw design and reverse barrel temperature profile.

Injection moulding

Prior to injection moulding, the compounded pellets were oven dried at 105 °C to obtain a pellet residual moisture content below 0.3 wt%. The compounded pellets were injection moulded with a BOY 35 machine (BOY Spritzgiessautomaten, Neustadt-Fernthal, Germany) into ISO multipurpose injection moulded test specimens (dogbone) type A (ISO 3167 2014). The barrel temperature of the injection moulder was 180 °C, and the mould was kept at 60 °C. The injection speed was 90 $mm*s^{-1}$. The mould was filled with a screw speed of 100 rpm with 2 bar back pressure. The cooling time was 30 s. The injection moulding parameters were the same for all composites.

Fibre morphology

The fibre length was measured by 2 methods. Firstly, using the Bauer McNett (BM) process (TAPPI T233 1998), a known amount of fibre (by weight) was carried by turbulent water through a cascade of sieves with increasingly finer mesh (14, 30, 50, 100, 200 mesh number). The fraction retained in each sieve was oven dried and weighed. The proportion of fibre bundles (shives) was determined with a Pulmac shive analyser (Pulmac Systems, Williston, Vermont) using a 0.15 mm screen (~100 mesh) (TAPPI T274 sp-97 1998). Secondly, the length, width, and coarseness were measured using an FQA-360 fibre analyser (OpTest Equipment Inc, Hawkesbury, Ontario, Canada). The proportion of fibres above the critical fibre length of 0.8 mm (Thumm and Dickson 2013) was also recorded.

The composites were prepared for confocal microscopy by cutting and polishing (320 to 4000 grit) 2 cross-sections from 1 tensile test piece per treatment examined. The composites were imaged with a Leica SP5 II confocal laser scanning microscope (Leica Microsystems, Mannheim, Germany). The excitation wavelength was 488 nm, the detection band was 519 to 568 nm and the field of view was 388 × 388 µm. The cross-section dimensions (200 per treatment examined) and fibre/PP fraction (20 images per treatment examined) were measured using ImageJ 1.52i (Abramoff *et al*. 2004).

The fracture surfaces of failed tensile test pieces were coated with chromium using an Emitech K575X sputter coater (Quorum Technologies Ltd, Kent, United Kingdom) and imaged using a JEOL JSM6700F (JEOL Ltd, Tokyo, Japan) scanning electron microscope (SEM) at 3 kV.

Fibre extraction

Fibres (for length measurement using an FQA-360) were separated from the PP matrix by Soxhlet extraction in boiling xylene (≥ 98.5%, Sigma-Aldrich, New Zealand). One gram of material was placed in a cellulose thimble which was sealed using a second thimble. The sealed thimble was placed into a round bottom flask with xylene (200 mL) and an anti-bumping granule. The samples were boiled for 4 h. The thimble was then placed into a Soxhlet extractor and the extraction ran overnight. The thimble was then dried at 105 °C for 1 h.

Fibre chemistry

Water extractives were determined by extracting 1 g of fibre in water (100 mL) at 20 °C for 24 h on an orbital shaker. The fibres were separated from the extract *via* glass fibre filter paper (GF/C, Whatman) and the extract was freeze-dried for gravimetrical determination (ASTM D1110 2013).

Dichloromethane (DCM) extractives (largely water-insoluble extractives) were measured by extraction using a Soxtec apparatus (Foss, Hilleroed, Denmark) for 1 h.

The sulphur content of the fibres was determined by inductively coupled plasma-mass spectrometry (ICP-MS) according to EPA Method 6020A (SW-846) (1998). All the above analyses were performed in duplicate.

Composite characterisation

The densities of injection moulded samples were determined using a water displacement technique (ASTM D792 2008). All mechanical properties were normalised by dividing the property by the density.

