

Polyurethanes and Isocyanates
used as adhesives in
Composite Wood Products

Dr Chris Phanopoulos



Contents

1.	A historical introduction to wood composites	03
2.	Introduction to the types of isocyanate- and polyurethane-based resins	07
3.	Mechanisms of adhesion and how isocyanate-based resins work	10
4.	Types of wood composites	18
4.1	Oriented Strand Board (OSB)	19
4.2	Medium Density Fiberboard (MDF)	28
4.3	Eco-binders	35
4.4	Engineered lumber	36
4.5	Plywood and Laminated Veneer Lumber (LVL)	41
4.6	Wood Fiber Insulation Boards (WFIB)	43
4.7	Other types of wood composites	45
	Acknowledgements	46
	References	47
	Norms and standards listed	48
	Glossary of terms	49

1. A historical introduction to wood composites

Wood is an abundant natural resource and the source of many natural polymers such as cellulose, lignin and hemicellulose. Despite the large number of trees, which provide wood and these other components – and regardless of the fact that the wood is a renewable resource – improvements to its efficient utilization are required. One of the main reasons for this is the increasing demands on land usage, diminishing areas for tree cultivation and forestry. Although there are ways of improving tree growth rates, they remain a relatively slow-growing crop. Additionally, there are growing environmental and ecological pressures limiting the social will to exploit, for industrial purposes, certain types of trees and forests. For example, old growth hardwood forests, which provide unique habitats for increasingly threatened flora and fauna, can no longer be harvested for industrial use.

For these reasons, methods to increase the efficiency of wood and wood composite utilization are continually sought.

Gluing of wood into composites has been practiced for most of the history of civilized man, even before resources were limited and before environmental aspects were considered important. The main reason for this is that composite wood assemblies allow for the efficient use of exotic, expensive and aesthetically pleasing but rare wood species. For example, highly valued wood veneers can be glued on to the surface of

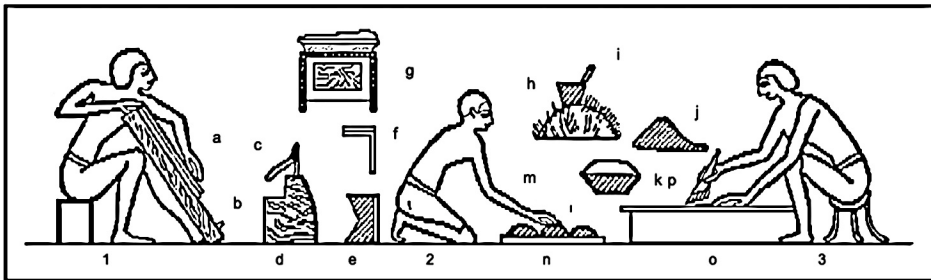


Figure 1. Schematic of an ancient Egyptian mural depicting the gluing of wood veneers. Mural record of veneering discovered in the sculpture of Thebes (scene from tomb of Rekhmire, Theban tomb 100), dated in the reign of Thothmes III, C. 1500 B.C. Reproduced from "Manners and Customs of the Ancient Egyptians," Wilkinson.¹

1. Workman exhibiting an example of veneering: Piece of dark-colored wood (a) applied to a lighter piece. (b) Adze (c) fixed in block (d) and from which b has apparently been cut (e) Ruler or straight edge. (f) Right angle or square. (g) View of a finished, veneer cabinet or stand.
2. Workman pressing sandbags, (l) and (m), probably heated, on plywood assembly (n) while the glue dries and sets. (h) Pot of glue, over fire (h,i) Lump or cake of glue (j) and (k) probably dish of crumbled glue.
3. Workman spreading glue on sheet of veneer. (p) Brush for spreading glue (or knife for cutting veneer). (o) Stand or table on which veneer is laid to spread glue (or to cut veneer).

cheaper, more abundant wood species. Such applications are predominantly of aesthetic value and require no more than permanence of bond without any significant mechanical performance. Some of the earliest evidence of gluing wood comes from early Egyptian artifacts. Figure 1 shows ancient Egyptian artisans gluing wooden veneers.

From those early times it was known that the use of glued wooden constructions overcame some of the problems associated with the anisotropy of wood and that more uniform properties could be achieved.

The improved uniformity of performance was gradually, over time, stretched to incorporate the use of waste materials from milling operations such as chips for the production of particleboards. The value of such wooden composites was rapidly recognized as it provided wooden articles of relatively uniform performance without excessive waste generation.

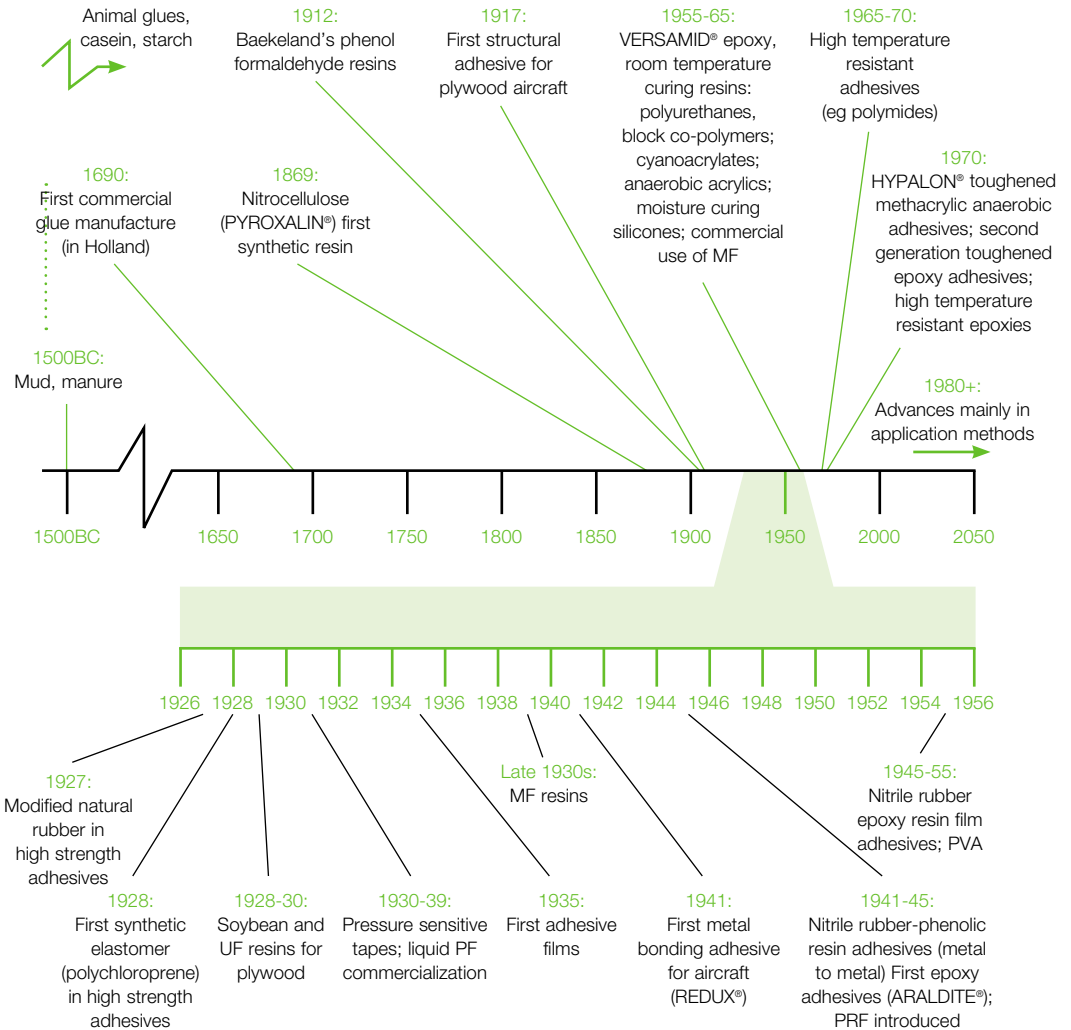
In time, the performance demands on the composites grew and the supply of local materials diminished and alternative composites to the traditional chipboard and plywood were sought. From these constraints, wafer board, oriented strand board (OSB) and medium density fiberboard (MDF) were born. Wafer board was a short-lived precursor composite to OSB.

As the use and types of composites developed, increasing demands were put on the resin in terms of how it can contribute to the production efficiency of the panels as well as how the final performance can be influenced.

In its earliest beginnings, biological sources of bonding materials were used. These included blood, milk (casein), bones and manure from animals and starch from plants. Mud was also used extensively for binding materials and is still employed today in some developing countries, for example, in the production of mud-bound straw used as bricks for domestic house construction. Resins based on these natural materials provided strong and durable bonds as long as the assemblies were not used in severe conditions and their use was limited to interior applications. The resins tended to embrittle, crack and delaminate as a result of exposure to sunlight, oxygen, and temperature and humidity changes. There was therefore a big demand to develop durable resins, which could withstand such adverse environmental conditions.

It was not until the 19th century however, that synthetic resins were invented and steps towards real durability were possible (see Schematic 1). By 1912 Baekeland's phenol formaldehyde (PF) resins were developed and being used commercially. These resins were originally used in molding applications, but their adhesive potential was quickly recognized. Resin developments (new materials and application techniques) evolved quickly from the end of the First World War.

Schematic 1: Timeline of resin developments^{2,3}



By the late 1950s, rapid developments in adhesive systems had ended. Since then, developments have mainly concentrated on improving the performance of existing technologies. These improvements have focused on processing ease and speed, use rate and final panel properties. Additionally, the number of applications has increased to include demanding applications such as structural engineered lumber.

Gluing of wood is currently a large worldwide industry, utilizing both large volumes of wood and resins. Resin types used however, vary from region to region, as do the species of wood. The types of resins used to some extent reflect the types of wood composites made and the designated end use.

By far the largest resin technology in terms of volume is urea-formaldehyde (UF) resin⁴. The success of UF resins can be attributed to their low cost and high cure speed. However, due to the nature of the chemistry, UF resins can only be employed in interior quality composites since hydrolysis of the resin is relatively easy. Hydrolysis of UF resins results in loss of bond integrity. It also results in the production of formaldehyde. Formaldehyde emissions have become the subject of much concern. As such, measures have and are being taken in the form of legislation or improved industry standards to reduce the level of formaldehyde emitted from wood-based articles. Melamine modified urea formaldehyde (MUF), melamine formaldehyde (MF), melamine urea phenol formaldehyde (MUPF), phenol formaldehyde (PF) and phenol resorcinol formaldehyde (PRF) all provide increasing improvements in resistance to hydrolysis and in reducing or eliminating formaldehyde emissions. In this order however, resin costs increase dramatically. But in applications that require hydrolytic resistance (for example in exterior use applications), these resins are used successfully and their market share is large. Resorcinol formaldehyde is so resistant to hydrolysis that it is used in a number of demanding wet applications such as boat construction and other marine applications. The chemistry of the formaldehyde-based polycondensate resins has been frequently and adequately reviewed by other authors, and the interested reader is directed to these for further information.

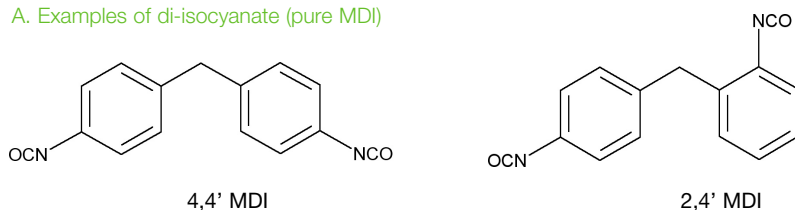
Formaldehyde-based polycondensate resins have a long history of use in composite woods. The use of isocyanate-based resins started in the second half of the last century. Despite its relatively short history, the use of isocyanates has grown continuously as a result of the outstanding performance levels (e.g. processing ease and speed, physico-mechanical properties including modulus and strength and environmental performance including durability, moisture resistance and no resin origin formaldehyde emission) that can be realized, even at very low resin consumption rates. Some of these aspects will be referred to in detail in the following sections.

