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Investigating the extent of urea formaldehyde resin cure in medium density fibreboard: Characterisation of extractable resin components

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ABSTRACT

Panel mass and nitrogen losses indicate medium density fibreboard (MDF) panels bonded with differing urea formaldehyde (UF) resins readily lose some 40–70% of resin components on exposure to cold water soaking. Analysis reveals these labile extractable resin components to be low molecular weight UF oligomers which were not present in such amounts in the original UF resins. Panel emissions appear linked to the relative proportions of these extractable UF resin condensation products. Furthermore, results indicate that when applying resin to fibre, resin components may chromatographically separate and become unavailable to cross-link into a fully cured resin matrix. Differences in wood fibre extractives, resin chemistry or application methodology gave minor differences in extractable resin components, but a greater resin loading contributed to lower relative resin extractability.

1. Introduction

Urea formaldehyde (UF) resin is primarily used in the manufacture of medium density fibreboard (MDF) and how this resin is dispersed and cured on MDF fibre is a key determinate of panelboard properties [1]. An adequate pressing time and temperature are required to achieve resin cure with all resin components cross-linking to form a fully cured resin matrix. Typically, UF resin hydrolytic stability and emissions have been the focus of UF resin developments and cure studies [2–4]. UF resin is susceptible to hydrolysis which can contribute to formaldehyde emissions from panels [1,2,5–10] and is inherently associated with release of urea or urea-derived species. While high urea extractability into water upon recycling of MDF is known [11,12], it has also been determined that significant quantities of UF resin components are readily extractable into water from MDF panels [13,14]. Mass and nitrogen content losses suggest both urea- and urea-methylene species are labile in panels with some 40–70% of resin components lost on cold water soaking of MDF. However, in contrast similarly extracting fully cured pure UF resin gave little or no loss [14]. Furthermore, an assessment of resin-fibre combinations found resin content appears to be a key factor in resin component loss [14]. Greater resin loadings contribute to proportionately lower resin extractables compared to resin loadings more typical of MDF. The relatively high water extractability of UF resin components from MDF may infer UF resin is not fully cured. Such an implication, together with fibre-adhesive interface interactions [15,16] indicates that UF resin cure on MDF fibre may be complex and differs to that of pure resin.

Reported here are findings from a comprehensive study evaluating the relatively high water extractability of UF resin components from MDF panels and the relationship between this and the extent of UF resin cure in this product. The effects of fibre chemistry and extractable wood components are investigated with respect to the degree of resin cure achievable in MDF panels and corroborate findings reported in the first part of this study [14]. The chromatographic separation of UF resin fractions is compared to the molecular weight profiles and chemistry of MDF panel extractable resin components. These results provide insights into the nature of how UF resin cures in MDF and resulting panelboard properties. Outcomes of this study provide opportunities for UF resin developments to enhance MDF performance, panel emissions and UF resin efficiency.

2. Methodology

2.1. Materials

The urea formaldehyde (UF) resins used were standard, proprietary MDF resin formulations sourced from Dynea New Zealand Ltd (now Aica NZ Ltd). These resins were E0 and E1 resins which vary in urea content. The wax used was Mobilicer 739 emulsion wax obtained from ExxonMobil NZ Ltd. Lactic and acetic acids were technical grade chemicals and used as received. The MDF fibre was produced from *Pinus radiata* chips and the fibre dried to

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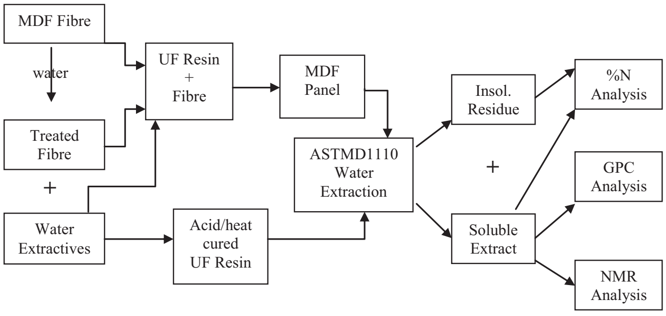

Scheme 1. Overview of methodology and approach used to prepare, extract and analyse MDF panels, extracted residues and water soluble extracts editing has created two full stops.

6–8% moisture content prior to resin application. Kraft fibre was obtained by resuspending lap pulp sheet (CHH Paper, NZ) in water with the dispersed fibre filtered and air dried. The cotton fibre was personal care grade cotton wool purchased locally. Shown in Scheme 1 is an outline of materials and treatments used, cured resin or panels formed and extraction and chemical analysis undertaken.

2.2. MDF extractives

Unresinated MDF fibre was extracted with either water, dichloromethane (DCM) or sodium hydroxide (NaOH) solution (0.1 M) at 20 °C for 24 h [see supplementary material]. The fibre suspension was then filtered and further washed. The filtrate was either concentrated to dryness (DCM) or freeze dried. The extracted wet fibre was forced-air dried (<55 °C) to 12% MC. In the case of the NaOH extract filtrate, this was neutralised prior to freeze drying.