The tensile properties were measured using an Instron 5566 (Instron, Norwood, MA, USA) universal test machine fitted with a 10 kN load cell and an external extensometer (ISO 527 1997). The crosshead speed was 5 mm/min. The gauge length was 115 mm, and the extensometer length was set to 25 mm. Ten specimens were tested for failure to obtain the average Young's modulus (modulus of elasticity - MoE), maximum tensile strength (modulus of rupture - MoR) and elongation at break.

The flexural properties were measured with the same instrument according to ASTM D790 (2010). The crosshead speed was 1.3 mm/min. The support span to depth ratio (L/d) was 16 to 1 giving a span of approximately 50 mm. Ten specimens for each treatment was tested for failure to obtain the average MoE and MoR

Samples for the Izod notched impact strength were prepared and tested (ASTM D256 2010). The samples (12.6 mm × 63.5 mm × specimen thickness) had a 45° notch machined into each one using a Ceast Notchvis (Ceast, Turino, Italy). Seven Izod specimens for each treatment were tested at 3.46 m/s, a 150º angle, and a 0.5 J hammer using a Ceast Resil impact testing machine (Ceast, Italy).

Statistical analysis

For analysis of variance (ANOVA) a 5% significance level ($\alpha = 0.05$) was used and the Fischer least significant difference test ($\alpha = 0.05$) was applied to determine significant differences between means. All other significant differences were also based on $\alpha = 0.05$.

RESULTS AND DISCUSSION

The strength (MoR) and stiffness (MoE) of the injection moulded CTMP fibre composites were significantly greater (6 to 7% and 10 to 11%, MoR and MoE, respectively) than those made with MDF fibres (Table 2). There were no significant differences in strength and stiffness due to extractives treatment (discarded *vs.* forwarded) (Table 2). Therefore, subsequent analysis disregarded extractives treatment as a variable for these properties.

Table 2. PP Composite Physical Properties

ID	Fibre	Flex. MoR (MPa)	Flex. MoE (GPa)	Tens. MoR (MPa)	Tens. MoE (GPa)	Impact (kJ/m^2)
07 ForLo	MDF	71.8 ± 0.2	3.58 ± 0.02	47.6 ± 0.2	4.24 ± 0.11	3.93 ± 0.10
08 ForMed	MDF	74.5 ± 0.4	3.75 ± 0.04	48.5 ± 0.9	4.47 ± 0.07	3.97 ± 0.10
09 ForHi	MDF	73.9 ± 0.4	3.72 ± 0.02	49.0 ± 0.2	4.40 ± 0.12	4.07 ± 0.26
03 DisLo	MDF	68.8 ± 0.5	3.42 ± 0.02	46.1 ± 0.2	4.20 ± 0.07	4.38 ± 0.37
06 DisMed	MDF	73.8 ± 0.4	3.63 ± 0.02	49.4 ± 0.5	4.43 ± 0.13	4.25 ± 0.25
19 ForLow	CTMP	76.3 ± 0.4	3.86 ± 0.02	50.1 ± 0.2	4.83 ± 0.12	4.31 ± 0.12
20 ForMed	CTMP	78.6 ± 0.5	4.04 ± 0.04	51.5 ± 0.3	4.98 ± 0.12	4.36 ± 0.26
21 ForHi	CTMP	78.7 ± 0.4	4.06 ± 0.01	51.9 ± 0.2	4.80 ± 0.08	4.19 ± 0.20
23 DisLo	CTMP	77.0 ± 0.4	4.07 ± 0.01	50.3 ± 0.2	4.85 ± 0.12	4.17 ± 0.17
22 DisMed	CTMP	76.3 ± 0.3	3.84 ± 0.03	50.2 ± 0.4	4.62 ± 0.33	4.26 ± 0.26
n, for ANOVA		10	10	10	10	10
Discard-forward						
F		0.7294	0.5052	0.2466	0.9644	7.3300
p-value		0.4412	0.5165	0.6456	0.3817	0.0537
MDF-CTMP						
F		9.8746	12.7733	8.4340	20.6581	10.4058
p-value		**0.0348**	**0.0233**	**0.0439**	**0.0105**	**0.0321**
% Difference		6.7	9.7	5.6	10.7	3.4
Interaction						
F		0.1083	0.5399	0.0222	0.3625	30.9455
p-value		0.7586	0.5032	0.8887	0.5796	**0.0051**

