Labile Extractable Urea-Formaldehyde Resin Components from Medium-Density Fiberboard*

Warren J. Grigsby James E. P. Carpenter Armin Thumm
Rosie Sargent Nancy Hati

Abstract

Urea-formaldehyde (UF) resin is the predominant adhesive used in the manufacture of medium-density fiberboard (MDF). While it is well known that this resin is susceptible to moisture and hydrolysis, the present study determined that MDF panels lose a significant quantity of UF resin components in panel water soaking tests. Panel mass and %N losses indicate that MDF panels lose 48 to 66 percent of resin components during water soaking tests. Chemical analysis revealed that the labile extractable resin components included urea and monomeric and low-molecular-weight UF oligomers. Panel formaldehyde emissions were linked to the proportions of extractable UF resin oligomers. The results have implications for panel performance and the extent of resin cure achievable in manufacturing MDF.

Urea-formaldehyde (UF) resin is used primarily in the manufacture of medium-density fiberboard (MDF; Dunky 1998). Given a susceptibility to hydrolysis, typically UF resin hydrolytic stability and emissions have been the focus of UF resin developments (Dutkiewicz 1983, Brown 1990, Dunky 1998, Kavvouras et al. 1998, Fleischer and Marutzky 2000, Abdullah and Park 2009, Park and Jeong 2011). Furthermore, UF resin hydrolysis and formaldehyde emissions are inherently associated with release of urea or urea-derived species. In recent work, it has been determined that a significant quantity of UF resin components is readily extractable by water from MDF panels (Grigsby et al. 2014a, 2014b). Such a significant proportion of the panel board resin leachable into water contrasts with little or no losses of fully cured pure UF resin under similar soaking procedures (Grigsby et al. 2014a). This relatively high water extractability of UF resin from MDF infers that the resin is not fully cured, which may have implications for efficiencies in MDF panel board processing.

Reported in this article are findings from a comprehensive study evaluating the relatively high water extractability of UF resin components from MDF panels. Panel properties of typical MDF panels bonded with E1- and E0-type UF resins were evaluated, and their respective proportions of labile UF resin components extractable by soaking MDF panels in water were determined. The chemistries and molecular weight profiles of these extractable resin components were determined by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) analysis. The results of this article complement recently published findings from the comprehensive study evaluating the degree of resin cure achievable in MDF with respect to the method of resin application and loading and cure temperature, and also the effects of wood fiber extractives on UF resin cure and panel extractability (Grigsby et al. 2014a, 2014b).

Materials and Methods

Materials

The UF E1- and E0-type resins used were proprietary MDF UF resin formulations sourced from Dynea NZ Ltd. (now Aica NZ Ltd.). The wax used was Mobilicer 739

The authors are, respectively, Research Leader, Scientist, Scientist, Process Engineer, and Scientist, Scion, Rotorua, New Zealand (warren.grigsby@scionresearch.com [corresponding author], james.carpenter@scionresearch.com, armin.thumm@scionresearch.com, rosie.sargent@scionresearch.com, nancy.hati@scionresearch.com). This paper was received for publication in March 2014. Article no. 14-00030.

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Table 1.—Panel properties of medium-density fiberboard (MDF) panels produced from blowline (commercial, Comm) and mechanical blending (laboratory, Lab).

Panel description	Resin (%)	Density (kg/m^3) Average	Density (kg/m^3) Core	Internal bond strength (MPa)	24-h cold-water soak thickness swell (%)	Formaldehyde emissions (mg/liter)
8-mm Lab MDF panels						
Lab E0	9.1	677	622	0.53	14.05	—
Lab E1	8.5	703	623	0.72	10.91	0.70
3-mm MDF panels with E0 resin						
Comm 5	4.8	876	853	1.29	112.87[a]	0.27
Comm 12	12.9	837	824	2.04	23.06	0.13
Comm 14	13.3	831	813	2.12	23.21	0.12

[a] Produced with unwaxed fiber.

emulsion wax obtained from ExxonMobil NZ Ltd. Glacial acetic and lactic acids were technical-grade chemicals and, where stated, were used as hardeners. The MDF fiber was produced from *Pinus radiata* chips and was dried to 6 to 8 percent moisture content (MC) prior to resin application. Commercially produced 3-mm MDF panels (Comm, blowline) with three different resin application rates (5%, 12%, and 14%) using the same E0 UF resin were sourced directly from a New Zealand MDF manufacturer.

MDF panel preparation and testing

Mechanically blended laboratory (Lab) panels were prepared with dried MDF fiber using standard laboratory procedures. Resin, lactic acid hardener (where stated), and emulsified wax (0.5% [wt/wt] fiber) were premixed and applied to the fiber using standard mechanical-blending techniques. The resinated fiber (~12% MC) was formed into a mattress. The mattress was then hot pressed (19 s/mm) at 180°C to a target average density of 720 kg/m^3 using an optimized position-controlled program. For each panel set, at least three 260 by 290-mm panels were prepared.

Unpressed resinated fiber was also prepared as above. Where stated, this fiber was first resinated and either left at ambient temperature or cured by heating in an oven (105°C) for 30 minutes. Panel testing was done using AS/NZS4266:2004 (Standards Australia/Standards New Zealand 2004), and panel emissions were measured using standard protocols for the Japanese desiccator method JIS A 1460:2001 (Japanese Standards Association 2001) and were initiated within 2 to 3 weeks of panel manufacture.

Resin cure

Resin (20 g) was combined with glacial acetic acid (0.42 g) and stirred. The treated resin was placed in an open pan and then cured by heating at 100°C for 30 minutes.

Analysis

Cured resin, resinated fiber, and panel section samples were rapidly ground up (12 mesh) with a Wiley mill and extracted with water at 20°C for 24 hours. Samples were analyzed by a commercial analytical laboratory (Veritec) using a modified ASTM D1110-84 (ASTM International 2013) procedure as follows. For each sample, 1 g of ground material was stirred in 300 mL of water at 20°C for 24 hours. The residual resin or fiber was then isolated by filtering and drying (105°C). The extract was either concentrated to dryness in an oven or freeze-dried. Where stated, Kjeldahl methods were used to determine %N in extract solutions. Weight loss is defined as the mass loss from resin, resinated fiber, or panel upon extraction with water.

Nitrogen (%N) contents were determined directly with resin, fiber, or panel samples. Nitrogen analysis used a LECO CNS-2000 combustion furnace analyzing original and residue samples.

GPC used a Polymer Laboratories GPC and Polymer Labs Mixed-E column. The eluting solvent was dimethylsulfoxide (DMSO) operating at 50°C. Polyethylene glycol molecular weight (MW) standards were used and spanned the MW range of the UF resin components. Freeze-dried pure UF resins and panel extracts were evaluated. Reference extracts of water-soluble MDF fiber components were also analyzed.

NMR employed a Bruker 400-MHz NMR using standard ^{1}H NMR pulse sequences. Deuterated DMSO was used as a solvent for pure resin and extract (freeze-dried) samples.

Results and Discussion

MDF panel properties

MDF panels prepared in this study have properties typical of those manufactured either by blowline or mechanical blending (Table 1). Soaking in cold water for 24 hours resulted in panel thickness swell values of 10 to 26 percent, which is normal for each panel thickness and resin loading. Internal bond (IB) strength values ranged between 0.5 and 2.1 MPa and were also consistent with panel resin loadings for each panel type. Analysis of formaldehyde emissions were consistent with the E1- and E0-type UF resins used. However, like IB values, panel emissions appeared related to resin loading, with the greater E0 panel emission associated with the lowest (5%) resin loading (0.27 mg/liter).

Extractables mass balance on panel soaking

Using ASTM D1110-84 methodology, ground MDF panel sections were extracted with water to obtain a full mass balance for nitrogen-containing resin components extractable from the MDF panel samples (Table 2). Using this methodology, the extraction of UF resin components is rapid, and the high extractability of UF resin components was not due to hydrolysis (Table 3; Grigsby et al. 2014b). In comparing the mass and nitrogen contents (%N) of the original panel samples, extracted panel residues, and the isolated water fractions, the majority of the panel nitrogen

(92% to 98%) could be accounted for in all samples. This methodology also provided an indication of the quantity of nitrogen-containing resin components extractable from the panel samples on water soaking (Grigsby et al. 2014b). As an example, based on the nitrogen content (%N value) in the blowline-blended Comm 14 panel residue, some 50 percent of nitrogen or resin urea–containing components were removed by water extraction (Eq. 1). In other samples, the extracted resin component losses ranged between 48 and 66 percent based on %N contents in extracted panel residues (Tables 2 and 3). Using mass loss values, these same panels were calculated to lose some 52 to 68 percent of resin components (Eq. 2; Grigsby et al. 2014b):

$$\%\mathrm{N\ removed} = ([\%\mathrm{N\ original}] - [\%\mathrm{N\ extracted\ residue}]) \div [\%\mathrm{N\ original}] \times 100 \qquad (1)$$

$$\%\ \mathrm{Calculated\ resin\ loss} = ([\mathrm{resin\ mass\ loss}]/[\mathrm{resin\ loading}]) \times 100 \qquad (2)$$

where [resin mass loss] = [sample mass loss] – [fiber-only mass loss].

Table 2.—Nitrogen balance on extraction of commercial (Comm) medium-density fiberboard panels according to ASTM D1110-84 for 24 hours at 20°C.[a]

Mass balance nitrogen (1-g basis)	Comm 5	Comm 12	Comm 14
Resin loading (%)	**4.8**	**12.9**	**13.3**
% panel residue (mass)[b]	**89.4**	**85.6**	**88.2**
% panel extract (mass)[b]	**3.3**	**4.1**	**4.2**
%N in panel[c]	**1.94**	**5.23**	**5.41**
%N in residue[c]	**0.65**	**2.56**	**2.68**
N in extract (mg/liter)[d]	**132**	**268**	**272**
%N extracted[e]	66	51	51
N in 1-g sample (mg)[f]	19.4	52.3	54.1
N in residue (mg)[f]	5.8	21.9	23.6
N in extract (mg)[g]	13.2	26.8	27.2
%N extracted[h]	67.8	51.4	50.2
%N in extract[i]	40	66	64
Sum N in residue/extract (mg)	19.0	48.8	50.8
Difference	0.4	3.5	3.4
% difference	2	7	6

[a] Values in bold have been measured and other values were calculated.
[b] Filtrate and residue masses are reported on an ovendry (105°C) basis but are uncorrected for original fiber/panel %MC (moisture content).
[c] %N by elemental analysis.
[d] Nitrogen by Kjeldahl.
[e] % nitrogen removed from sample based on %N residue.
[f] Calculated from %N and mass values.
[g] Kjeldahl value per extract volume.
[h] Calculated using N (mg) values.
[i] Calculated on N (mg) and extract mass.

The MDF panel (Comm 14) was also extracted over shorter time periods to ensure that any resin component loss was not influenced by extraction time and resin hydrolysis (Dutkiewicz 1983, Kavvouras et al. 1998). Although extraction at either 2, 6, or 24 hours gave some variability in panel sample mass losses, the %N extracted values were similar (Table 3). This result indicates the water extraction of resin components to be relatively rapid, with the %N removed almost independent of extraction time, and resin hydrolysis (Dunky 1998) an unlikely predominant cause for nitrogen loss during extraction.

Resin curing

Given the relatively high extractability of UF resin components from MDF panels, extraction of cured, pure resin was evaluated. Acid-promoted cure of pure UF resin led to <2 percent mass loss after water extraction when curing with acetic acid (100°C; Table 3; Grigsby et al. 2014a, 2014b). In contrast, similarly heating the pure resin in the absence of a hardener resin led to ~48 percent mass loss of resin (Table 3). Despite the mass loss differences, extracted resin samples showed a minor enrichment of

Table 3.—Results of water extraction of selected medium-density fiberboard (MDF) panels, fiber, and resin samples according to ASTM D1110-84 for 24 hours at 20°C, unless otherwise stated.

Fiber/panel/resin sample	Resin (%)	%N Original	%N Residual	%N Extracted[a]	Extracted residue (%)[b]	Filtrate mass (%)[b]
MDF fiber only (pressed, no resin)	—	0.07	0.04	—	90.7	4.4
Control E0	9.1	3.69	1.28	65	88.1	7.6
Control E1	8.5	3.19	1.56	51	88.7	7.2
E1 resin + hardener	8.0	3.00	1.38	54	89.3	7.5
Timed extraction						
Comm 14, 2 h	13.3	5.41	2.81	48	88.7	4.9
Comm 14, 6 h	13.3	5.41	2.82	48	90.2	8.5
Comm 14, 24 h	13.3	5.41	2.68	51	88.2	4.2
Type of cure						
Uncured fiber (E0)	10.7	4.34	1.70	61	87.7	11.8
Cured fiber (E0)	10.8	4.36	1.47	66	92.6	13.6
Panel (E0)	11.5	4.67	1.66	65	89.0	4.9
Pure resin						
E1 resin (no hardener)		36.3	38.5	106	52.4	41.6
E1 + 3% acetic acid		37.2	39.9	107	98.1	1.1

[a] Represents an actual enrichment of nitrogen (106%) or proportionate loss of the formaldehyde component (methylene) on extraction of the cured urea-formaldehyde resin.
[b] Filtrate and residue masses are reported on an ovendry (105°C) basis but are uncorrected for original fiber/panel %MC (moisture content).

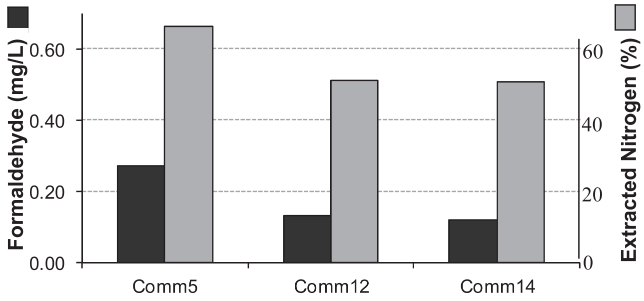

Figure 1.—A comparison of extracted nitrogen values (%N loss) and formaldehyde emissions for blowline medium-density fiberboard panels prepared with differing resin loadings.

nitrogen (urea species) in the residual, extracted resin material, which was indicative of a loss of UF resin methylene, ether components, or both.

UF resin was also variously cured on fiber to further compare cure achieved with pure resin or within the MDF panel. Mechanically blending E1 resin and fiber led to panel water extraction mass losses of ~7 percent (Table 3). A panel mass loss of 7.2 percent suggests a mass loss of ~3 percent due to resin or a calculated resin loss of ~33 percent (Eq. 2). There were no differences in the amount of nitrogen extracted (50%) from panels when a hardener was added to the resin. Furthermore, applying E0 resin to wood fiber and then either pressing fiber into a panel, curing as an unpressed mat (100°C), or leaving without any heating gave comparable results. While samples had 9 to 12 percent mass losses on water extraction, a comparison of %N in residual, extracted resinated fiber material revealed that similar levels of extractable nitrogen (~60%) were removed (Table 2). This evaluation shows that once applied to fiber, heating and cure may not influence the amount of extractable resin components.

MDF panel resin loading

The commercial MDF panel series produced with E0 resin was evaluated to distinguish whether the degree of resin extractability was influenced by varying resin loading (5% to 14% resin content; Table 2, Fig. 1). Extraction revealed panel mass losses were greater with higher resin loading. However, it is evident from using Equation 2 that this does not directly indicate the proportion of resin lost on extraction (Grigsby et al. 2014a, 2014b). Using %N values (Eq. 1) revealed that the 5 percent panel lost some 67 percent of nitrogen compared with values of 51 percent for the corresponding 12 and 14 percent panels, a result consistent with the wood matrix effect influencing resin cure (Xing et al. 2005) and that for resin–fiber combinations established over a greater (10% to 50%) resin content range (Grigsby et al. 2014a, 2014b). A comparison of panel formaldehyde emissions revealed a relationship ($R^2 = 0.95$) of greater formaldehyde emissions with panel resin component extractability (Fig. 1).

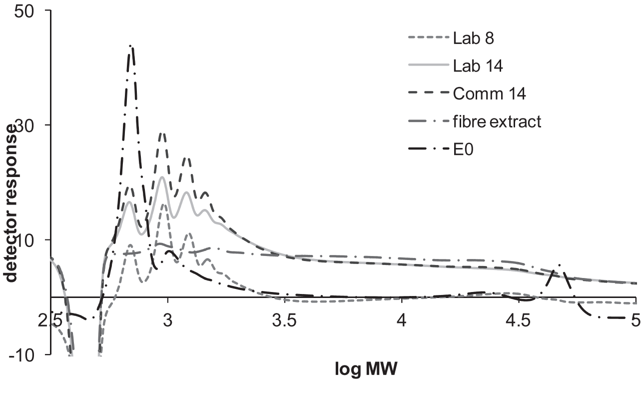

Figure 2.—Relative molecular weight (MW) profiles of the E0 urea-formaldehyde resin and various water extracts of medium-density fiberboard panels varying in resin loading and application, being either blowline (Comm 14) or mechanically blended (Lab 8 and 14) panels.

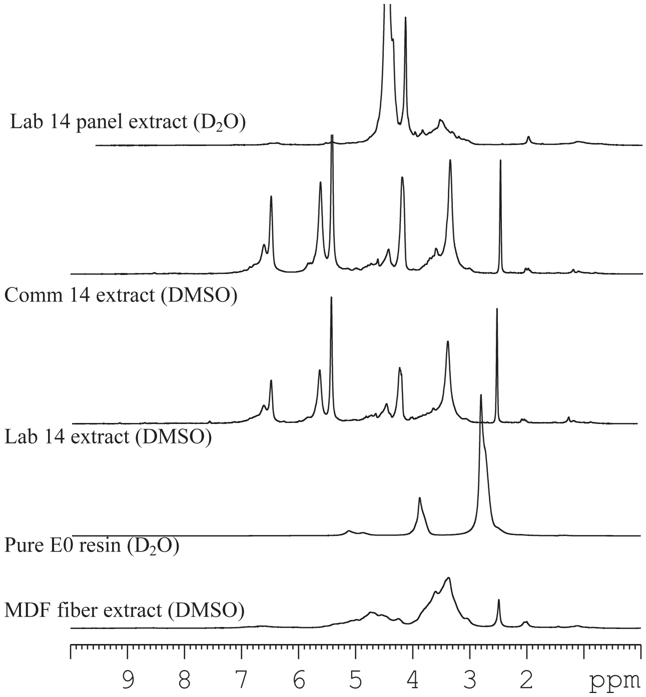

Figure 3.—^1H nuclear magnetic resonance spectra of the E0 urea formaldehyde resin and corresponding blowline (Comm) and mechanically blended (Lab) medium-density fiberboard (MDF) panel extracts. DMSO = dimethylsulfoxide.

Chemistries of extractable panel resin components

GPC analysis of panel extracts provided MW profiles of the extractable components from panels (Fig. 2). GPC revealed the panel extracts to consist of both wood fiber extracts and UF resin components, the latter dominating the extract MW profiles. MW profiles of the 14 percent Comm and Lab panel extracts showed that these UF resin components ranged from monomeric to low-MW oligomeric species. These oligomers extend to UF hexamers and, collectively, dominate the monomeric components when compared with the original E0 resin. Extracts of mechanically blended panels differing in resin loading (Lab 8% and 14%) had similar MW profiles and proportions of oligomers. No high-MW oligomeric or polymeric UF resin fractions were present in any panel extracts. Based on mass balance data and %N values

(Tables 2 and 3), it was evident that the low-MW oligomeric resin components were not present in the original UF resins in the proportions isolated on panel extraction. This suggests that oligomers were likely formed on panel hot pressing rather than by resin degradation or hydrolysis subsequent to panel manufacture.

The ^{1}H NMR spectra of the E0 resin and corresponding panel extracts from blowline (Comm) and mechanically blended (Lab) panels are given in Figure 3. Both the pure resin and the extracts show key peaks attributable to methylene and ether linkages (3.4, 4.2, and 4.5 ppm; Angelatos et al. 2004). The resin spectrum is dominated by the methylol species (2.8 ppm). As established by GPC and mass balance data, NMR further confirms that the extractable resin components dominate fiber extractives in panel extracts as evident by the relative size of carbohydrate peaks (3.5 and 4.5 ppm) and fractionation of this material in either D_2O or DMSO solvent. Moreover, the similar proportions of peaks due to $>$N-CH_2-X and NH_2 and –NH- chemical species (Angelatos et al. 2004) corroborate the GPC data that extracted resin components were composed mainly of low-MW UF monomers and oligomers, including methylenediurea-type species.

Conclusions

The results presented in this article and those available from the greater study (Grigsby et al. 2014a, 2014b) have demonstrated the high extractability of UF resin components from MDF panels on water soaking. Despite achieving satisfactory panel properties, the MDF panels bonded with E1 and E0 UF resins lose some 48 to 66 percent of resin components on water soaking, whereas fully cured pure UF resin loses $<$2 percent mass. These labile UF resin components were readily extractable and determined to consist of low-MW UF oligomers not originally present in the UF resin. It can be inferred that UF resin components likely chromatographically separate when applied to fiber and that, because of their dispersal throughout the wood fiber matrix, only limited amounts of resin components couple together. This implies that UF resin cross-linking is possible only in a limited proportion and that a significant proportion of UF resin does not fully cure and participate in panel bonding. Panel emissions are then linked to not only free formaldehyde but also these labile resin oligomers.

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