For the preparation of fibre with additional water extractives, a water filtrate containing extractives was used to soak fresh MDF fibre. This wet fibre was then forced-air dried. “Rewetted” fibre was briefly immersed in water then similarly dried.

2.3. Resin cure

Pure E1 resin was cured at 105 °C for 30 min with either acetic acid 3% (w/w) or wood fibre extractives. The fibre extractives were added to the UF resin on a resin solids basis and ranged from 2 to 13% (w/w) additions.

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q1000. Resin samples (2–4 mg) were enclosed in Hermetic pans and heated at 10 °C/min from 20 °C to 220 °C. Exothermic heat flows were monitored for the onset of the UF resin cure exotherm and the evolved heat calculated using TA Universal Analysis software.

2.4. MDF panel preparation

All laboratory panels were prepared with dried MDF fibre being either control fibre or the variously treated fibres. Resin (either E1 or E0), emulsified wax (0.5% w/w o.d. fibre) and any additive were pre-mixed and applied to the fibre using standard mechanical-blending techniques. The resinated fibre (*ca.* 12% MC) was formed into a mattress and hot pressed (19 s/mm) to a target average density of 720 kg/m^3 using position-control to a thickness of 9 mm. A minimum of three 260 × 290 mm panels were prepared for each variable studied. Where stated, a set of 3 mm panels was also produced using the above press schedule. All panels were conditioned at 65% relative humidity and 20 °C.

Additionally commercially-produced blowline blended 3 mm MDF panels using the same E0 resin were sourced directly from a New Zealand MDF manufacturer.

For the double resin application, initially only half of the UF resin was applied to the fibre and the resinated fibre then oven cured (105 °C, 30 min). The second (half) proportion of resin was then applied to this MDF fibre and then a pre-press mattress formed and pressed as above.

Panel formaldehyde emissions were measured using standard protocols for the Japanese desiccator method JIS A 1460:2001 and were initiated within 2–3 weeks of panel manufacture.

2.5. Analysis

Water extraction of cured resin and panel sections (within a fortnight of manufacture) were ground up and analysed by a commercial analytical laboratory (Veritec, NZ) using ASTM D1110-84 methodology as follows. Sample (1–2 g) was stirred in water (100 mL) at 20 °C for 24 h, unless stated [supplementary material]. The residual, extracted resin or fibre material was isolated on filtering and dried to constant weight (105 °C). Where stated, the water soluble extract was concentrated to dryness either in an oven or by freeze drying. Results and calculated mass balances are reported on an oven dry basis [14].

Nitrogen analysis (%N) was determined on resin and fibre samples using a LECO CNS-2000 combustion furnace as previously described for both original, residue and extract samples [14]. The resulting %N values were compared and the losses (or enrichment) in %N calculated by comparing the residual %N and original %N values [14].

Thin layer chromatography (TLC) separation of E1 UF resin was undertaken on cellulose coated plates using standard laboratory procedures. The UF resin was applied as spots and the plate then eluted with water. The plate was removed after the solvent front attained 10 cm and separated bands (nominally R_f=0.2, 0.4, 0.6, 0.8, 1.0) were removed from the plate, extracted with DMSO and then analysed directly by GPC. To highlight resin components TLC plates were stained with iodine vapour.

Gel permeation chromatography (GPC) analysis employed a Polymer Laboratories GPC system operating a refractive index detector and a Polymer Labs Mixed-E column. The eluting solvent was dimethylsulfoxide (DMSO) operating at 50 °C and 0.5 mL/min. Polyethylene glycol molecular weight (MW) standards (600, 1470, 4100, 23,000) were used and spanned the MW range of the UF resin components. Pure UF resins (freeze dried), recovered TLC sections and panel extracts (freeze dried) were evaluated. Reference extracts of DMSO-soluble MDF fibre and cellulose materials were also analysed.

Nuclear magnetic resonance (NMR) employed a Bruker 400 MHz NMR using standard ^{1}H NMR pulse sequences. Both deuterium oxide and deuterated DMSO were used as solvents for pure resin and extract (freeze dried) samples.

3. Results

3.1. Effect of wood components on UF resin cure

Differential scanning calorimetry (DSC) was employed to analyse the cure of E1 UF resin mixed with various MDF fibre extractive fractions (Fig. 1, Table 1). For pure resin the onset of curing was 106 °C with *ca.* 85 J/g heat evolved during cure [10,17,18] compared to using acetic acid as a cure catalyst which gave the lowest cure onset (53 °C) and greater enthalpy (169 J/g) on resin curing. Adding MDF fibre extractives caused lower cure onset temperatures with 13% (w/w resin solids) water extractives

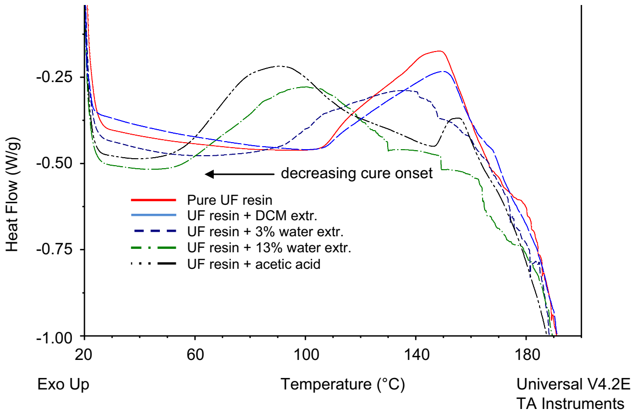

Fig. 1. DSC thermograms showing cure profiles of E1 UF resin promoted by various wood extractive fractions.

Table 1
DSC analysis results for the cure onset and enthalpy of E1 UF resin cure promoted by various wood extractive fractions.

Sample	Evolved heat (J/g)	Onset temp. (°C)	Max. peak (°C)
UF resin (pure)	85	106	149
UF resin 3% acetic acid	169	53	93
UF resin 3% water extractives	113	94	140
UF resin 13% water extractives	149	59	106
UF resin non-polar DCM extractives	87	107	151

reducing the cure onset to 59 °C compared to 94 °C for 3% extractives addition. In contrast, addition of non-polar (DCM) fibre extractives did not alter the onset temperature of resin cure. While DSC analysis confirmed fibre extractives may promote resin cure at lower temperature, the relatively lower enthalpies indicate that at a 100 °C resin cure may not be complete for pure resin or resins exposed to lower extractives content as noted previously [10,12,14,17,18].

Pure E1 resin was mixed with various wood extractives and cured at 100 °C (30 min) to determine the relative extractability of each cured resin. Mass losses were variable ranging from $<1\%$ mass loss on curing with acetic acid to *ca*. 50% mass loss for resin heated in the absence of an acid hardener (Table 2) [14]. Resin samples heated with added wood fibre water extractives led to lower mass losses compared to samples containing non-polar (DCM) or neutralised (NaOH) wood extractives. Addition of 13% water extractives to resin (w/w on solids) resulted in a significantly lower resin mass loss than a 3% extractives addition. A 13% w/w extractives content represents a third of water extractives possible from MDF fibre at an equivalent 10% resin loading. This indicates it is possible for UF resin to attain full cure on MDF fibre. In contrast to mass loss, samples generally show a minor enrichment of nitrogen (urea species) in the residual, extracted resin material. This %N enrichment indicates a loss of UF resin methylene, ether components, or both.

Overall, these results further confirm that wood extractives may increase UF resin cure and cross-linking at 100 °C, consistent with DSC findings. Achieving full cure led to little resin mass loss on water extraction, whereas under-cure of the UF resin can lead to significant resin mass losses.

3.2. *Effect of MDF extractables from differing fibre types on resin cure*

Given the impact of fibre water extractives on curing pure resin, the effects of these wood extractives were further investigated in MDF panels prepared from differently treated fibre types. Compared to the control panel (9% mass loss), panels prepared with fibre without extractives have lower mass losses, while fibre or resin containing additional extractives had relatively greater mass losses (Table 3, Fig. 2). This was likely due to fibre pre-treatment, rather than apparent differences in extractable resin losses. Panels prepared with cotton or Kraft fibre had mass losses of 4.3 and 8.3%, respectively. Analysis of extracted panel residues found between 45 and 54% of nitrogen (%N) was lost across the panel series (Fig. 2) with the control E1 panel (51%) comparable to that reported previously for MDF panels [13,14]. The lowest extractable nitrogen contents were those with a two-part resin application (45%) or with additional extractives (47%). The highest nitrogen losses were associated with panels prepared from Kraft and cotton fibre which had %N losses of 61 and 67%, respectively. This indicates the necessity of extractives or other lignocellulosic components as contributors to resin cure.

Panel formaldehyde emission values ranged between 0.4 and 0.8 mg/L. Panels prepared with resin mixed with either lactic acid

Table 2
Results of water extraction of cured UF E1 resin combinations with various wood fibre extractives or acid hardener according to ASTM D1110-84 for 24 h, 20 °C.

100% Resin samples	Extracted residue mass (%)	Original% N (%)	Residual% N (%)	%N Extracted (%)[a]
Pure E1 resin, no hardener	52.4	36.3	38.5	106
3% Water extractives	62.0	35.1	37.8	108
13% Water extractives	91.3	34.5	36.8	107
3% NaOH extractives	60.4	35.4	38.8	109
$<1\%$ DCM extractives[b]	53.2	35.8	38.0	106
$<1\%$ NaOH/DCM extractives	50.7	35.8	38.4	107
3% Acetic acid	98.1	37.2	39.9	107
3% Acetic acid and 2% extractives	100.0	36.4	38.7	106
3% Acetic acid and 5% NaOH extractives	95.0	35.0	39.0	112

[a] Values $>100\%$ represent an enrichment of nitrogen, or proportionate loss of carbon component (methylene, ether), on extraction of the cured resin [14].

[b] DCM extractives used in relatively low amounts due to the relatively low extraction yield of this material from MDF fibre [13].

Table 3
Results of formaldehyde emissions and water extraction of selected MDF panels according to ASTM D1110-84 for 24 h, 20 °C. (results uncorrected for panel %MC).

Panel sample	**Resin loading (%)**	**%N Extractable (%)**	**Mass loss[a] (%)**	**Formaldehyde emission (mg/L)**
MDF fibre only (pressed, no resin)	–	–	4.4	
Control E1	8.5	51	9.0	0.70
Rewetted fibre	8.1	50	6.1	0.62
Fibre without extractives	8.4	52	4.2	0.58
Fibre with additional extractives	9.4	47	8.0	0.57
Resin with extractives[b]	7.1	53	7.6	0.77
Resin with extractives (no wax)	8.8	53	8.5	0.84
Resin with hardener[c]	8.0	54	7.5	0.76
Resin with hardener fibre no extractives	7.8	49	4.9	0.60
Double resination	9.0	45	7.3	0.48
Differing fibre type				
Kraft	8.4	61	8.3	–
Cotton	3.6	67	4.3	–

[a] Filtrate masss reported on an oven dry (105 °C) basis.

[b] Only 13% fibre water extractives (w/w resin solids) was added due to high resin viscosity. *Note*: addition of the total fibre extractables (4% of fibre) would have given 39% w/w extractives in resin.

[c] Lactic acid was added as hardener.

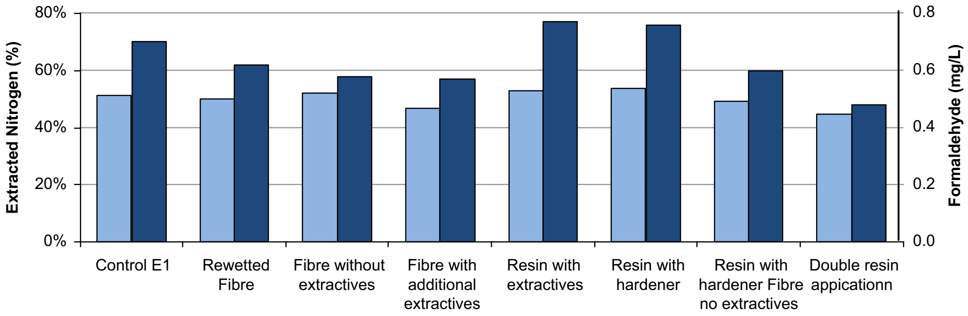

Fig. 2. A comparison of extracted nitrogen values (%N loss, light blue) and formaldehyde emissions (dark blue) for MDF panels prepared with differing fibre treatments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Results of formaldehyde emissions and a comparison of water extraction results of MDF panels with differing UF resins and resin loadings according to ASTM D1110-84 for 24 h, 20 °C. (results uncorrected for panel %MC).

	Resin loading (%)	Filtrate mass[a] (%)	%N Extracted (%)	Formaldehyde (mg/L)
Mechanically-blended panels with differing resins				
E0	9.1	7.6	65	–
E1	8.5	7.2	51	0.70
Lab 3	7.8	5.6	42	1.05
Lab 4	7.4	4.5	48	1.03
Blowline-blended panels varying in E0 resin content				
Comm 5	4.8	3.3	66	0.27
Comm 12	12.9	4.1	51	0.13
Comm 14	13.3	4.2	51	0.12
Mechanically-blended panels varying in E0 resin content				
Lab 5	6.0	3.6	63	0.35
Lab 12	11.5	4.9	65	0.18
Lab 14	14.1	6.2	70	0.15

a. Filtrate masses are reported on an oven dry (105 °C) basis.

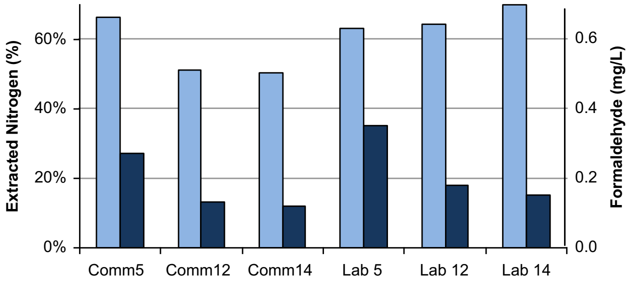

Fig. 3. A comparison of extracted nitrogen values (%N loss) and formaldehyde emissions for MDF panels prepared by either blowline (Comm) and mechanical-blending (Lab) with differing resin loadings.

or extractives had relatively higher formaldehyde emissions (0.77 mg/L, Table 3). Double resin application gave the lowest formaldehyde emission value (0.48 mg/L). However, with this sample it was possible some formaldehyde was volatilised on initially curing the first resin addition on fibre. Lower emissions were also noted for "rewetted" fibre, a likely consequence of volatiles loss when washing and redrying fibre and this may also be the case for other pre-treated fibres. Panel emissions correlate with %N losses from panels ($R^2=0.7$) implying a strong link between extractable resin components and emissions. The fibre differences do not impact panel emissions, but adding hardener or extractives to resin led to greater emission values indicating their presence may have impacted cure.