Note: ± 95% confidence intervals; significant p-values from ANOVA (α=0.05) are bolded; ID 05 DisHi removed to balance the ANOVA

There was also a significant difference in impact energy (3%) between composites made with MDF and CTMP fibres, but there was a significant statistical interaction between fibre type and extractives treatment (Table 2). Therefore, a subsequent analysis of impact energy included the extractives treatment.

There was a general trend of improved flexural and tensile properties with increased refining energy. However, apart from tensile MoR (MDF fibres) which did show a significant correlation (Pearson correlation coefficient $r = 0.86$, $p = 0.03$), the trends were not consistent or strong enough to be statistically significant. For this reason, the refining level was also removed as a variable for all property assessments.

Strength and Stiffness

To compare the results, excluding any influence of refining energy, a regression analysis was applied to the mechanical property data using refining energy as the independent variable (Fig. 2). The mechanical properties were then predicted using 300 kWh/t as a reference (Table 3). By experience, the energy of 300 kWh/t in the pilot-scale facility relates to conventional refining energies in commercial MDF mills. On this basis, CTMP fibre composites showed a 7 to 8% increase in MoR over MDF and an 11 to 12% increase in MoE.

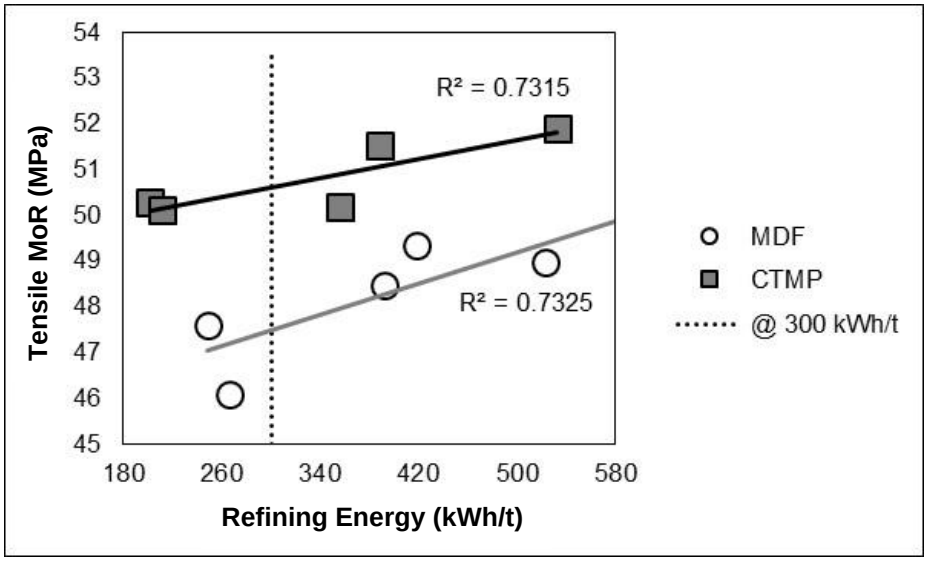

Fig. 2. Tensile MoR at a range of refining energies

Table 3. PP Composite Physical Properties at 300 kWh/t

	Flex. MoR (MPa)	Flex. MoE (GPa)	Tens. MoR (MPa)	Tens. MoE (GPa)
CTMP	77.1	3.96	50.6	4.82
MDF	71.5	3.56	47.5	4.30
Difference (%)	7.8	11.2	6.6	12.0

Fibre properties

The significant differences in mechanical properties between the MDF and CTMP composites were not evident in the physical properties of the fibres prior to compounding (Table 4). There were also few differences in fibre properties extracted from, or in, the composites (Table 5). The exception was the fibre width (and perimeter) with the CTMP fibres being significantly wider (larger) than the MDF fibres. This is attributed to swelling of the fibre wall due to lignin softening (Eriksson *et al*. 1991). As there was no difference in fibre length between the MDF and CTMP fibres, greater fibre diameters would result in lower aspect ratios for the CTMP fibres.