2. Introduction to the types of isocyanate- and polyurethane-based resins

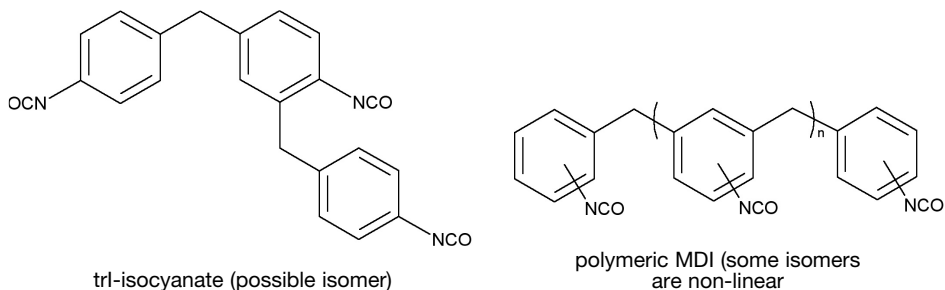
Isocyanate and polyurethane resins are generally based on the family of products called methylene diphenyl di-isocyanate, or MDI for short. These materials are characterized as moisture curable aromatic polyisocyanates. Examples of different types of MDIs are illustrated in Schematic 2. Some of the more common types of curing reactions are shown in Schematic 3. For more detailed background information about the different grades of isocyanates that are available, as well as more information about the chemistry, the reader is directed to The Polyurethanes Handbook⁶.

Schematic 2: Examples of MDI molecular structures.

A. Examples of di-isocyanate (pure MDI)



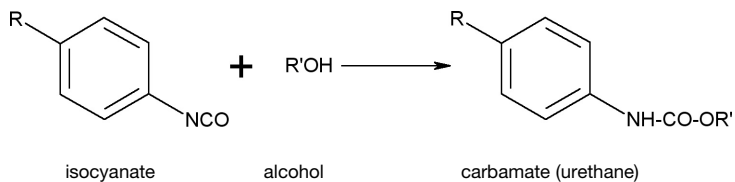
B. Examples of higher oligomer MDIs



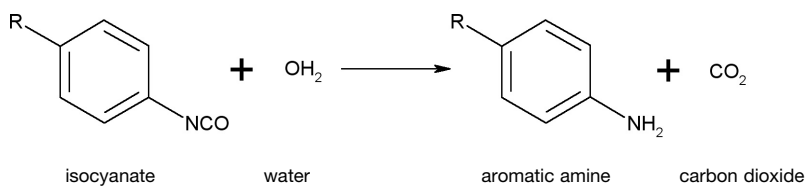
Commercially available pMDI is usually a mixture of di-, tri-, tetra- etc. isocyanates of specific molar ratios.

Schematic 3: Some characteristic reactions of isocyanates.

A. Urethane formation

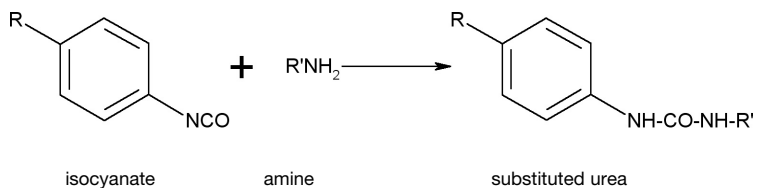


B. Blowing reaction

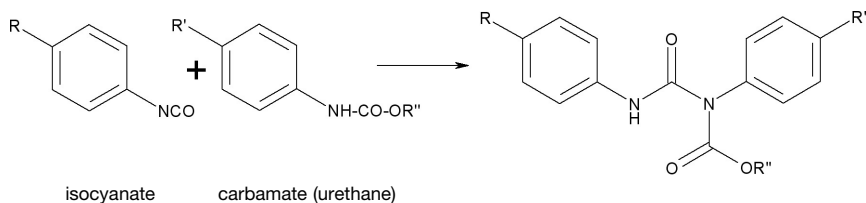


Carbamic acid forms as an intermediate, but this decomposes releasing carbon dioxide giving rise to the amine.

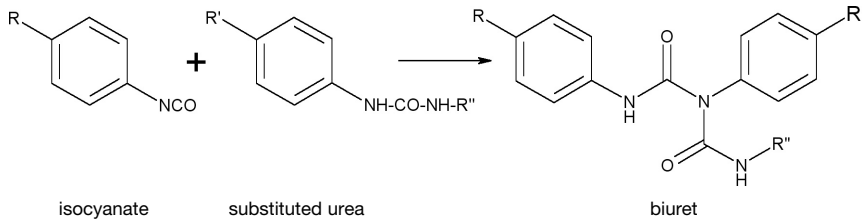
C. Urea formation



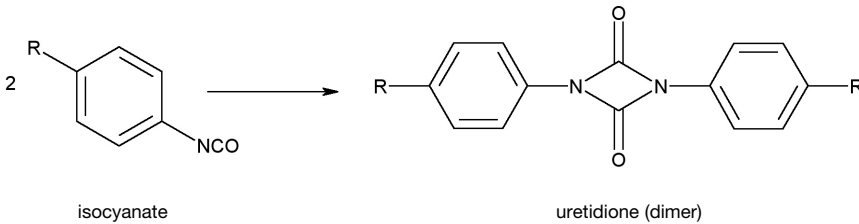
D. Branching reactions – allophanate formation



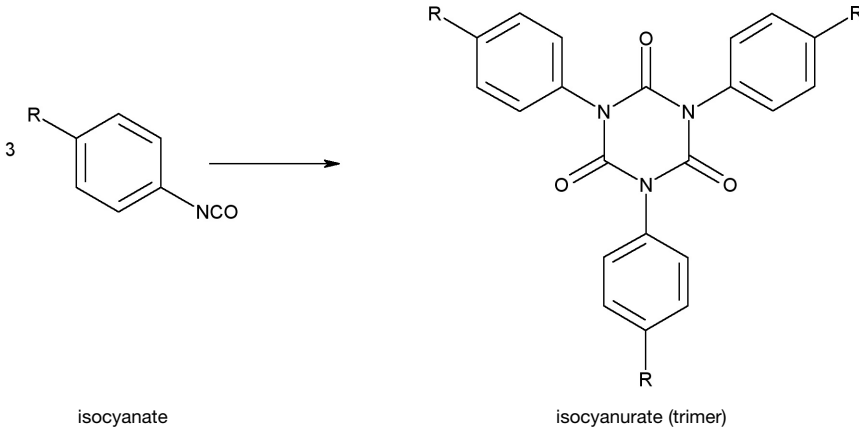
E. Branching reactions: biuret formation



F. Isocyanate-isocyanate reactions: dimers



G. Isocyanate-isocyanate reactions: trimers



Isocyanates used in wood composite manufacturing vary depending on the type of wood composite and the required end performance. Unlike the polycondensate resins, isocyanate-based resins are comparatively insensitive to the species of wood being employed for the various composites. Generally speaking, for the smaller particle composites such as medium density fiberboard (MDF), particleboard (PB) and oriented strand board (OSB) (see figure 2), polymeric grades of methylene diphenyl di-isocyanate (or pMDI) are used. Often, however, the isocyanate will be chemically modified in some way to provide some performance differentiation, either from a processing perspective or from a desired physico-mechanical performance perspective.



Figure 2. OSB (left) and MDF (right) panels (face view).

For example, a recent and effective resin innovation to aid the processing for OSB is a modification that increases the speed of cure, thus shortening the pressing time. With MDF on the other hand, the specific processing method requires that resins with increased water affinity are used. Chemical modification by grafting of hydrophilic groups onto the MDI molecule allows this desired effect to be realized.

Further, large particle wood assemblies – for example, plywood, glulam, parallel strand lumber (PSL) etc – can not be bonded with standard pMDI other than under selective conditions. For such assemblies, formulated resins are needed. Formulated resins (which may be physically blended or chemically modified isocyanates) are useful in these applications due to specific processing needs (e.g. room temperature cure for I-beams, long open assembly times for glulam and tack for laminated veneer lumber), as well as exact mechanical performance requirements (e.g. gap filling, resistance to creep).

Examples of these types of composites are shown in Figure 3.

3. Mechanisms of adhesion and how isocyanate-based resins work

In order to explain some of the particular performance characteristics of isocyanate-bonded wood, it is desirable to outline some of the more important features of the specific mechanism of adhesion of isocyanates to wood. A more detailed discussion on the mechanisms of adhesion in general, and with regard to isocyanates specifically, can be found elsewhere^{5,6,7}.

In summary, there are five main theories of adhesion. Most adhesive applications can be attributed to one or a combination of several of these theories. The main theories of adhesion are⁵:

- (i) formation of primary bonds, such as covalent or ionic bonds, between the adhering bodies,
- (ii) formation of secondary bonds, such as hydrogen bonds, dipole-dipole interactions, van der Waals forces etc. between the adhering bodies.



Figure 3. I-beam and glulam.

- (iii) electrostatic forces can form due to the flow of electrons from one bonding component to the other
- (iv) mechanical interlocking can result when a liquid flows into the cracks and other macroscopic irregularities of a solid and then hardens, so holding the two bodies together
- (v) formation of a diffusion interphase, which can occur when mutual inter-diffusion of adhering bodies occurs, generating an indistinct boundary between the two bodies (e.g. welding of metals or plastics).

While the manufacturing details of the different wood composites vary in detail (see below), the general principles of how isocyanates stick seem to be universal. In the following outline of the bonding processes, examples are mainly drawn from solid wood bonding in general and OSB in particular.

Isocyanates are applied to the surface of the wood particles (fibers, chips, strands, veneers, lumber) by an appropriate method. Resin application methods vary depending on the type of composite. Typically this is done by spraying, pouring or rolling. The resin, as for all adhesion systems, is then required to wet the surface and spread over it.

Isocyanates wet wood reasonably well and uniformly. The contact angles are reasonably low and in most applications the achieved level of wetting is adequate. Typical contact angles for isocyanates on various lignocellulosic substrates are given in Table 1. It should be noted that on porous substrates such as wood, penetration of the resin into the wood makes measuring the contact angle difficult (see Figure 4). Therefore the recorded values in Table 1 are after one minute of contact time.

The resin then spreads and penetrates into the wood. The extent of penetration of the resin (see example in Figure 4) depends greatly on the species of wood, moisture content, type of surface cut, whether the isocyanate is applied to early or late wood, the age of the surface and so on. Furthermore, it depends on the viscosity, surface tension and reactivity of the resin used, as well as on the prevailing temperature and to some extent the relative humidity.

Substrate	Region	Contact Angle/ $^{\circ}$
Aspen	earlywood	14
	latewood	14
	early/latewood interface	57
Pine	earlywood	29
	latewood	19
	early/latewood interface	54
Wheat	outer culm	55
	inner culm	35
	leafy sheath	50
	node	68

Table 1. Contact angles of isocyanate on various lignocellulosic surfaces

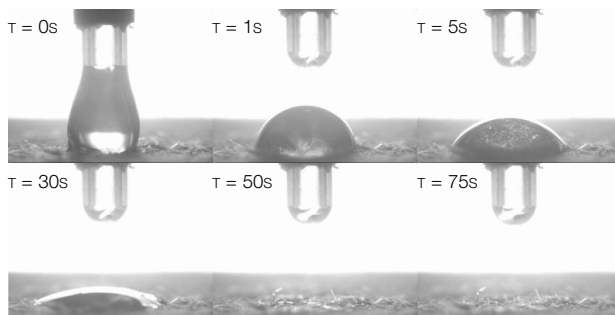


Figure 4. Series of optical micrographs showing the changing shape and penetration of resin droplets that have been in contact with wood surfaces over a period of a few minutes.