3.3. *Effect of resin chemistry variables on MDF extractables*

UF resins varying in urea content (E1 and E0) and urea addition sequence (Lab 3 and 4) were evaluated for differences in MDF panel water extractable contents. Panels formed with E1 and E0 resins had 51 and 65% extractable nitrogen content respectively (Table 4), the latter consistent with previous findings for low Formaldehyde:Urea (F:U) resins [14]. In contrast, panels formed with the two resins varying in resin synthesis style (Lab 3 and 4 E1 resins) had relatively lower extractable nitrogen (42–48%) and mass loss (*ca.* 5%, Table 4). The Lab 4 resin (42% N% loss) has greater urea included during resin synthesis, while Lab 3 (48% N% loss) had a proportionately larger urea post-charge. Across these results, the differences in extractable %N values indicate mole ratio may contribute to nitrogen extractability. This is consistent with lower F:U resins being more susceptible to hydrolysis and water soaking [1]. However, any differences in panel extractability due to F:U mole ratio during condensation and urea addition rate do not appear conclusive.

Resin distribution and resin-fibre interactions can differ between blowline- and mechanically-blended MDF panels [15,19]. MDF panels (E0 resin) were evaluated to distinguish whether their degree of resin cure and extractability was influenced by how the resin was applied (Table 4, Fig. 3). Although water extraction of panels revealed mass losses were greater with increasing resin loading (5–14%) for both resin application methods, this does not directly indicate the proportion of resin lost on extraction [14]. %N values of extracted panel residues reveal the blowline 5% panel lost some 67% nitrogen compared to values of 51% for the corresponding 12 and 14% panels. This is consistent with previous findings for the wood matrix effect [14]. For the mechanically-blended panels, extracted nitrogen values ranged between 58 and 67%. Analysis of panel formaldehyde emissions revealed mechanically-blended panels had relatively higher formaldehyde emissions than the corresponding blowline blended panels, but this may relate to panel pressing and history with the latter panel set tested 2–3 weeks later (Fig. 3). However, across the blowline- and mechanical-blended samples, the panels with 5% resin content had greater formaldehyde emissions in both panel sets.

3.4. *Chromatographic separation of UF resin components*

UF resin separation using chromatography was undertaken because previous studies have shown UF resin is mobile and distributed through the wood fibre cell wall on resin application [15]. UF resin separation by thin layer chromatography (TLC) is reported, but limited to examples using modified silica or cellulose with polar solvent [20–22]. Shown in Fig. 4 is UF resin separation achieved on cellulose TLC plates with water as carrier solvent. UF resin was observed to separate with some UF resin material carried at the solvent front.

The TLC plate (Fig. 4) was divided into five sections and the UF resin components from each section recovered for gel permeation

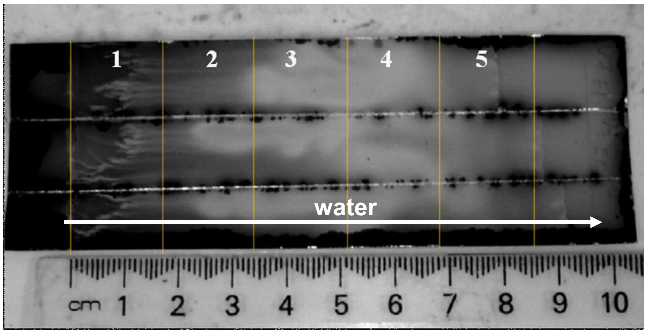

Fig. 4. Image of UF resin chromatographic separation on cellulose eluting with water. UF resin components observed as lighter coloured regions (TLC plate has been stained with iodine vapour).

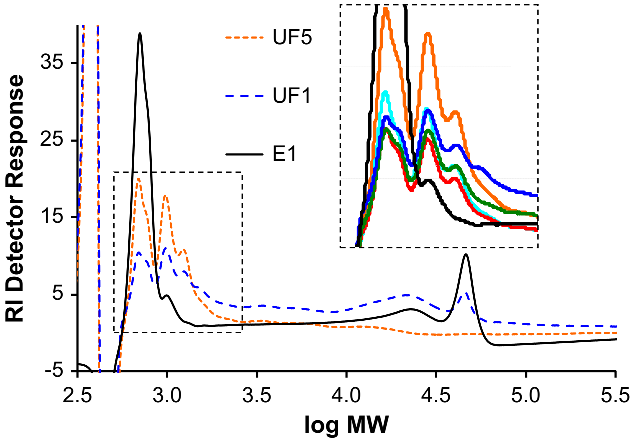

Fig. 5. GPC molecular weight profiles of UF E1 resin fractions obtained by TLC chromatographic separation. Inset are UF fractions UF1-, UF2-, UF3-, UF4- and UF5- as identified from Fig. 4. Profiles are reported as relative MW based on PEG standards and have any soluble-cellulose material subtracted from each MW profile.

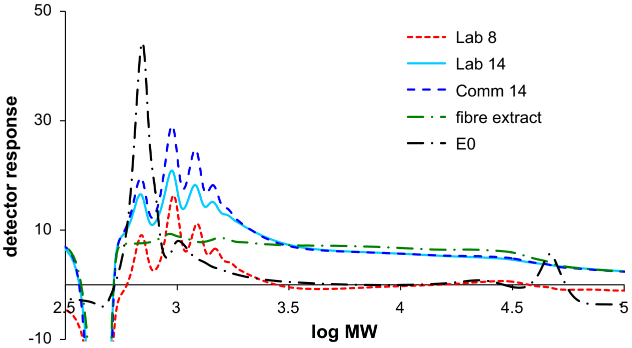

Fig. 6. Molecular weight profiles of the E0 UF resin and various water extracts of MDF panels varying in resin loading and application, either blowline (Comm 14) or mechanically-blended (Lab 14 and Lab 8) and fiber extract.

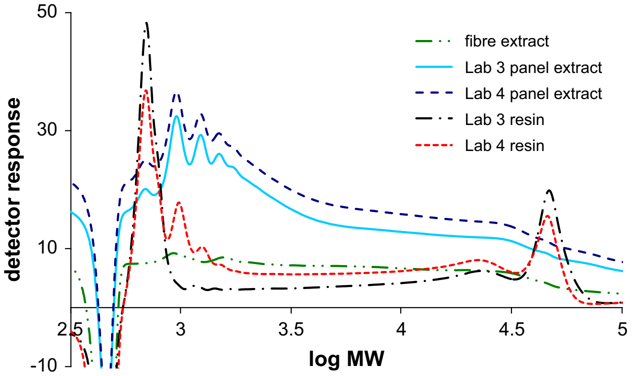

Fig. 7. Molecular weight profiles of UF resins varying in urea addition during synthesis (Lab 3 and 4) and their respective MDF panel water extracts.

chromatography (GPC) analysis. GPC molecular weight (MW) profiles of the E1 resin and TLC fractionated UF components are given in Fig. 5. GPC revealed Section 1 (UF 1) to have a similar high MW profile as the pure UF resin, but proportionately minor contributions from lower oligomeric MW fractions. In contrast, Section 5 (UF 5) with greatest water mobility on cellulose, had no high MW UF species, being dominated by low MW oligomeric and monomeric UF species. Sections 2–4 (UF2, UF3, and UF4, Fig. 4, inset) have MW profiles intermediate of UF 1 and UF 5 with a trend toward lower MW components with greater chromatographic mobility.

Combination of TLC and GPC confirms UF resin components are mobile within a cellulose matrix. Resin components were observed to separate on cellulose with this separation dependent on resin component MW.

3.5. Chemistry of MDF panel extractable resin components

The chemistry of UF resin components extractable into water was assessed primarily with ^{1}H NMR and GPC analyses. GPC analysis of the blowline and mechanically-blended panel extracts show these extracts consist of fibre extractables and UF resin components [supplementary material]. Molecular weight profiles of the 14% Comm and Lab panel extracts showed monomeric and low MW oligomeric UF resin components (Fig. 6). These oligomers appear to extend up to UF pentamers and hexamers with proportionately more oligomeric than monomeric components observed in each extract compared to the original E0 resin which was dominated by monomers. No high MW oligomeric or polymeric UF resin fractions were present in these panel extracts. The blowline (Comm) panel extract had slightly more oligomeric species than the mechanically-blended (Lab) extract. Extracts of mechanically-blended panels differing in resin loading (Lab 8 and 14%), had similar MW profile and proportions of oligomers.

The panel extracts from differing UF resins had similar MW profiles (Fig. 7). The Lab 3 and Lab 4 panel extracts show monomeric and oligomeric components which extend to UF pentamers and hexamers. These panel extracts also show higher proportions of the low MW UF oligomers compared to the original resins, which have distinctly different MW profiles in this region. In general, the GPC data show the predominance of low MW UF oligomers with relatively lower proportions of UF monomers recovered by panel extraction. There appeared little distinction between these panel extracts despite differences in original UF resins used. Based on mass balance and %N data values, it was also evident these low MW oligomeric resin components were not present in the original UF resins in the proportions isolated on panel extraction. This indicates oligomers were likely formed on panel hot-pressing, rather than by resin degradation or hydrolysis post-panel manufacture.

^{1}H NMR spectra of the Eo resin and corresponding MDF panel extracts from blowline (Comm) and mechanical-blended (Lab) panels are given in Fig. 8. The pure resin and the extracts show key peaks at 3.4, 4.2 and 4.5 ppm attributable to methylene and ether linkages ($>N–CH_2–N<$, $>N–CH_2–O–$ and $–O–CH_2–O–$) with the pure resin spectrum dominated by the methylol species (2.8 ppm) [23,24]. NMR confirmed the panel extracts also contain fibre extractives which have characteristic peaks of carbohydrates

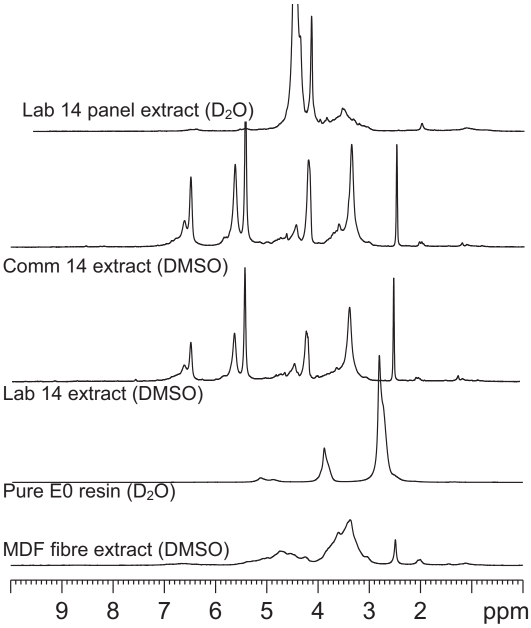

Fig. 8. ^{1}H NMR spectra of the E0 UF resin and corresponding blowline (Comm) and mechanically-blended (Lab) MDF panel extracts. NMR solvent used given in brackets.

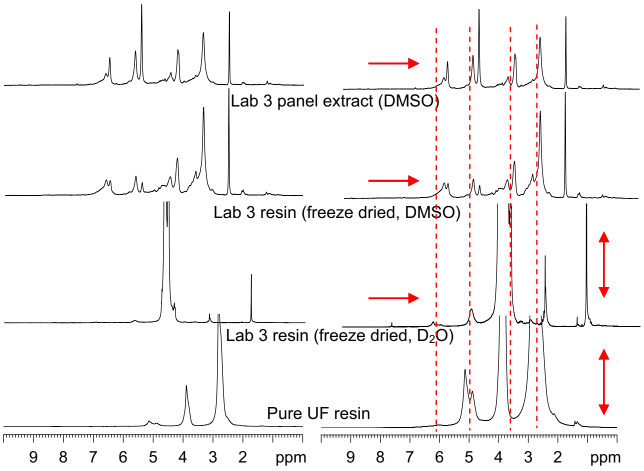

Fig. 9. Original (left) and same spectra scaled (*Y* axis) and aligned (right) ^{1}H NMR spectra of the Lab 3 UF resin and corresponding MDF panel extract.

at 3.5 and 4.5 ppm. It was evident resin components dominate the fibre extractives in each extract, consistent with the mass balance data for panel extractions and GPC profiles (Table 3, Fig. 6). In comparing each extract there also appeared little difference in chemistries due to resin application (Comm, Lab) which was similarly found with GPC analysis (Fig. 6). Fig. 9 is a comparison of NMR spectra of the Lab 3 resin and corresponding MDF panel extract. Methylene and ether peaks were present in both the extract and resin, but the pure resin was dominated by the monomeric, methylol component (2.8 ppm) consistent with GPC analysis (Fig. 7). Furthermore, the extracts identify similar proportions of peaks due to $>$N–CH$_2$-X and NH$_2$ and –NH– chemical species [23] which corroborate GPC data that extracted resin components were mainly composed of low MW UF oligomers.

4. Discussion

The high extractability of low MW UF resin species (Figs. 5 and 6) likely arises from the *in situ* condensation of monomeric, dimeric and low MW UF resin components within the fibre during hot-pressing, while degradation of cured resin on pressing or cure inhibition by carbohydrates are also possible contributors [1]. It is hypothesised that on application the high resin mobility [15,19] and chromatographic effect of the fibre allow the monomeric, dimeric and low MW UF resin components to separate from higher MW resin species. Due to their dispersal throughout the wood fibre matrix, only limited amounts of resin components actually couple together. An inability to further cross-link into a fully cured resin matrix is leading to the observed high levels of low MW, labile extractable resin species [10,14]. This is consistent with resin chemistry and proportions of monomeric and dimeric species in UF resins (Figs. 5–7). With proportionately more resin present on fibre it is likely there will be more opportunity for resin components to associate and cross-link, forming a more integral resin matrix. This is the “fibre effect” [14] in which greater resin loading contributes to relatively lower proportions of extractable resin components and associated lower panel emissions.

Fibre extractives promote resin cure and their presence is sufficient to induce full resin cure. Extractives mixed with pure resin can fully cure resin and inhibit water extraction losses (Table 2). However, in panels the addition of extractives or hardener to resin led to similar extracted panel %N values as control MDF panels (Fig. 2). An absence of fibre extractives however, led to panels with greater resin extractability (54%,) than panels formed with fibre with additional extractives (47%, Table 3). This result was further complicated by higher formaldehyde emissions on adding extractives or hardener which indicates their addition may confer a differing resin cure to that without added hardener. Nonetheless, a key finding in this study is the high extractability of heated, pure resin without acid hardener (Table 2) which was comparable to that from an MDF panel. This result implies the UF resin cure on fibre may be fundamentally different to that achievable with acid-promoted cure of pure resin.

Outcomes of this comprehensive study indicate a significant quantity of UF resin may not fully participate as a binder in MDF. That is, the effective UF resin loading of components contributing to panel bonding may be lower than the applied resin loading. The threshold for achieving an integrated, fully cured UF resin on fibre appears [14] greater than the highest resin loadings used in this study (14%). Furthermore, a relatively high extractability of UF resin components was observed across all four UF resins investigated. Some 40–70% of nitrogen-containing resin components appear to be UF oligomers (Figs. 6–9) which likely do not provide adhesive bonding, but were contributors to resulting panel emissions. Instead adhesive bonding is likely only achieved by the higher MW fractions present in the UF resin. However, practically, monomeric, dimeric and very low MW UF components are necessary in UF resins as they provide UF resin solubility and water tolerance. Use of greater resin content also reduces relative resin extractability while more resin is also beneficial for panel properties.

5. Conclusion

It was evident from mass and %N losses that MDF panels bonded with differing UF resins can lose some 40–70% of resin components on water extraction whereas fully cured pure UF resin loses <5% mass. Panel water soaking shows these resin components appear to be labile and readily solubilised with chemical analysis revealing the extractable resin components to be low MW UF oligomers. Analysis and mass balance indicate these extractable oligomeric species were not present in such amounts in the original UF resins.

This study has demonstrated the cure of UF resins on wood fibre may be fundamentally different to that of pure resin. Resin components may chromatographically separate when applied to fibre. This leads to some UF resin components being dispersed within the fibre wall and unavailable to cross-link into a fully cured resin matrix. This results in high proportions of low MW oligomeric UF resin condensation products which are readily extractable in water. While the presence of fibre extractives, differences in resin chemistry or resin application may give minor differences in panel extractability, there was a strong fibre effect, where greater resin loading led to lower resin component extractability. Results also imply panel emissions were linked to the relative resin extractability. The outcomes of this study provide a basis for understanding the nature of resin cure on fibre and mechanisms contributing to UF resin extractability. These present opportunities for resin developments to control resin cure and extractability for the enhancement of panel properties.

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References

[1] Dunky M. Int J Adhes Adhes 1998;18:95–107.
[2] Park BD, Jeong HW. J Appl Polym Sci 2011;122:3255–62.
[3] Park BD, Jeong HW. Int J Adhes Adhes 2011;31:524–9.
[4] Park BD, Lee SM, Roh JK. Eur J Wood Wood Prod 2009;67:121–3.
[5] Abdullah ZA, Park BD. J Appl Polym Sci 2009;114:1011–7.
[6] Brown SK. Polym Degrad Stab 1990;27:121–43.
[7] Dutkiewicz J. J Appl Polym Sci 1984;29:45–55.
[8] Fleischer O, Marutzky R. Holz Roh Werkst 2000;58:295–300.
[9] Kavvouras PK, Koniditsiotis D, Petinarakis J. Holzforschung 1998;52:105–10.
[10] Xing C, Deng J, Zhang SY, Riedl B, Cloutier A. J Appl Polym Sci 2005;98:2027–32.
[11] Roffael E, Dix B, Schneider T, Kraft R. Holz Roh Werkst 2003;61:73–4.
[12] Hennecke U, Roffael E. Holz Roh Werkst 2006;64:305–11.
[13] Grigsby W, Thumm A, Carpenter J. J Wood Chem Technol 2012;32:149–64.
[14] Grigsby WJ, Carpenter JEP, Sargent R. J Wood Chem Technol 2013 http://dx.doi.org/10.1080/02773813.2013.861850, in press.
[15] Grigsby WJ, Thumm A. Eur J Wood Wood Prod 2012;70:337–48.
[16] Grigsby WJ, Murton K, Thumm A. Appita J 2013;XXX:XXX (-XXX).
[17] Stefke B, Dunky M. J Adhes Sci Technol 2006;20:761–85.
[18] Xing C, Zhang SY, Deng J. Holzforschung 2004;58:408–12.
[19] Grigsby WJ, Thumm A. International wood adhesives conference. South Lake Tahoe, CA, USA: Forest Products Society; 2009.
[20] Ludlam PR. Analyst 1973;98:116–21.
[21] Schindlbauer H, Dabernig G. Fresenius' Z Anal Chem 1984;319:399–402.
[22] Schindlbauer H, Schuster J. Ger Plast 1981;71:19–22.
[23] Angelatos AS, Burgar MI, Dunlop N, Separovic F. J Appl Polym Sci 2004;91:3504–12.
[24] Chuang IS, Maciel GE. J Appl Polym Sci 1994;52:1637–51.