The lengths of the extracted fibres (*i.e.* after compounding and injection moulding) were in the range expected for this wood fibre type (Dickson and Sandquist 2018), and there was no indication that the fibre treatment influenced the fibre length retention during compounding and injection moulding. There was also no evidence that the physical properties of the fibres were responsible for the observed differences in composite properties. Therefore, other factors related to the fibre treatments were responsible.

During the CTMP treatment, the addition of sodium sulphite resulted in lignin sulphonation evenly across the cell wall (Richardson 1998) and increased the amount of acid groups on the surface. This also decreased the contact angle and hydrophobicity of the fibre surface (Börås and Gatenholm 1999). It has been shown that the presence of added (sulphonated, kraft) lignin can enhance the effect of MAPP and improve tensile properties (Peltola 2010; Graupner *et al*. 2014). The maleic anhydride reacts with hydroxyl groups making the fibre surface more hydrophobic and the esterification of the cellulose surface increases its surface energy closer to that of the matrix (Li *et al*. 2007). It is possible that

the improved composite properties observed for the CTMP composites were due to the sulphite treatment increasing the efficiency of the lignin-MAPP interaction compared to the MDF fibres.

Table 4. Properties of MDF and CTMP Fibres Prior to Compounding

ID	Fibre	Mean Fibre Length (mm)	LWL[a] (mm)	Fibre Width (µm)	BM[b] Fines (%)	Pulmac Shives (%)
07 ForLo	MDF	1.90 ± 0.08	2.87 ± 0.05	37.4 ± 0.8	3.8	14.6
08 ForMed	MDF	1.44 ± 0.09	2.54 ± 0.07	34.5 ± 1.2	5.0	2.1
09 ForHi	MDF	0.96 ± 0.05	1.87 ± 0.07	31.2 ± 0.8	13.2	0.4
03 DisLo	MDF				3.3	27.9
06 DisMed	MDF				6.8	2.2
05 DisHi	MDF				4.3	0.4
19 ForLo	CTMP	1.72 ± 0.27	2.78 ± 0.17	36.1 ± 2.8	8.0	13.0
20 ForMed	CTMP	1.56 ± 0.14	2.69 ± 0.11	34.9 ± 1.6	7.3	0.4
21 ForHi	CTMP	1.51 ± 0.10	2.58 ± 0.09	36.2 ± 1.3	5.6	0.0
23 DisLo	CTMP				7.8	20.7
22 DisMed	CTMP				3.2	3.7
n, for ANOVA (MDF-CTMP)		6	6	6	11	11
F		0.3512	0.7431	0.5952	0.0250	0.0033
p-value		0.5853	0.4373	0.4835	0.8779	0.9555

Note: ± 95% confidence intervals; a: length weighted fibre length; b: Bauer McNett; significant p-values from ANOVA are bolded

The CTMP treatment also reduced the pulp yield by roughly 4 to 5% (Richardson *et al*. 1990) and resulted in the swelling of the fibre wall (Eriksson *et al*. 1991). This raises the possibility that a more open, porous surface, allows for greater mechanical interlocking between the PP-MAPP and the fibre surface (Zhou *et al*. 2016). Additionally, the yield loss of the CTMP fibres meant that more fibres were required per given mass compared to the MDF fibres. Therefore, the CTMP reinforced composites may be expected to contain a greater fibre volume fraction and a corresponding increase in surface area. However, no significant difference in fibre volume fraction was seen based on microscopy measurements (data not shown). Therefore, there was likely only a minor effect of volume fraction on properties.

Fibre and composite chemistry

The CTMP fibres had significantly lower DCM extractives than the MDF fibres but neither fibre type showed differences in DCM extractives resulting from forwarding the extractives pressate or discarding it (Table 6). Therefore, the level of DCM extractives seen were due to the pulping type, not the final course of the extractives pressate. Much of the CTMP extractives would have been removed earlier in the system (Fig. 2). Studies have shown improvement in flexural properties after the removal of extractives (Saputra *et al*. 2004; Sheshmani *et al*. 2012; Chen *et al*. 2014), with a suggested mechanism being an improvement in interfacial bonding. The improvement in tensile and flexural properties of the CTMP fibre composites over the MDF composites (Table 3) was possibly a

combination of a) improved mechanical interlocking due to fibre wall swelling and roughness and b) improved interfacial adhesion due to the removal of extractives.

Table 5. Properties of MDF and CTMP Fibres after compounding (extractives pressate feed forward).

ID	Fibre	Mean Fibre Length (mm)	LWL (mm)	Fibres ≥ 0.8 mm (%)	Fibre Width (µm)	Fibre Perim. (µm)	Fibre Wall Area, (µm²)	Fibre Wall Thick. (µm)
07 ForLo	MDF	0.46 ± 0.01	0.59 ± 0.01	3.0 ± 0.6	41.3 ± 0.9			
08 ForMed	MDF	0.39 ± 0.01	0.51 ± 0.01	1.1 ± 0.5	39.5 ± 0.9			
09 ForHi	MDF	0.43 ± 0.01	0.54 ± 0.02	2.4 ± 1.0	41.4 ± 0.4	106 ± 3	451 ± 20	5.2 ± 0.2
19 ForLo	CTMP	0.41 ± 0.01	0.51 ± 0.01	1.6 ± 0.7	42.5 ± 0.9			
20 ForMed	CTMP	0.41 ± 0.01	0.51 ± 0.01	1.8 ± 0.7	42.6 ± 0.7			
21 ForHi	CTMP	0.41 ± 0.01	0.51 ± 0.01	1.9 ± 0.7	43.1 ± 0.3	111 ±2	469 ±18	5.2 ± 0.2
n, for ANOVA (MDF-CTMP)		6	6	6	6	400	400	400
F		0.7444	2.4825	0.5597	8.8856	5.7055	1.7516	0.3861
p-value		0.4369	0.1902	0.4960	**0.0407**	**0.0174**	0.1864	0.5347

Note: ± 95% confidence intervals; significant p-values from ANOVA are bolded

The sulphur content was in the range expected after CTMP sulphonation (Richardson *et al*. 1990). The lower sulphur content of the fibres where the extractives were discarded (ID 22 DisMed, Table 6) indicated a substantial amount of the added sulphite was likely removed with the extractives pressate.

Composite fracture surfaces

Although it is speculated that the differences between CTMP and MDF fibre composites are due to the nature of the fibre-matrix interface, there were no obvious qualitative differences between the fracture surfaces of the tensile tested composites that could be discerned by SEM. Both the MDF and CTMP fibre composites were dominated by fibre fracture (Fig. 3a). Where fibre pull-out was present, it was only minor, and PP fibrils could be seen between the fibre wall and the surrounding PP (Figs. 3b and c). These fibrils indicated a strong attachment between the fibre and the polymer, and that failure occurred at the fibre-PP interface by the necking and rupture of the polymer. Similar fibrils have been described in PP-wood particle composites and attributed to the compatibiliser (MAPP) increasing toughness through a localised effect adjacent to the fibre surface (Hristov *et al*. 2004a; Hristov *et al*. 2004b). The dominant failure mechanism was fibre wall axial failure as evidenced by the exposed fibre cross-sections and the large number of axially failed cellulose microfibrils (Fig. 3b). Some cell wall delamination was also visible, most noticeably but not restricted to, the interface between the S1 and S2 layers of the fibre wall. Such delaminations are common at interfaces between the layers of wood cell walls due to changes in microfibril angle and lignin content (Donaldson 1995; Putoczki *et al*. 2007).

Table 6. Chemical Analyses of MDF and CTMP Fibres and PP Composites

ID	Fibre	Sulphur Content (%)	Water Extract. (%)	DCM Extract. (%)
07 ForLo	MDF			
08 ForMed	MDF	<0.01	7.45 ± 0.02	0.75 ± 0.09
09 ForHi	MDF			
03 DisLo	MDF			
06 DisMed	MDF	<0.01	3.51 ± 0.01	0.70 ± 0.04
05 DisHi	MDF			
19 ForLo	CTMP			
20 ForMed	CTMP	0.47 ± 0.004	6.92 ± 0.03	0.39 ± 0.02
21 ForHi	CTMP			
23 DisLo	CTMP			
22 DisMed	CTMP	0.39 ± 0.005	5.06 ± 0.04	0.38 ± 0.04
n, for ANOVA (MDF-CTMP)			8	10
F			0.100694	72.59259
p-value			0.76175	**<0.0001**

Note: ± 95% confidence intervals; significant p-values from ANOVA are bolded

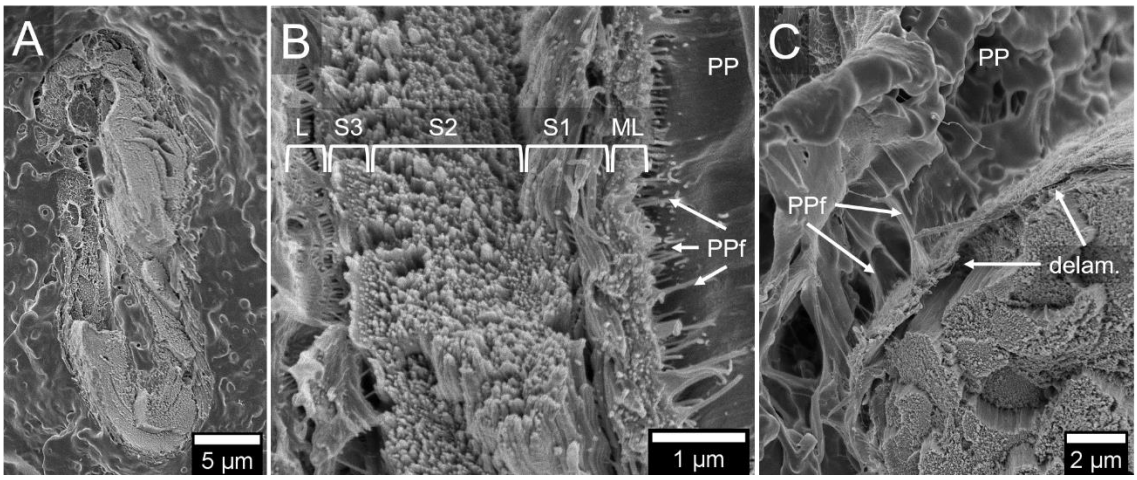

Fig. 3. Fracture surfaces of tensile tested samples: A) MDF, fractured fibre, B) MDF showing fibre wall detail and PP fibrils (PPf) where ML is the middle lamella; and S1, S2, S3 are the layers of the secondary wall, L is the flattened cell lumen, and PP is the PP matrix, and C) CTMP showing delamination (delam.) between S1 and S2 layers.

Impact Energy and Extractives

Retaining the extractives pressate (*i.e*. forwarding the extractives) significantly reduced the impact energy (approximately 5 to 7%) for the MDF composites compared to the other fibre treatments (Fig. 4). The MDF composite with retained extractives pressate also had higher water-soluble and DCM extractives than the CTMP composites (Table 6). Sheshmani *et al*. (2012) showed only small improvements in impact strength after the removal of extractives (at a laboratory scale) compared to much larger increases in tensile and flexural properties. Likewise, results in this study showed different responses for impact energy and flexural/tensile properties due to extractives. This points to different

mechanisms or degrees of interaction between extractives and the matrix/interface for flexural/tensile properties and impact properties. In this study, the removal of extractives was related to the pulping conditions and the use of the pressate stream in a pilot-scale biorefinery. This is a complex system (Pasco and Suckling 2001) and may not relate well to laboratory-based extractions.

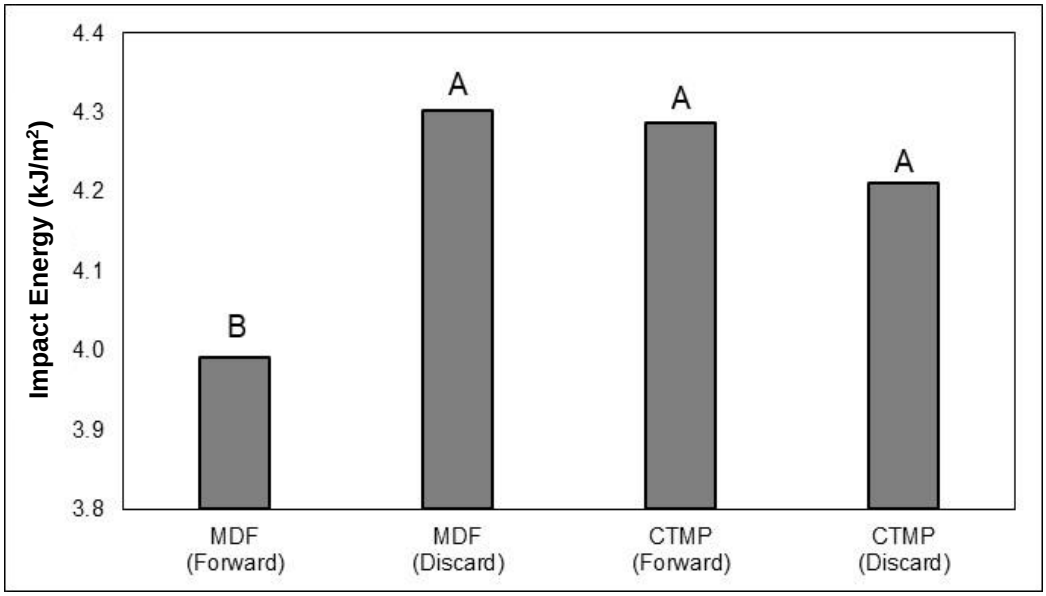

Fig. 4. Comparison of impact energies of PP composites containing MDF and CTMP fibres, with (Forward) and without (Discard) extractives. Treatments with the same letter are not significantly different (Fischer's least significant difference).

CONCLUSIONS

1. Higher pulp refining energy resulted in significantly higher tensile MoR for the MDF fibre composites. No other tensile or flexural properties showed a significant effect of refining energy.
2. When adjusted to a common refining level of 300 kWh/t, the CTMP fibres gave a 7 to 12% improvement in composite strength and stiffness compared to the MDF fibres.
3. The removal of extractives improved composite properties. Firstly, the removal of extractives during the CTMP pulping likely improved the fibre-PP interface. This along with improved mechanical interlocking, improved the mechanical strength and stiffness of the CTMP composite relative to the MDF. Secondly, the impact performance of MDF fibre composites improved 5 to 7% by discarding the extractive stream, rather than depositing it with the fibre.
4. These results indicated a significant advantage of a CTMP pre-treatment over conventional MDF processing for PP composite reinforcement using wood fibres. No analysis of chemical or capital related costs was conducted to determine if this would be a cost-effective process for generating wood fibre for composites.

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