Isocyanate-based resins have been found to penetrate rapidly and to a reasonable depth. In many cases the depth of penetration has been found to be up to 1mm or more. In many traditional gluing applications, such deep penetration is often seen as inefficient use of the resin. In extreme cases, such excessive penetration can result in the phenomenon called glueline starvation where there is insufficient resin left at the interface between the two substrates to be bonded. Starved gluelines do not adhere particularly well. In the case of isocyanates however, the resin penetration has been determined to be of critical importance. The Huntsman research laboratories in Everberg, Belgium, have found that a

depth of at least 0.25-0.3mm must be reached for the resin to impart adequate adhesive strength. This distance is greater than the typical depth of the wood surface damage due to the cutting process. The resin is required to consolidate the weak damaged layer, which would otherwise cause a deterioration in performance due to it being a fragile layer in the assembly.

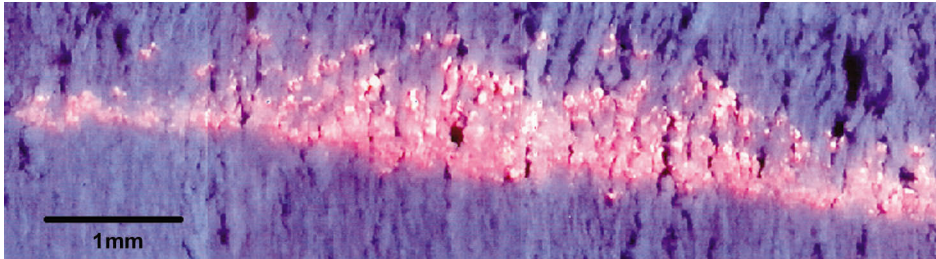


Figure 5. Optical fluorescence micrograph of isocyanate penetration into tangentially cut pinewood. A single drop of resin is applied to a defined surface of a pre-conditioned wood sample. A second similarly cut and conditioned wood is placed on top and the assembly is pressed and heated to effect cure of the resin. The assembly is then sliced perpendicular to the surface on which the resin was applied. The slices are then observed under an optical microscope. Using a combination of specific incident light and the employment of fluorescing additives to the resin (red), high contrast resin/wood (blue) images can be realized.

Once spread and penetrated, the resin seems to react predominantly with water to produce a comparatively highly cross-linked polyurea matrix.

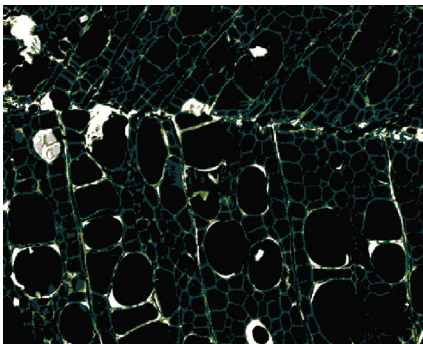
It has been found that penetration of resin beyond the 'critical' 0.3mm level is still beneficial. Additional strength (in some cases) can be realized but, more importantly, the resistance to thickness swell of the wood is improved. Increasing the depth of penetration (as well as the spread) of the resin increases the volume of resin-modified wood. This is responsible for the excellent thickness swell performance characteristics of isocyanate-bonded wood.

There will be regions where the resin does not penetrate beyond the damage layer of the wood (as illustrated in Figure 5 at the edges of the penetrated region). Even in these regions the resin has still been found to benefit the thickness swell performance as the resin in these areas acts as a barrier, restricting the movement of water, which would cause the swelling.

Figure 5 is an image from a single slice of a droplet of isocyanate cured between two pieces of wood. The true penetration behavior is three-dimensional. In this particular case, the shape of the penetrated resin is similar to a relatively flat, slightly elongated disc. The shape and orientation of the penetrated resin has a strong impact on the derived performance of the composite.

By controlling the wood (species, moisture content, grain angle, age of surface, extractives contents and distributions) and the quality of the resin (surface tension, reactivity, viscosity, hydrophilicity) a wide range of penetrated resin 'shapes' can be achieved. The penetrated resin, once cured, can be seen as a type of inhomogeneous filler that has a definite shape. The preferred shape is dependent upon the particular performance required. As an example, in lap joints the highest performance in terms of strength is achieved with 'cigar-like' penetrated resin shapes orientated in the direction of the strain. This is because such shapes will minimize stress concentrations at its tips.

The penetration behavior of isocyanate resins into wood can be investigated in more detail using x-ray microscopy, which provides much higher spatial resolution than optical microscopy as well as providing chemical information⁸. Figure 6 is a characteristic x-ray micrograph of isocyanate in wood and shows that the resin penetrates and interacts with the wood in a specific manner. The resin moves into the wood and preferentially locates itself in one of four specific regions. Firstly, some of the resin remains at the wood-to-wood interface. It should be noted, however, that although the resin accesses the inner cell wall surfaces of fractured cells, only the inner surfaces of the large vessel lumen are wetted. The inner cell wall surfaces of the more abundant parenchyma and tracheid cells are not wetted. Secondly, the resin runs into the ray cells, which are exposed on the macroscopic wood surface. Thirdly, the resin can be seen as discrete isolated drops at some distance from the wood-to-wood interface in the lumen of the large vessels. It is most probable that the resin accesses the lumen of the cells exposed on the surface since the grain angle will not always be perfectly parallel to the macroscopic surface of the wood. Having entered the lumen of the vessels, the resin can flow along the inner cell walls some distance. The resin appears to wet the inner cell wall of the vessels rather well, but does not always fill the cavity. Finally, the resin can also be seen in the connecting pits between cells. Resin does appear to fill the free space of the pits and does wet the primary cell walls in these areas.



Notice the location of isocyanate:

1. At the interface between the pieces of wood.
2. In the ray cells.
3. On the inner cell wall surfaces of the lumen of large vessels.
4. In the connecting (simple) pits of the vessels.

The anatomical features referred to are described in detail in Desch H. E.⁹

Figure 6. Typical x-ray micrograph of resin penetrated wood (resin appears bright)

From x-ray microscopy studies there is an indication of the possibility that the resin reaches a fifth location within the wood: inside the cell walls. The evidence for this is

tentative. The resin in the cell walls is of course not evident in images such as that shown in Figure 6. But spot x-ray absorbance spectra from the cell walls indicate the possibility of isocyanate in the cell walls, Figure 7.

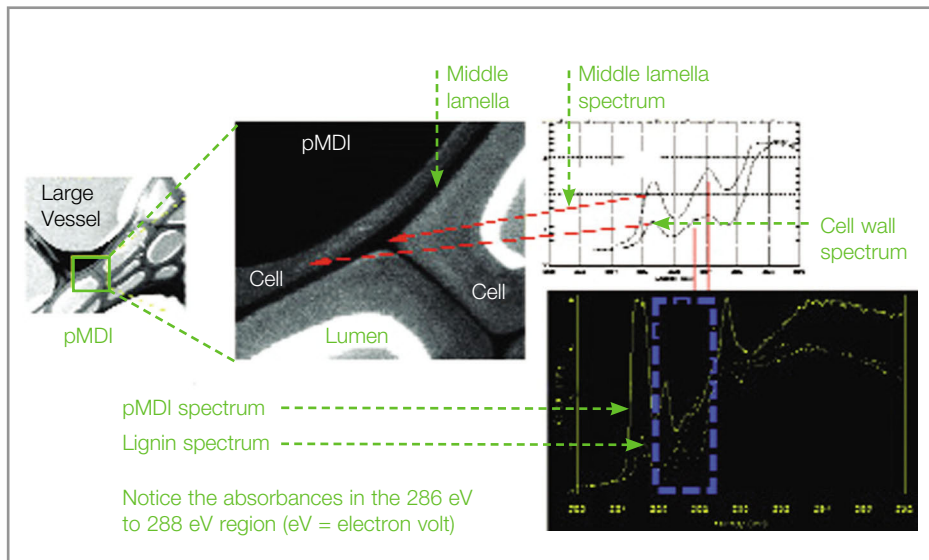


Figure 7. X-ray transmission images near bonded interface + spectra showing pMDI associated with cell wall, but not with middle lamellae.

Supporting evidence that resin enters the cell walls comes from solid state NMR spectroscopy^{7,10,11}. Using careful experimental processes it is possible to assess the relaxation times of various nuclei both of the resin and of the wood. Examples of such results are shown in Table 2. As can be seen, the relaxation times of both the lignosic and the hemicellulosic components of the wood are strongly affected by the presence of isocyanate. To achieve this level of influence, there needs to be some intimacy between the resin and the wood components. Lignin is of course found both inside and on the outside of cell walls, and so the inferred interaction could be occurring either in the middle lamellae or inside the cell walls. However, hemicellulose is only found in appreciable quantities inside the cell walls, strongly suggesting that the interaction is within the cell walls. This interaction is probably a secondary bond formation (van der Waals forces, dipole-dipole interactions, London dispersion forces or possibly even stronger hydrogen bonds) between the isocyanate and the wood component.

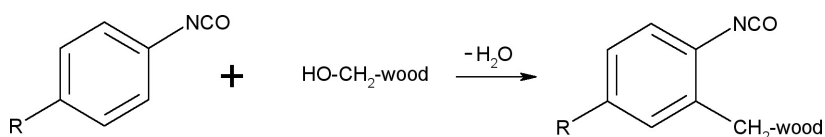
Fourier transform infrared (FTIR) studies of the interactions of isocyanates with wood have not shown any significant chemical interactions, except to show changes to some of the aromatic ring substitutions in the 700-900cm⁻¹ region of the spectrum. It is unclear from the work whether the aromatic rings involved were of wood or isocyanate origin. Surface analytical studies of isocyanate-treated wood have helped to clarify the results¹². Laser

		$^1\text{HT}_{1\rho}$ (ms)			
	Chemical shift ppm	Aspen (neat)	PF coated aspen (cured*)	Isocyanate coated aspen (uncured)	Isocyanate coated aspen (cured*)
Lignin	56	7.8	7.4	3.8	12.3
	155	9.2	8.2	3.8	11.0
Cellulose	65	8.6	8.1	8.5	11.6
	73	9.1	8.9	6.9	12.7
	75	8.7	9.3	7.1	11.6
	84	8.2	8.9	6.2	11.6
	89	10.7	11.8	6.3	13.9
	105	8.9	9.4	6.4	13.3

*cured = 140°C

Table 2. Relaxation data ($^1\text{HT}_{1\rho}$) of wood components comparing neat wood with isocyanate on wood. Work completed by Marcinko and Rinaldi.^{7,8}

ionization mass analysis (LIMA), a sensitive, surface-specific analytical tool, reveals the formation of a family of wood and isocyanate reaction products. New mass fragments were seen when di-isocyanate was cured in the presence of wood or lignin. The observed mass fragments are consistent with the formation of a methylene bridge product formed by the condensation of a methylol phenolic wood component to an aromatic ring of the isocyanate (see schematic 4).



Schematic 4: Methylene bridge formation between wood and isocyanate by isocyanate-aromatic ring substitution.

This type of structure has been proposed by others, most notably by Pizzi¹³. This product would explain the changes in the FTIR spectrum, which are consistent with a change in the ring substitution of aromatic ring groups. To be seen in infrared, the abundance must be quite high, and so it is suspected that the ring-substituted reaction product is easily and abundantly generated. But the question remains as to which components of wood are involved in the reaction. Model compound studies with LIMA showed that lignin definitely could be a contributing component. If this is true, then the isocyanate must have accessed either the components inside the cell walls or those in the middle lamellae. Why then, is

there only tentative evidence of the presence of isocyanate components in the cell walls by x-ray microscopy? The problem is most likely due to the fact that in the x-ray study, water-cured pMDI, or polyurea, was used as the model for isocyanates. If the isocyanate in the cell walls was predominately not cured to polyurea, but some other material, the reference material (polyurea) used for the x-ray mapping would not be appropriate. Extended studies using alternative references are needed to clarify the situation.

There is further evidence suggesting that isocyanates access the interior of cell walls. In diffusion studies in which thin slithers of wood are immersed in pMDI, initially typical Fickian type diffusion is seen to occur (Figure 8). The coefficient of diffusion of isocyanate into wood is large. It is several orders of magnitude faster than that of other common wood resins such as urea formaldehyde and phenol formaldehyde⁵, and even faster than water. After the initial Fickian uptake, an equilibrium or steady state is established. With prolonged immersion, however, a second uptake stage is seen followed by a subsequent loss of mass or net outward diffusion of components from the wood. The extent of mass loss exceeds the potential mass loss due to the reaction of the isocyanate with the water in the wood. The second uptake stage is thought to be due to a morphological change in the wood. This is induced by the concentration gradient of the isocyanate and which subsequently allows for further entry of isocyanate. It is suspected that this second stage of isocyanate diffusion is into the wood matrix itself (i.e. into the cell wall).

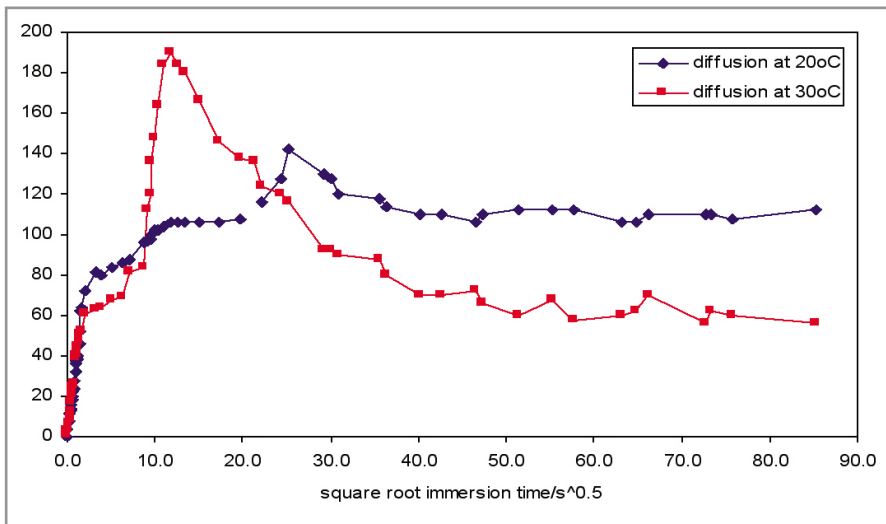


Figure 8. Diffusion profile of isocyanate (pMDI) into aspen at different temperatures (image generated in Huntsman R&D labs).

The subsequent mass loss is due to the leaching of low molecular weight wood components (extractives), which dissolve into the now continuous liquid isocyanate path and move out of the wood. These components are in fact reactive with isocyanates and the resultant effect is that the isocyanate reservoir solidifies.

The long-term strength performances of variously extracted types of wood, which have been bonded with isocyanates, indicate that the extractives that migrate, from the wood into the isocyanate, toughen the otherwise brittle water-cured polyurea. This enables the resin to withstand and accommodate the high levels of stress that the glue line experiences when water ingress into the wood occurs.

Hence at a certain loading, isocyanates wet, spread and penetrate into wood to produce a type of polyurea mechanical interlock. The resin does however penetrate into the cell walls from the cell lumen, where it interacts with the lignins and hemicelluloses via a series of secondary bonds as well as by the formation of primary bonds with the lignins. At the same time, some wood extractives are removed from the wood into the resin and interact to provide some elasticity to the otherwise brittle polyurea. In this way, an anchored (hydrogen-bonded, ring-substituted reaction product) diffusion interphase of moisture-cured isocyanate (polyurea) is established and is responsible for the binding of the wood particles.

It should be noted that this is the mode of isocyanate bonding for most wood composites in which 'solid' wood particles are employed. The situation with wood fibers, as in MDF, is slightly different. In the fiberization process, the wood is cleaved in the middle lamella and so the isocyanate, which is subsequently added, contacts — at least initially — a loose lignin-rich surface. The complete bonding process involved in this case has not yet been fully elucidated.

4. Types of wood composites

There are many different types of wood composites manufactured and used for a wide range of different applications. Each requires a different property set. It is not the purpose here to cover all the different types of possible composites. However, a few examples of the types of composites will be covered to demonstrate the range of processing steps and conditions which resins must accommodate to be used in these applications. Table 3 below summarizes the types of composites made, the geometry of the wood particles used, as well as some of the common resins used in their production.

Composite name	Abbreviation	Primary wood particle type	Typical dimensions (mm)	Types of resins employed	Examples of applications
Oriented strand board	OSB	Strands	100 x 40 x 0.4	pMDI, PF	Roof, floor and siding panels. Web stock in I-beams
Medium density fiberboard	MDF	Fibers	Individual wood cells up to a few mm length	MDI, MUF, UF	Window frames, cabinetry, furniture
Particleboard	PB	Chips	10 long	pMDI, UF	Cabinetry, furniture
Plywood	PLY	Veneers	1-3 thick	UF, PF, PRF	Boats, furniture, construction including roofing
Laminated veneer lumber	LVL	Veneers	1-3 thick	PF, PU	Broad span structural element
Glulam	Glulam	Lumber	50 x 100 cross section	PF, PU, PRF	Broad span structural element, vertical supports, bridges
I-beams	IB	Lumber flanges and panel webs		PU, PF	Floor joints
Strand lumber	PSL	Strands	150 x 25 x 3	PF	Broad span structural

Table 3. Summary of types of typical wood composites, primary wood particle geometries and types of resins used.

4.1 OSB

4.1.1 Manufacturing process

Trees are usually harvested within about 150-200 kilometers of a manufacturing plant. They are felled and the branches removed in the field. The logs are then typically transported by road or rail to the manufacturing site and stored in wood yards in stacks until needed. The preparation of logs prior to cutting into strands varies from mill to mill, but essentially they go through the same steps. The logs are cut to standard lengths and in some instances soaked in large water baths or ponds. These baths may be heated (especially in cold/freezing climates to thaw the wood) and may contain biocides and other additives. This process softens the wood, which makes subsequent processing steps easier. The logs are brought into a de-barker, removing the outer and inner bark of the tree. Subsequently logs are conveyed to stranding knives.

Several logs can be stranded simultaneously. Logs are aligned length-wise and rotating blades are driven across them perpendicular to their length. Consequently the generated strands have radial or tangential faces with the grain direction parallel to the faces. Higher relative tangential face content strands can be generated if logs are allowed to rotate during the stranding operation.

Stranding knives are mounted on a rotating disc. They are angled out of the plane of the disc so as to cut strands of approximately 0.3-0.8mm thickness. The blades also have perpendicular cutting edges, which define the length of the stands. They are typically of the order of 7-15cm long and 2-5cm wide.

The strands are then separated into two streams (face and core) and conveyed to dryer tubes. They make several passes through the dryers (single pass dryers are common in Europe, while triple pass dryers are more common in the U.S.). The dryers are set at temperatures up to 600°C. The heated gases usually have depleted oxygen levels to reduce the potential of combustion and thermal oxidative degradation of the wood.

The wood is usually dried to an average moisture content of about 4-12% (depending on whether the strands are face or core quality and depending on the type of resin to be used; PF resins require drier wood than isocyanate resins). However, since the strands are flash dried, the water from the strand surfaces is stripped out of the wood. This leaves the cores of the strands relatively wet and the surfaces relatively dry.

The strands are then blended with resin. Often the strands are held in bunkers after drying to cool them and to allow the residual intra-strand moisture to equilibrate; otherwise any resin applied will contact relatively hot and dry wood surfaces. To blend the resin with the wood, the wood strands are fed into rotating drums, which are angled to allow tumbling of the strands while still moving them forward. A number of resin dispensing heads are positioned along the length of the rotating drum through which the resin and other materials such as waxes can be applied.

The dispensing heads commonly employed are called 'spinning disc-heads'. Such heads provide excellent resin distribution over the surfaces of the tumbling strands.

In addition to the resin, waxes are also sprayed on the wood. Waxes are employed as aids to improve the water resistance and thickness swell of the wood. There are different philosophies as to whether resin or wax should be sprayed first on the wood. Biocides, fire retardants, dyes and so on may also be applied to the wood at this stage.

The resin loading applied is such to achieve a particular set of desired properties. Typically for MDI resins, loadings are of the order of 1.5-8% by weight based on the oven-dried weight of the wood, this is compared to 6-12% for liquid PF resins. Wax loadings are usually around 1%.

The resinated strands are then conveyed to the mat lay-down system. In OSB production, it is common to lay down several layers of strands, such that the strands (and hence the grain direction of the strands) in each layer are orientated perpendicular to each other. Typically three layers of strands will be laid – two outer or face layers and a single core layer. The bottom-most face is laid down first, such that the strands are orientated parallel to the conveying direction. The core layer is laid above the bottom face and is orientated perpendicular to the conveying direction. Finally the top face is laid down with the same orientation as the bottom face. The face layers are usually of a higher moisture content than the core.

Mat lay-down and orientation is achieved by tumbling the strands over a series of comb-like rotating wheels. Strand dimensions can vary enormously and the orientating combs are not 100% effective, which can result in some degree of disorientation. This misalignment remains in the final product and is responsible for lowering the final performance. Much effort is made by the machine suppliers and the panel producers to maximize the strand orientation.

Commercial products vary in the face-to-core ratio as a matter of producer preference and depending on the application and final thickness of panel required. However, as a general rule of thumb, the thickness ratio of face-to-core is between 40:60 to 60:40.

The mats are then conveyed into a heated press. Presses may be multi-daylight static presses (Figure 9), or, increasingly common are continuous presses (Figure 10). Presses are heated to 170-240°C and the mats pressed to target thickness at a certain rate and for a specified time. Standard OSB thicknesses range from 3mm to over 30mm. During pressing, water in the higher moisture content surface layers is converted to steam and it is believed that this is conducted into the core of the mat by virtue of the temperature, vapor pressure and water gradients. The condensation front of steam is thought to be the principal heating mechanism of the mat. The heat activates the curing of the resin, which in the case of MDI is the reaction of the isocyanate with the water and steam (as well as with some of the wood components). Typically for isocyanate-based resins, core temperatures are required to reach 105-120°C to achieve the desired degree of cure throughout the thickness of the mat. The total pressing time will depend on the overall moisture content, mat density, resin loading, resin type, press platen temperature, wood species and so on.

Controls on the pressure cycle are required to accommodate wood decompression and any panel spring back due to relaxation phenomena. The press is then opened and the edges of the consolidated panels are trimmed and conveyed to cooling racks. After this the panels are cut to the desired dimensions.



Figure 9. Multi-daylight press.



Figure 10. Continuous press (seen in background).

4.1.2 Resin developments

For most applications, polymeric MDI is employed in OSB manufacture. However, since pMDI is a strong adhesive for both wood-to-wood bonding and wood-to-metal bonding, it cannot be used easily in the face layers of the mat. This is because it can cause sticking of the mat to the press platens. Several options to overcome this problem have been found:

- (i) Lay-down of weakly-bound wood flour facings which are subsequently sanded off
- (ii) Lay-down of thin UF-bonded outer face layers which may subsequently be sanded off
- (iii) Use of PF or MUPF resins in the face layers
- (iv) Application of external release agents such as soaps and waxes, which are sprayed either on the press platens or on the mat.

While each of these approaches has been successful in a number of manufacturing plants, they do have particular problems associated with them. These problems fall principally into five categories:

- (i) Economic – build-up of material on the platens can cause extended down time for clean up; speed of application, subsequent cure or post treatments can reduce output; waste volume is often increased; the approaches require additional material purchases
- (ii) Hygienic – dust and atomized sprays are released into the atmosphere potentially causing health and safety issues
- (iii) Efficiency – incomplete coverage of the resin technology, or in the case of external sprays if chips flip over, then wood adhesion to the platen is not avoided
- (iv) Aesthetics – soap sprays can cause a darkening of panel surfaces. PF faces have dark red/brown spots across the panel surface and these can be deemed as visually less pleasing than the light, wood colored panels generated with isocyanate resins (Figure 11)
- (v) Properties can be compromised e.g. fungal resistance and thickness swell.

Increasingly, the most commonly adopted approach is the use of soap spray. This works well although there is often a risk of incomplete spray application and strand flipping. However, in conjunction with continuous presses, which 'peel' the panels from the presses, such technologies are being used successfully.

Despite the cost-effectiveness of these technologies in avoiding press sticking, efforts are being made to develop innately releasable isocyanate resins. This approach is by far the most attractive to avoid press sticking, as it would avoid:

- (i) performance compromise
- (ii) the need for additional production steps
- (iii) the cost of additional hardware investment
- (iv) application failures.

The releasable isocyanate resin would need to maintain high wood-to-wood adhesion and all other expected isocyanate benefits (cure speed, high mechanical properties, excellent water resistance and so on) but would also need to show zero adhesion to the metal press platens.

Various approaches have been evaluated and developed with varying degrees of success. But a truly releasable isocyanate without performance compromise still eludes the industry.

Figure 11 shows the aesthetic benefit of employing releasable isocyanates without the use of external soap sprays. 100% MDI-bonded panels produced using standard soap release systems give darker colored panels, which is probably due to the thermal decomposition of the soaps during hot pressing. Use of releasable isocyanates gives rise to light colored panels. Huntsman has developed a range of tailored soap release systems (e.g. I-Release® OSB 9110) for different presses, which show no or very limited thermally-induced discoloration.

In addition to external soap systems, Huntsman has developed a series of internal additive systems (I-Release® OSB 9120 and I-Release® OSB 9122) based on synthetic polymers which, provide excellent release from, for example, conti presses – without compromising performance and build-up on the belt.



Figure 11. Surface color of soap released OSB panel (right) and new development releasable isocyanate technology (left).

A second area of much interest is also related to production improvement, namely faster cure. At manufacturing sites where production rates are limited by the press capacity, accelerated cure of resin would be extremely beneficial. Commercial success has already been achieved with regard to resins with increased cure rates.

Huntsman Polyurethanes has developed a range of resins that exhibit accelerated cure rates and can reduce pressing times by as much as 10-20%. An example of this type of resin is I-Bond® OSB PM 4310. Second generation fast cure systems, so called enhanced fast cure (EFC) are now being developed which will cure even faster.

Such resins are only beneficial if the derived performance is not compromised and the performance standards expected from isocyanate resins are still realized. By controlling the types of interactions and chemistry of cure appropriately, the acceleration of cure is achieved without compromising any of the mechanical performance characteristics of the derived panels. Table 4 lists some of the typical cure and performance characteristics of some of the accelerated cure resins in comparison to those of reference or conventional isocyanate-based resins.

Methods to increase the cure rate of isocyanate resins could potentially adversely impact the storage stability of the resin. However, the fast cure or 'FC' range of isocyanates from Huntsman is tailored to minimize this and typically a six or even 12-month shelf-life is still achieved.

Property	Unit	15 mm thick panel		18 mm thick panel	
		Standard isocyanate-based resin	Fast cure isocyanate-based resin	Standard isocyanate-based resin	Fast cure isocyanate-based resin
Density	Kg.m ⁻³	612	611	608	607
MOR – major	MPa	25.9	29.5	30.6	28.3
MOR – minor	MPa	17.1	21.6	13.0	16.1
MOE – major	MPa	5385	5154	5684	5160
MOE – minor	MPa	2784	3059	2147	2719
Internal bond strength	MPa	0.39	0.50	0.49	0.42
Rate increase	%	-	10	-	15

Table 4. Cure and mechanical properties of accelerated-cure, isocyanate-bonded OSB compared to standard isocyanate-bonded panels.

4.1.3 Uses

OSB panels are used for a number of applications. These include construction (roofing, siding, flooring, I-beam webbing), hoarding, packaging and concrete molding. In the US, by far the biggest use is in domestic house construction. Increasingly, such composites are also being employed for similar applications in Europe, especially in the UK and Germany and to a lesser extent in the Benelux. Some examples of these applications are illustrated in Figures 3 and 12.

In most of these markets, OSB competes mainly with plywood. This should not be a surprise as both OSB and plywood are wooden composite panels composed of layers of wood with perpendicular grain directions. Since OSB is somewhat cheaper to produce and does not require the use of large diameter (old growth) trees, it could be expected that OSB would have captured the plywood market. There is evidence that, at least to some extent, this is the case. OSB has grown rapidly in line with the increase in demand for composite

wood panels. Plywood demand however seems to have somewhat stagnated, although it remains a large and valuable market. Recently cheap, yet adequate quality, softwood plywood imported from South America into North America and Europe has resulted in some increase in plywood consumption.



Figure 12. OSB roofing.

In all the application areas mentioned, OSB meets or exceeds the requirements and national performance standards, allowing the substitution of traditional plywood by OSB. This is somewhat true whether PF-or isocyanate-based resins are employed. However, isocyanates remain preferable because:

- (i) Isocyanates cure at faster rates than PFs and so increase press capacity
- (ii) Isocyanates give rise to aesthetically advantageous clear gluelines
- (iii) The resin loading of isocyanate-bonded panels is significantly lower than with PFs and storage facilities at production sites can be minimized
- (iv) Isocyanates can adhere to wetter wood compared to PFs, so reducing:
 - a. the energy consumption of manufacture – less drying and therefore lower energy consumption and
 - b. the volatile organic compound (VOC) emissions – less drying lower decomposition rates of wood and removal of less volatile organics. This makes isocyanate-based resins rather more environmentally friendly than alternative resins,
- (v) Isocyanate-based resins do not emit formaldehyde and so meet the zero formaldehyde standard of panels
- (vi) Isocyanate-based resins easily pass the EN300 standard.

4.1.4 Typical performance characteristics

All properties of panels depend on:

- (i) Quality of wood (species, defects, dimensions)
- (ii) Density of panel, density profile and geometry of sample
- (iii) Resin loading (and resin type)
- (iv) Stress application direction (with regard to grain direction of wood)
- (v) Thermal, strain and moisture history of panel (both during manufacture and during post conditioning/service).

Strength and thickness swell are of particular importance for the main performance requirements of panels. Typical performance requirements of specific panel types are listed in Table 5.

Performance Characteristic	Units	Standard	Standard pass value	I-Bond® resin	
Resin loading	%			2-4	4-6
Panel thickness	mm		10-18	10-18	10-18
Panel density	gcm ⁻³	EN 323	0.65	0.64-0.67	0.64-0.67
Parallel MOR	N.mm ⁻²	EN 310	22	33-42	39-45
Perpendicular MOR	N.mm ⁻²	EN 310	10	11-12	>15
Parallel MOE	N.mm ⁻²	EN 310	3500	5500-6300	6000-6700
Perpendicular MOE	N.mm ⁻²	EN 310	1400	>1500	>1900
Internal bond strength (dry)	N.mm ⁻²	EN 319	0.32	0.35-0.45	0.7-0.9
Internal bond strength (wet aged)	N.mm ⁻²	N1087-1	0.13	>0.15	>0.15
Thickness swell	%	EN 317	<15	5-10	6-10

Table 5. Typical performance values of isocyanate-bonded OSB panels.

Performance characteristics such as core and face strengths (for tongue and groove joints), nail-ability, nail and screw holding strengths, machinability, durability and creep (for example, ASTM D-3434, EN ISO 9664/1995, EN 302-2/1992 and ASTM D-4680-98), fungal (for example, ASTM D-4300-98a and D-4783-98a) and insect resistance and fire resistance, can be important depending on the application.

With regard to biological and fire resistance, the required properties are usually achieved by incorporating appropriate additives. Care must be taken in the selection of these additives as many classes of potential chemicals can interact with the resins. This interaction can reduce both resin binding capability and the biocidal (or fire resistance)

efficiency of the additive. However, there are many compatible additives that give acceptable performance without compromising resin or additive efficiencies, for example borates. For further information, the reader should contact resin suppliers.

With specific regard to fungal and bacterial resistance, isocyanates do seem to have a slight advantage over competitive resins such as phenol formaldehyde. Fungal infestation is strongly dependent on panel swelling due to moisture ingress. Isocyanate-bonded panels show a delayed onset of swelling and generally swell less than PF-bonded panels. Fungal infestation is thus slower and to a lesser degree. In this way isocyanate-bonded panels demonstrate a limited fungistatic property.

4.2 MDF

4.2.1 Manufacturing process

Wood from a wide range of sources is used in the production of medium density fiberboards (MDFs). Newly harvested wood remains the principal source for this application. However, industrial and even domestic waste wood can be employed. Industrial wood waste may be both raw lumber and composite wood.

Initially the wood is reduced to rough chips just a few centimeters in length. It is soaked and heated (150°C) and conveyed into a refiner or defibrator. By a combination of moisture, temperature, pressure, pressure changes and mechanical grinding, the chips are reduced to individual wood fibers. The defibration step and the quality of the derived fibers have a significant impact on the final panel properties. In the ideal state, the wood is separated into its individual fibers without causing excessive damage such as reduction of the natural fiber length (species dependent). If conditions are not controlled, the defibration step can result in non-separated fiber bundles and/or truncated fibers with fully exposed lumen. Hence the conditions of defibration are critical.

Fibers are generated by cleaving adjacent cells from each other by 'breaking' the connecting middle lamellae layers. In this way, small wood fibers are generated which have a high surface lignin content.

From the defibrator, fibers (Figure 13) are discharged directly into the so-called 'blowline'. The blowline is a long and narrow pipe (ca. 100-120mm diameter), which conveys the fibers from the refiner to a dryer. The fibers move through the blowline in a turbulent manner at very high speeds. The internal pressure of blowlines ranges from 6-10 bars at the refiner end and the temperature varies along the length from about 180-190°C at the inlet to 50-100°C at the outlet. Super-heated high pressure steam is employed to generate the temperatures.



Figure 13. Wood fibers used in MDF production.

Despite high moisture levels and temperatures in the blowline, it is at this point that resins are typically added. The preferred resin addition position along the blowline varies from producer to producer. Generally, the resins are pumped into blowlines at high pressure either just after the refiner or just before the outlet at the dryer. Some producers prefer early resin addition as this maximizes the mixing of the resin and fibers due to the turbulent flow in the blowline and the large number of fiber collisions – both of which help distribute the resin. Others prefer to add the resins late in the blowline to minimize potential pre-cure due to heat and moisture.

Isocyanate-based resins for this type of panel production are usually modified to help improve the heat and moisture tolerance of the resin, hence emulsifiable MDI, or eMDI, is employed. Emulsified isocyanates have improved water stability/compatibility and with gentle mixing form reasonably stable emulsions in water (see Figure 14). The emulsifiable resin is pumped via a static mixer where it is emulsified in water and then metered into the fiber flow in the blowline. It has been found that emulsified isocyanates can be added anywhere along the length of the blowline without any detriment to the final product performance. Typically for isocyanate-based resins, 3-7% by weight of resin is added to the wood furnish.

It is perhaps surprising that isocyanates can be injected into blowlines without causing a subsequent loss of adhesive quality. High temperatures and moisture levels would normally be expected to cause hydrolysis of the isocyanate functionality, the -NCO group, which would then react further with more isocyanates to ureas. However, since the residence time of the isocyanate in the blowline is only a few seconds, only very limited consumption of resin occurs at this stage.



Figure 14. Comparative photograph: dispersions of isocyanates in water after standing for 40 minutes. The image on the right shows the instability of standard isocyanates while the image on the left shows the emulsion stability of emulsifiable isocyanates.

Initially it was believed that turbulent flow of fibers resulted in a good distribution of the isocyanate when it was injected just after the refiner. However, as has been said above, resin addition at the end of the blowline does not adversely affect performance and so must also result in good distribution.

Waxes as release aids and thickness swell reducers and other additives are also usually added to the fiber at this stage.

Blowlines may become blocked due to the deposition of material on the walls. Blockages usually occur at bends in the blowline where fiber flow is reduced and eddies form.

Analysis of blockage material reveals that it is composed mainly of lignin, fiber and resin. Due to high temperatures and moisture levels, the lignin on the surface of the fibers is mobile. The lignin separates from the fiber and is deposited on the blowline inner walls in regions of reduced flow rate. This phenomenon occurs even without the addition of resin. When resin is added, it may get deposited on the isolated lignin, effectively gluing it in place and into which wood fibers can also get deposited. The rate of material deposition increases, reducing the diameter of the blowline; complete blockage can then be rapid.

It is therefore vital that blowline pressure is monitored continuously so blockages can be removed as soon as they start forming.

Based on the observation that resin becomes associated with the lignin – which is initially deposited, so aggravating the blockage – attempts to add the resin at the end of the blowline were evaluated and found to be acceptable. Without resin, the deposited lignin can still ‘flow’ to some extent and is eventually pushed out of the blowline, although blockage can still occur under certain circumstances.

The fibers, steam, resin and other additives exit the blowline and enter a dryer tube. The wet, resinated fibers are exposed to a stream of hot, dry air, lowering the moisture content

of the fibers to under 10-12%. The fibers are conveyed to bunkers after being separated from the large volume of air and moisture via cyclones.

From the bunkers, the fibers are conducted to a fiber lay-down system. The fibers are dropped by gravity onto a conveyor system to a pre-determined thickness depending upon the target density and thickness of the panel to be prepared. The fiber lay-down is often informally described as a snow-like effect, since the fibers and loose bundles of fibers gently float down from the lay-down unit onto the conveyor system.

The loosely formed mat may then be pre-pressed to help the integrity of the mat. The conveyor system conducts the mat into the press. Again, presses may be single or multi-daylight static or continuous. Presses that are continuous are commonly used in MDF production, especially in Europe where production capacity is largest. A range of different types of continuous presses are used in MDF manufacture.

Presses are typically heated to 175-220°C. Application of pressure is usually controlled to achieve a relatively uniform density profile or a smooth u-shaped profile without discontinuities. Press times are similar to those used in OSB or slightly slower. Decompression steps are used at the end of the press cycle to avoid explosive decompression and consequent “blows” or loose non-adhering internal voids in the panels.

Due to the nature of the wood particles, release of the panel from the press platen surfaces is usually easier than that of OSB. Even so, internal release aids such as Montan wax or more recently synthetic waxes are often employed. These waxes are added to the fibers in the blowline usually below 1% based on dry wood weight. Some isocyanate systems are pre-blended with release agents for this application. Internal release agents such as I-Release® MDF 9132 are used in MDF production.

From the press, panels (Figure 15) are conveyed to cooling racks, after which they are trimmed and, if necessary, sanded to the required thickness. The total process is illustrated in Figure 16.



Figure 15. Example of MDF panel after sanding and trimming.

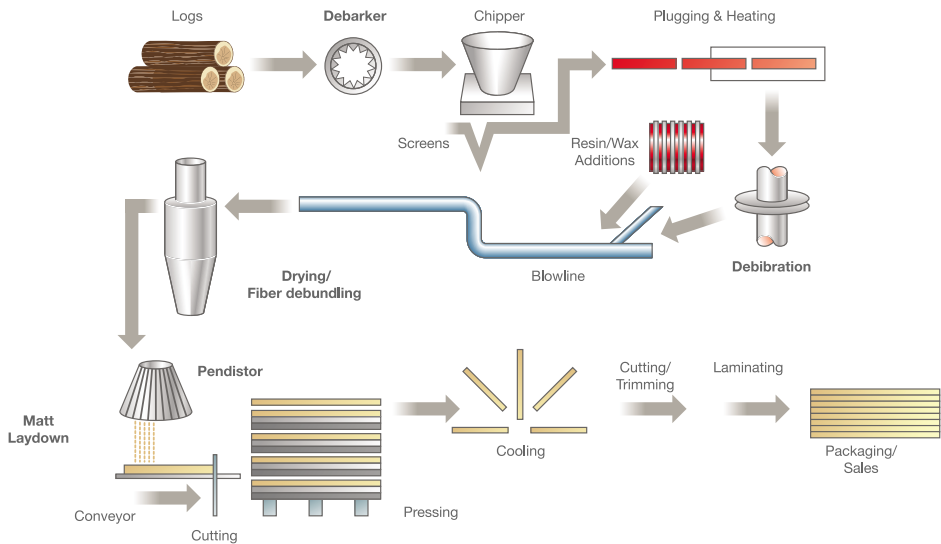


Figure 16. Schematic of MDF production process showing blowline and dryer.

Alternative blending techniques are currently being assessed. One of the forerunner techniques is dry blending, in which the wood is refined as described above and then dried. Only after the drying step is resin then added. One of the complicating issues with this approach is the need to de-ball loosely held together bundles of fibers in order to get a good distribution of the resin on the wood.

As mentioned above, emulsifiable isocyanate (I-BOND[®] MDF EM 4330) is well suited for the production of MDF. In some instances, it is possible to use unmodified, polymeric MDI when appropriate blending and resin application equipment is used. However, generally speaking, the performance of panels made using eMDI is superior to those made with pMDI. Comparative studies of these two resins have consistently shown that eMDI outperforms its parent pMDI (see Table 6). The reasons for this are not fully understood, but it is most probably due to differences in resin distribution on the one hand and the nature of the water interaction and affinity with the different types of isocyanate (during the blending and drying steps) on the other.

Property	Units	eMDI	pMDI
Resin loading	%	4	4
Density	gcm ⁻³	0.72	0.71
Internal bond strength	Nmm ⁻²	0.65	0.55
Internal bond strength after wet aging	Nmm ⁻²	0.2	0.15
Modulus of rupture	Nmm ⁻²	0.43	0.35
Thickness swell	%	6	8

Table 6. Comparative mechanical performance of eMDI vs. pMDI-bonded MDF.

4.2.2 Resin developments

Developments in release technologies have been mentioned above in the context of OSB production. In MDF, release is equally important. Montan wax, a relatively old but successful release technology, has been employed with isocyanate-based resins for MDF. Under normal circumstances, the wax is pre-blended with the isocyanate and is therefore an internal release system. The availability of this wax is becoming increasingly limited and alternatives are required. Within the last few years, other solutions based on synthetic waxes have been successfully developed and employed when pre-blended with the isocyanate resin and when applied separately.

Although release of MDF panels is comparatively easy (compared to, say, OSB), when choosing an appropriate release agent it is not only release from the press that needs to be addressed. Post manufacture treatments and production steps must also be considered, especially post treatments related to panel surface quality. Paintability and lamination are two such examples. The release technologies mentioned above do not adversely affect these production steps.

In MDF, urea formaldehyde (UF) and melamine modified urea formaldehyde (MUF) are the most abundantly used resins. The nature of UF resins renders panels suitable for interior quality only. Modification with melamine improves quality and performance as well as reducing formaldehyde emission levels. However, UF resins cure extremely rapidly (4-8 seconds/millimeter (s/mm) compared to 8-13 s/mm for MDI). The melamine modification does reduce cure speed, but generally such resins remain marginally faster than isocyanates. However they remain lower performing and less durable than MDI-based systems. There is therefore a desire to employ faster isocyanate quality resins in MDF to increase mill capacity and reduce fixed costs. Such technology is now becoming available.

Fast cure resins are particularly important in thick panel production. In the production of such panels, steam injectors are used in the presses to help heat the thick panels to enhance cure rates.

Some of the properties of UF- and MUF-bonded panels can be improved by hybrid resin technologies, in which UF/MDI and MUF/MDI systems are used. Such hybrid systems result in reinforced panel properties compared to the neat formaldehyde-based polycondensate resins¹⁶. This technology is used with success.

Another area for future resin development is linear expansion, which is expansion of a panel in the plane of the surface. Unlike thickness swell, increasing the resin loading of a panel does not improve the linear expansion. The mechanism by which wood expands in this way is not known.

4.2.3 Uses

MDF panels have excellent 'machinability' properties. They can be cut, profiled, engraved and otherwise shaped and decorated with a fine, well-defined finish. Many of the applications of MDF exploit this characteristic.

Applications include furniture, cabinets and shelving, door paneling and frames, window frames, flooring and signposts. As always, the specific application defines the thickness, density and density profiles required as well as the type and quantity of resin. For instance, garden furniture and kitchen cabinets require low thickness swell performance at a range of thicknesses; internal door panels are thin (2-3mm) and do not require significant resistance to swelling; sign post and shop front signs require both low thickness swell and linear expansion.

Due to the excellent machinability of MDF, panels are also used extensively in do-it-yourself (DIY) applications.

Another use of MDF is molded parts. After blending the fibers with resin, they can be used in molding applications to make complicated shapes and parts with well-defined and finished surfaces.

4.2.4 Typical Performance Characteristics

MDF panel performance ranges from internal non-structural applications to semi-exterior applications. To succeed in this range of applications a wide variety of performance capabilities are needed. Typical performance characteristics based on resin loading and panel thickness are given in Table 7.

Performance Characteristic	Units	Standard	I-Bond® resin
Resin loading	%		4-6
Panel thickness	mm		10-12
Panel density	gcm ⁻³	EN 323	0.7-0.8
Parallel MOR	N.mm ⁻²	EN 310	0.4
Parallel MOE	N.mm ⁻²	EN 310	3500
Internal bond strength (dry)	N.mm ⁻²	EN 319	1-1.5
Screw holding (face)	N	EN320	1400
Thickness swell	%	EN 317	4-8

Table 7. Typical performance characteristics of MDF panels.

4.3 Eco-binders

Eco-binders and agricultural waste panels are the generic names given to the resin and the non-wood lignocellulosic composites respectively. The types of panels that can be made with these materials depend on the physical dimensions of the raw material and the types of fibers. Generally speaking, composites based on non-wood lignocellulosic materials are reduced to chip, particle, strand or MDF-type panels.

A wide range of raw materials can be used in this application, examples of which are wheat straw, rice straw, rice husks, sugarcane bagasse and hemp. Each of these substrates has particular associated difficulties, but generally speaking the issues can be summarized as:

- (i) Dust – high dust contents reduce mechanical integrity of panels and ‘consume’ high levels of resin
- (ii) Low-density ‘pithy’ material – pith contents in bagasse and wheat straw can be high. Pith is a low-density material, which again ‘consumes’ high levels of resin and weakens the final panel
- (iii) Silicon content – silicon levels can be extremely high in rice husks and rice straw and in the nodes of wheat straw culms. Resins do not wet such materials well and so lead to points/regions of poor adhesion

- (iv) Mixed surface qualities – this is particularly applicable to wheat straw, which is often split, revealing the inner surface. Resins are then required to adhere to both a waxy outer and a porous inner surface of the same piece of furnish. This potentially results in poor wetting or starved gluelines or weak boundary layers
- (v) Low lignin contents – as detailed above, isocyanates have a particular affinity towards the aromatic content of lignocellulosic materials but are relatively incompatible with the cellulose components. All the non-wood substrates have only relatively low lignin contents (and high cellulose contents), rendering them ‘difficult to bond’
- (vi) Bio-deterioration of stored raw materials. Since most of these products are harvested only once or twice per year, manufacturing sites need six monthly/yearly stock levels. Due to the low lignin contents (and low sugar in the case of bagasse) the materials are highly susceptible to fungal and bacterial infestation.

Despite these drawbacks, isocyanate-based resins do perform relatively well with such substrates and can give rise to higher mechanical performance panels than with other resins. Even so, mechanical performances are comparatively low compared to equivalent wood-based composites. Further, the panels can continue to be prone to fungal infestation.

Due to the relatively low properties and biological susceptibility, non-wood lignocellulosic panels of this type are typically used for interior cabinetry and furniture (after lamination) only, although some packaging quality panels can be produced.

The specific manufacturing procedures are essentially the same as for wood equivalent types, whether manufacturing MDF or chipboard or particleboard. Recent developments have helped improve the low panel performance such as the development of methods to split straw culms. There have been various developments in ways of removing waxy outer layers of the substrates and these have been reasonably successful, at least at the laboratory scale.

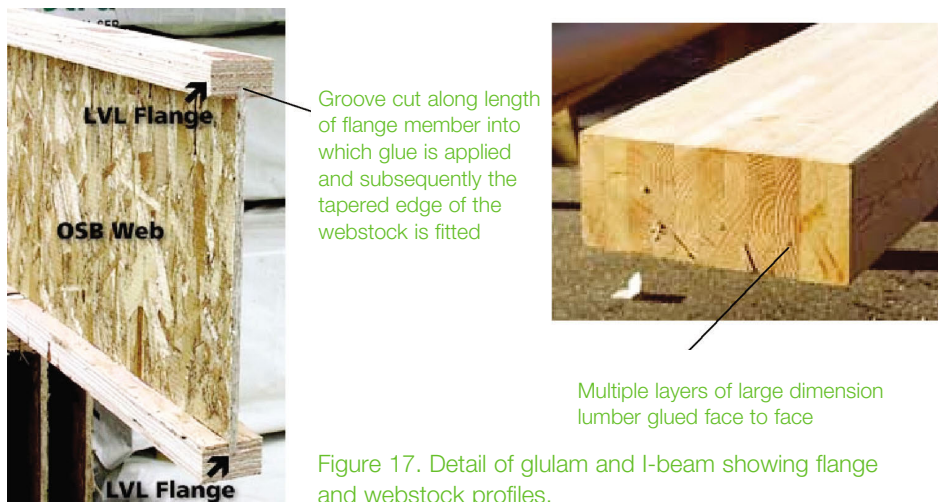
4.4 Engineered lumber

Engineered lumber is a generic name given to a range of composite constructs. The products are characterized by their load-bearing capabilities. The range of products in this category of composites includes glulam, laminated veneer lumber (LVL), oriented strand lumber (OSL), timber strand or parallam and I-beams. Such structures are often required to be long (tens of meters) and this is achieved by finger jointing individual pieces together. For this reason, finger-jointing applications are also considered as engineered lumber. Engineered lumber composites compete with solid sawn wood, which is increasingly unavailable in the quality and dimensions required. This application is therefore experiencing a large market growth.

4.4.1 Manufacturing processes

In manufacturing a structural lumber assembly, the wood is first conditioned to a defined moisture content and is usually freshly cut to the required dimensions. Resin is then applied. Resin application methods vary between producers and depend on the type of engineered lumber to be fabricated. Examples of resin application methods include ribbon, curtain and roller transfer coating as well as brush and spray application methods. Resin loading depends on the type of resin being used, but for phenol resorcinol formaldehyde resin is typically $200\text{-}400\text{ gm}^{-2}$, while for polyurethane-based resins the loading is typically $90\text{-}150\text{ gm}^{-2}$. A second piece of wood or wood composite is then brought into contact with the resinated piece. The two pieces (or more) are pressed together. The pressing step can be short (a few seconds), as in the case of I-beams, or relatively long (several hours), as with glulam. Generally, no heat is applied to the resin so it needs to cure at either room or at only modestly elevated-temperatures.

For I-beams (see Figure 17), grooves in the flanges (solid wood or LVL) are cut out and resin is applied through an aperture of controlled size. This is done using a pump. Tapered edge OSB or plywood panels (webs) are then pushed into the resinated grooves of the flanges. This is usually achieved by crowder-rollers. Since I-beams need to be of a certain length, flanges and web stock are often finger jointed previously or in situ. After the crowder-roller, the constructed I-beams are stacked in staggered piles. In the case of phenol resorcinol formaldehyde (PRF) resins, the loadings are relatively large and cure is comparatively slow. This can lead to resin overflow. Overflow results in unsightly resin flow lines (due to the deep red color of PRFs) over the web and flange and can cause undesirable adhesion between touching beams in the stack. Isocyanate-based resins, which are wood colored, cure faster and require lower volume usage. They therefore generally do not suffer from these problems.



On the other hand, the higher loadings of PRF resins are useful for gap filling in regions of the coupled substrate members where there is a lack of good contact.

Glulam (Figure 17) is prepared by application of resin to freshly prepared surfaces of long lumber (up to tens of meters). The wood is conditioned to a specific moisture content and resin is applied to one surface, usually by knife, brush or roller. A second piece of wood is placed on the glue line and its upper surface is similarly resinated. The process is then repeated for as many layers of lumber as required. Again, finger jointing is used to extend the lengths of the pieces of lumber, which are stacked to control the orientation of the wood growth rings with respect to the stack thickness. The growth ring curvatures of the upper and lower pieces curve away from each other to balance any internal stresses.

The stack of lumber is then mounted on a simple press and clamped. Clamping pressures vary but are usually not high. The press is often an A-frame type of press and where heating is needed steam is pumped into the central cavity of the press. Depending on the type of resin, the glulam assembly is clamped for up to 24 hours.

Due to the nature of the substrate, the gap-filling ability of the resin is more important for glulam than for I-beams. PRF resins achieve this property by formulation design and by inclusion of fillers such as wood dust.

4.4.2 Resin developments

Phenol resorcinol formaldehyde (PRF) resins are most commonly used in engineered lumber applications where only limited load-bearing performance is required. The patent literature describes a large number of modified polyvinyl alcohol (PVA) and acrylate resins, which need modification with isocyanate-based materials to improve performance. Some of these resins have been commercially successful.

Some grades of isocyanate modified PVAs are used successfully even in structural applications. The amounts of isocyanate addition vary, but are typically 5-15%, based on the weight of the principal adhesive. The poly-functional isocyanate additives (usually pMDI or eMDI) are said to increase the cross-linking density of the parent polymer, so increasing its strength and durability.

Two-component isocyanate-based adhesives are also described in the patent literature and have met with some commercial success. Two-component isocyanate- or polyurethane-based adhesives are composed of an isocyanate-bearing component and an isocyanate-reactive component, usually a poly-alcoholic material. Such materials resemble conventional polyurethane systems. Two component resins allow for a high degree of control of component viscosity, stability, reactivity and performance. Hence processability as well as performance can be optimized while avoiding issues such as shelf-life constraints and processing-performance compromises. However, such resin systems do require good mixing at specific component ratios and careful monitoring during use and application stages is needed.

Most recently, one-component urethane-based adhesives have been developed for these applications. Preparation of these resins essentially involves pre-mixing all the required components (as in the two-component system). Final complete cure is achieved by an auto reactive step or via reaction with moisture (in the wood, atmosphere or applied as a spray to the glue). In all cases, application and processing of the resin is easier for the panel fabricator (no mixing is required, only one set of pumps etc.) but, unless specific precautions are taken, the shelf life of the pre-mixed resins can be slightly compromised.

Examples of such resins are the family of one-component urethane resins, developed by Huntsman Polyurethanes. The resins are based on pMDI modified with polyether poly-alcoholic and polyaminic materials. The polyether polyols increase the compatibility of the isocyanate with the polar wood surface. They also increase the affinity of aromatic isocyanates to water and prevent excessive penetration of the resin. The materials also contain a molecularly in-built water-isocyanate reaction catalyst to allow rapid room temperature cure. These resins are usually applied to the wood surface and subsequently a fine water spray is applied (up to 30% by weight based on resin weight). This range of resins is designed to have cure profiles to meet different application demands. The range of cure profiles is given in Table 8.

Processing performance characteristic	Units	PU based autocatalytic structural adhesive	
		Slow cure	Fast cure
Application rate	gm ⁻²	90-120	90-120
Water application rate	% (on resin)	10-20	10-20
Prevailing temperature	°C	23	23
Open assembly time	min	15	2
Clamping time	min	15	5
Cure time	min	45-60	15-20

Table 8. Examples of handling and cure times of the structural PU family of resins.

A number of other resin producers also have one-component urethane resin systems for use in structural lumber applications.

4.4.3 Uses

Most applications of composites such as glulam and I-beams are load bearing (other examples include parallel strand lumber, laminated strand lumber, composite strand lumber etc.). For this reason, they are subject to stringent codes and standards. Standards are set at a national level, with each country requiring a particular set of performance tests. These tests range from initial strengths and bending moduli of

assemblies to long-term endurance and creep testing. Tests may include glueline thickness capability assessments and aggressive short-term hydrolytic ageing assessments.

Examples of the tests are EN 312 and ASTM D-2559. In Europe, the German test institute Forschungs-und Materialprüfungsanstalt, Baden-Württemberg, or MPA for short, is seen as the critical evaluator of resins for structural applications. Although other national tests may need to be passed, passing the MPA tests is usually seen as a strong indicator of success.

Structural applications for these types of composites include roof trusses, floor joists, support columns and cross beams. In the US, I-beams are mainly used in domestic house construction. I-beams and more commonly glulam are used in Asia, especially in Japan, for house construction and include vertical lumber applications. In Europe, glulam (and LVL)-type composites are used in large span buildings such as gymnasias and auditoria. Examples of I-beams and glulam have been shown in Figures 3 and 17.

4.4.4 Typical performance characteristics

Even at low resin dosage levels, structural PU resins achieve high performance levels. Not only is strength high but high wood failure levels are simultaneously realized.

Delamination of composite members due to wood movement or failure of gluelines needs to be avoided at all costs. To avoid delamination, the resin and the adhesive bond must be resistant to hydrolytic processes. They also need to resist peel forces caused by the movement of wood due to wetting and drying cycles. This requires some degree of elasticity in the resin to avoid stress concentrations adjacent to the glueline. Urethane resins of the types used in these applications combine a high degree of cross-linking with elasticity.

With regard to gap filling, especially for glulam type applications, the relevant standards assess performance up to a glueline thickness of 1mm. Although some urethane resins have passed the full thickness test, they are currently only given approval for a limited (0.3mm) glueline thickness due to the narrow nature of the standards that specify the use of PF type resins only. However, new standards are currently being drafted and these foresee the possibilities of polyurethane- and isocyanate-based resins.

4.5 Plywood and Laminated Veneer Lumber (LVL)

Plywood

4.5.1 Manufacturing process

Wet, large diameter logs are debarked and cut to manufacturer specific lengths. They are then mounted on a large lathe-like machine and rotated at high speeds. Initial cutting is conducted to eliminate irregularities and to 'round' the wood. After rounding, the log continues to turn and a knife, the length of the log, is brought into contact. The angle and pressure of the knife defines the cutting thickness. The log is then peeled into a single long veneer with grain perpendicular to its length. The veneers are then dried to a target moisture content. Drying of the veneers is often achieved in a relatively short time – a few minutes. Due to the nature of the wood, although an average moisture content is achieved, the moisture content distribution across the veneer is wide. Indeed, the higher the target average moisture content, the wider the distribution of moisture contents. For PF-bonded plywood, the target moisture content is of the order of 2-5%. For MDI bonding, the moisture content can be higher. The veneers are then cut to appropriate widths. Typically, the veneers will be of the order of 2-4 meters long (originally the length of the log) and 1-2 meters wide. Veneers are monitored for defects such as holes, loose and tight knots, wet spots, bark pockets, pith flecks etc. These parts are removed or stamped out and replaced by close-fitting plugs.

Resin is then applied to the surfaces of the veneers. Depending on the set-up of the manufacturing process, resin is either applied to one face of each veneer, or to both (the upper and lower) faces. In the former case, the top face resinated veneers are stacked with the non-resinated face down. Each veneer is resinated except for the top most. In the latter case, resinated and non-resinated veneers are stacked alternately. The resin can be applied in a number of ways, but roll coating is the most common. Curtain and ribbon coating, as well as some spray applications, are also used.

Irrespective of the resination process, the alternate veneers are stacked so that the grain direction is perpendicular to the preceding veneer.

The loose stack of veneers is then conveyed to a cold press where they are pressed together into so-called 'veneer-cakes'. After a certain period of time, the veneer cake is conveyed to a hot press to cure the resin, after which the panel is cooled and trimmed. Subsequent processing, such as surface or edge coating, can then be undertaken.

There are two main reasons for the cold pressing step:

- (i) The traditional resins used to prepare plywood are PFs. Phenol formaldehyde resins are slow curing resins. The dwell time in the hot press is therefore rather long while veneer stacks can be made at a high rate. Resinated veneer stacks can be held for up to eight hours before hot pressing. If the veneer stacks were not consolidated into veneer cakes by cold pressing, then the resins would dry out and bonding

would subsequently not be achieved. This is not a problem for isocyanate-bonded plywood since the isocyanate resins cure faster. In-press dwell times are therefore shorter and the holding time between resination and hot pressing is greatly reduced.

- (ii) The hot press feed inlets are narrow and loosely stacked veneers, which are not flat, would not be able to enter the press – the topmost veneers would simply roll back. Cold pressing the veneer stacks into the cakes reduces the stack thickness and straightens the otherwise curly veneers. Of course, originally, the small opening distances of the presses were only possible due to the need to prevent dry out of PF-bonded systems by employing the cold press. Small opening distances of presses lowers the capital cost of the press and reduces the total press occupancy times since the press can be closed and opened to full distance much faster. Hardware developed this way requires that newer resins, such as isocyanate used in bonding plywood, need to be cold pressed into veneer-cakes.

Consolidating veneer stacks into veneer cakes requires that the resin has excellent tack performance. Tack is not an innate characteristic of isocyanate resins.

4.5.2 Resin developments

Fast curing resins with high performance characteristics are required for the production of high quality plywood. Often high quality woods such as tropical woods are used, since this is necessary to achieve the high performance levels needed. Tropical woods can be difficult to bond due to high extractives contents and/or low porosities of the woods. Therefore resins with wide substrate tolerances are needed.

Isocyanates are required that are cost competitive with the older PF resins. This can be achieved by lowering the resin loading and/or by increasing the cure speed. Isocyanate and polyurethane resins meet these requirements rather easily since standards are easily achieved with low resin loadings and the resins are naturally faster curing. Further improvements can be made in both these aspects. However, improved application methods to uniformly resinate the veneers with the lower levels of resin do need to be developed and improved simultaneously.

Due to the peculiar production process, the resins employed for plywood need to impart a certain level of tack. Several ways to improve tack are being investigated by Huntsman Polyurethanes.

4.5.3 Uses

Plywood can be used in packaging, hoarding, sign making, construction (siding, flooring, roofing) and transportation (caravan and lorry flat bedding) as well as the most demanding applications such as marine applications (boats, yacht decking, piers and jetties). Since very high quality wood is often employed for plywood production, high water contact applications are possible. For such applications, the better quality resins should also be used.

Additionally, plywood can be used as webstock in I-beams (similarly to the use of OSB in this application).

For some of the less demanding applications, e.g. packaging, the lower quality softwood plywood grades can be used. It is important however to realize that softwood plywood quality is increasingly improving and the quality of softwood plywood is now of a very high standard.

Laminated Veneer Lumber (LVL)

Laminated veneer lumber has been grouped with plywood because it is a composite assembly of wood veneers. However, it differs from plywood in many aspects. The veneers are usually thicker than with plywood. The wood species is often softwood rather than the more typical hardwoods for plywood. The number of veneer layers is substantially higher for LVL than for plywood. And most significantly, LVL is not usually employed as a panel. Instead, it is cut into lumber type dimensions and is used in load-bearing applications as indicated in the section on engineered lumber.

4.6 Wood fiber insulation boards

4.6.1 Manufacturing process

Wood fiber insulation (WFI) panels are usually produced in one of two ways:

- a. Wet process
- b. Dry process (Figure 18)

The dry process is the newer production method and is considered more environmentally friendly than the original wet method due to its lower energy demands. Less energy is required as there is no need for drying the wood. MDI is usually employed in the dry process.

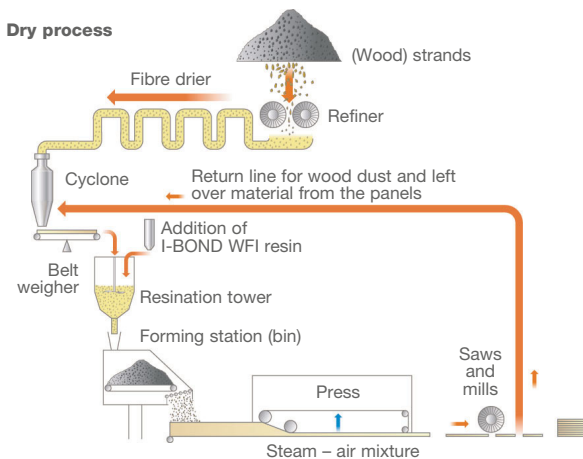


Figure 18 - Schematic of dry process WFI manufacture (original schematic supplied by Gutex)

The production of fibres, which is achieved in a similar fashion to the process described in the MDF section, is the same for both the wet and dry processes.

After the wood is dried, the fibres are conducted to a blender where isocyanate (I-BOND® MDI resin) is sprayed onto them. There are a number of different dry blenders on the market, but in all cases the principle is the same – the fibres are blown with a hot air stream and the isocyanate is atomized into the fibre stream. The resinated fibres are then laid as a pre-mat on to a conveyor system and transported into presses. Hot air is blown into the mat via porous textile press plates to cure the resin. No mechanical pressure is applied. The dry process allows for the preparation of thicker panels, up to 200mm.

4.6.2 Resin developments

Such special production processes require special MDI resins. Huntsman has developed and patented a high quality MDI, I-BOND® WFI 4370 specifically for this application. This highly reactive resin starts to cure upon contact with moisture or temperature or with the application of pressure.

As is the case with other composite wood applications, this press belt needs to be treated with an external release agent to prevent the pre-mat from sticking to the press belt. A release agent has been developed specifically for this application: I-Release® WFI 9162. The application of the release agent is by an external spray installation.

4.6.3 Uses

WFI has a wide range of insulation-based applications in the construction industry – flooring, interior sides of exterior walls, in-wall, power and plumbing lines and compression proof boards for flat roofs.

4.6.4 Typical performance characteristics

Some of their most distinct qualities are:

- (i) low thermal conductivity
- (ii) highest possible volumetric heat capacity
- (iii) superb water vapour permeability
- (iv) unsurpassed noise absorption
- (v) completely recyclable

The most important performance requirements and their range are listed in Table 9. The actual values of these characteristics are dependent on the exact application and thickness of the WFI board.

Performance characteristic	Units	Range
Nominal thickness	mm	20 – 200
Bulk density	kg/m ³	10 – 20
Thermal conductivity λD	W/mK	0.037 – 0.046
Thermal resistance RD	m ² K/W	0.0 – 5.45
Vapour diffusion factor	μ	3 – 5
Compression resistance/compression strength	kPa	50 – 200
Tensile strength perpendicular to the surface	kPa	7.5 – 40
Air flow resistance	kPas/m ³	≥100
Specific heat capacity	J/kgK	2100

Table 9 - Typical performance characteristics of WFIB

4.7 Other types of wood composites

There are a number of other types of wood composites that have not been mentioned including, most particularly, particleboard (PB). PB panels are produced in high volumes using virgin and recycled or waste wood as feed stock. The most abundant resins used in this type of panel manufacture are urea and melamine modified urea formaldehyde resins. Such resins are low cost, relatively fast cure and give rise to high strength, relatively high-stiffness panels. Urea formaldehyde does not have any hydrolytic resistance and so uses of derived panels are limited to interior applications (such as furniture). Increasing the melamine content in the resin formulations improves the hydrolytic resistance; high melamine content systems can be used in semi-exterior applications such as kitchen and bathroom cabinetry. However, increasing the melamine content increases the materials costs and reduces the cure rate of the resin.

As with plywood, the resins used to produce PB require tack to aid the production process. As before, isocyanates do not innately show tack and therefore the use of isocyanates in particleboard is limited to special niche applications. However, isocyanates can be used in combination with other resins as co-adhesives to improve the performance – especially as related to hydrolytic resistance and durability. Under certain circumstances cure speed enhancement can also be realized by adding MDI in some form to the formaldehyde-based polycondensate resins.

New developments with low-temperature, fast curing, MDI-based resins (e.g. I-Bond® PB EM 4352) are improving production efficiencies of the panels.

Acknowledgements

I would like to thank many of my colleagues without whose help this publication would not have been possible. While it is not possible to mention them all by name, specific thanks are given to Chris Skinner, Chris Moriarty and Bill Arndell for their help in providing figures and technical data.

Thanks are also due to several of my colleagues who were involved in the studies relating to understanding the nature of the interaction between isocyanates and wood. These include, in no particular order, Lieve Vanoverloop, Christel Van Den Bosch, Jacky Vanden Ecker, Ann Engelen, Steven Ramsdonck, Katia Smeets, Bill Daunch and especially Joe Marcinko. Also to Julien Devos and his team for all the analytical support they provided.

Special mention should be made to the following people for their specific contributions to some of the development studies: For fast cure and release in OSB – Chris Skinner, Jan Lauwers, Michel Van Tilt and Peter Stroobants. Wolfgang Pille-Wolf, Bruno Jung and Danny Geukens, Ian Fletcher (ICI Technology) and Jan William Leenslag were involved in the initial design stages of the isocyanate release studies. Finally for the engineered lumber resin developments Bill Newman, Joe Costa, Bill Arndell, