Resins in Panel Production

Editorial by NTL Chemical Consulting

Urea formaldehyde-based (UF) resins have, for many decades, been the standard adhesives used to bind the particles together in many composite wood products, including particleboards (PB), fiberboards (MDF), plywood (PLW), etc. As a result of their high reactivity and low cost, formaldehyde-based adhesives account for over 90% of the wood adhesives market volumes. However, due the poor water resistance of urea formaldehyde-based resins, a certain amount of melamine is added as a reinforcing component in UF resins, particularly for low-formaldehyde-emission panels and for moisture resistant boards. Additionally, phenolic resins (PF) deliver permanent resistance to water and climatic conditions, but are slow curing. They are, for example, mainly used for exterior/marine plywood and to some extent in oriented strand board (OSB) production.

In recent years, however, concerns have been rising about the health risks of formaldehyde. In 2004 the International Agency for Research on Cancer (IARC) classified formaldehyde as a 'known human carcinogen, Class 1B'. Concerns around formaldehyde emissions from wood-based panels, primarily those for indoor applications, is currently the most important driver for a move to formaldehyde-free adhesives. Pressure from the green building movement through market selection and certification programs, and emissions regulations from the California Air Resources Board (CARB), are leading manufacturers to look for ways to reduce formaldehyde emissions, or to eliminate formaldehyde entirely from product formulas. As a result of these pressures, the wood panel industry has adopted UF/UmF and MUF resins -- very low-emission resins – which reduce wood-based panels' formaldehyde emissions to a level close to that of natural wood.

In North America, polymeric methylene di-isocyanate (PMDI) is used mainly for OSB panels and, to a lesser extent, for PB and MDF panels. The cost of the PMDI resins is high, but they feature a faster reaction time compared to phenolic resins (PF); high bonding strength; and high resistance to water and climatic conditions. PMDI are considered to be 'formaldehyde-free' resin systems, but special precautionary protection measures must be adopted during production due to toxicity and their tendency to stick at metallic parts of the production line, so special handling measures are required. Today, the main adhesive systems used in the wood-based panels industry are UF, MUF, MUPF, PF and, to a lesser extent, PMDI resins, due to their high cost.

There has been strong research interest in bio-adhesives -- mainly soy-based adhesives --- in North America and China, and to a lower extent in Europe. The main reasons for this interest are legislation and the growing desire to use | more environmentally-friendly products which are not dependent on petrochemicals. To enable such a

Table 1: Limits for formaldehyde emissions from wood-based panels according to California Air Resources Board (CARB).

Material	CARB II (Phase 2)
Medium-density fiberboard (MDF)	0.11 ppm
Thin (<8mm) MDF	0.13 ppm
Particle Board (PB)	0.09 ppm
Composite Core Hardwood Plywood (HWPW-CC)	0.05 ppm
Veneer Core Hardwood Plywood (HWPW-VC)	0.05 ppm

transition for wood adhesives, the bio-based alternative must have properties comparable to the adhesives used today. Lignin, tannin, proteins and starch are some examples of the bio-based polymers that have already been examined as suitable for wood-adhesive applications. However, it has proven difficult to find an alternative that fulfills all the requirements for wood adhesives -- including availability; price stability; uniformity of properties; batch-to-batch or year-to-year performance consistency; and primarily the ability to compete in terms of cost. Lignin and starch are readily available, but they offer low reactivity and require modification. Protein (soy) is also generally available, and offers high viscosity. However, it has low water resistance and is sensitive to biological degradation, so denaturation is required. Tannin has good adhesion and good water resistance, and is fast curing, but geographically is not widely available. Starch emerges as one of the most promising raw materials for bio-based resins because of its relatively-lower cost and wide availability. Compared to other raw materials, starch can be easily extracted from many renewable agriculture resources. However, unmodified-starch contains a high number of hydroxyls, leading to weak wet bonding strength. Additionally, there is a lack of economically-viable crosslinkers for bio-adhesives that would satisfactorily increase reactivity, bonding strength and water resistance. The most common synthetic crosslinkers in use are glyoxal, hexamine, polyamides, isocyanates and epoxides. Moreover, there is little possibility of it is rather impossibility of substituting aminoplastic resins with natural products in the near- to medium-term because of the enormous annual volumes of urea formaldehyde resins used today around the world, and their relatively low cost.

In 1992, the California Air Resources Board (CARB) listed formaldehyde as a toxic air contaminant. The CARB regulations addressed concerns surrounding formaldehyde emissions from wood-based panels by implementing very low emissions standards for formaldehyde across a wide range of pressed board products. The federal government has adopted these regulations on a national scale. According to Standard ANSI A208.1 &2, the emissions limits were to be implemented in two phases. The initial Phase 1 (2009) standards are no longer in effect. The more stringent Phase 2 standards came into effect between 2010 and 2012. The emission limits determined by large chamber measurements in accordance with ASTM E1333 are shown in Table 1.

The CARB II regulations apply to products sold, supplied, used, imported for sale, or manufactured for sale in USA. While most domestic manufacturers have already been certified to the CARB standard, the bigger issue may be that a large number of imported products have yet to achieve certification. The regulations allow exemption from third-party certification for panel manufacturers using ultra-low-emitting formaldehyde (ULEF) resin systems (0.08 ppm for PB, 0.09 ppm for MDF and 0.11 ppm for thin MDF), or no added formaldehyde (NAF).

In May 2017, the US Environmental Protection Agency (US EPA) regulation to reduce formaldehyde emissions from composite wood products came into effect, but later the compliance date for all regulatory provisions was moved to December 2018. The California Air Resources Board (CARB) Airborne Toxic Control Measure (ATCM) to Reduce Formaldehyde Emissions from Composite Wood Products remains fully in effect, and CARB will continue to enforce the ATCM. CARB will accept products labeled as compliant with the US EPA TSCA Title VI regulation as also being compliant with CARB's Phase 2 formaldehyde emission standards, because the standards are identical.

European formaldehyde limits (Table 2) for wood-based panels are summarized in the harmonized standard EN 13986. At present the highest permitted formaldehyde emission limit for MDF, particleboard and OSB is at 8mg/100g board (E1 class). Germany, Austria, Denmark and Sweden require compliance at emission limits of 6.5mg/100g dry board. The European Panel Federation (EPF) decided to draw up its own standard (for example, . for PB: 4mg/100g; and for MDF: 5 mg/100g (thickness > 8mm) In 2011, EPF agreed on a reduction in formaldehyde emissions for CE labeled, uncoated wood panels for construction according

Table 2: Formaldehyde emission limits from wood-based panels according to European Standard EN 13986.

Board type	Emission class	Formaldehyde emission limit value	Test method
MDF, PB, OSB	E1	≤ 8.0 mg/100g oven dry board ≤ 0.1 ppm	Perforator EN ISO 12460-5 Chamber EN 717-1
Plywood (PW)	E1	≤ 0.1 ppm ≤ 3.5 mg/m^{2}h	Chamber EN 717-1 Gas analysis EN 717-2

to EN 13986. The new limit value must be determined using the chamber test method described in EN 717-1 and should not exceed 0.065 ppm. The Swedish multinational company IKEA also sets its own emissions limit: half of E1, thus called class E0.5 (0.05 ppm) (IOS-MAT-003), which is not yet recognized officially by the European Committee for Standardization (CEN),.

In Japan, stricter regulations were established concerning formaldehyde emission limits. In 2003, testing and certification requirements were established for composite wood building materials that contain formaldehyde. The Japanese Standards JIS A5905 and JIS A 5908 (Japan Industrial Standard: JIS; Japan Agricultural Standard: JAS) include four emission classes labeled as F*, F**, F***, and F****. The F** is more or less equivalent to European E1 class, the F*** and F**** classes cover much lower emissions than the E1 class. F**** emission is close to the emission of solid untreated wood, between 0.5 and 2.0mg/100g, or 0.008-0.01 ppm. Table 3 presents the emission classes for PB and MDF in Japan, as determined by Desiccator method according to JIS A 1460.

Finally, the regulations concerning formaldehyde emission limits for PB and MDF in Australia and New Zealand are shown in Table 4.

Over the past 30 years, emissions of formaldehyde from wood-based panels have fallen from approximately 3 ppm to less than 0.1 ppm. In 2014, the EU REACH Committee and the Classification, Labelling and Packaging regulation (CLP) reclassified formaldehyde as carcinogenic category 1B and mutagen category 2. New debate can therefore be expected in the future concerning even lower limits of formaldehyde emissions of wood-based panels.

Pressure from environmental and health regulators causes formaldehyde emission requirements to become more and more stringent. Resin suppliers must keep up with such legislation. NTL Chemical Consulting has been effectively engaged for many years in providing very-low-emission and cost-effective resin technology for its Asian customers for the manufacture of panels down to the level of natural wood (i.e. Super E0/F**** class) for export to the Japanese market.

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Table 3: Formaldehyde emission limits for wood-based panels according to Japanese Standards JIS A5905 and JIS A 5908 for PB and MDF.

Emission class	Formaldehyde emission limit value (Desiccator method JIS A 1460)		Formaldehyde emission limit value (Perforator method EN ISO 12460-5)
	mean	maximum	
F**	≤ 1.5 mg/L	≤ 2.1 mg/L	6.5 mg/100g oven dry board
F*** ≈ E0	≤ 0.5 mg/L	≤ 0.7 mg/L	2.5 mg/100g oven dry board
F**** ≈ SE0	≤ 0.3 mg/L	≤ 0.4 mg/L	1.5 mg/100g oven dry board

Table 4: Formaldehyde emission limits for wood-based panels in Australia and New Zealand according to Standards AS/NZS 1859-1 & 2.

Board type	Emission class	Formaldehyde emission limit value (Desiccator method AS/NZS 4266.16)
MDF, PB	E0	≤ 0.5 mg/L
PB	E1	≤ 1.5 mg/L
MDF	E1	≤ 1.0 mg/L
MDF, PB	E2	≤ 4.5 mg/L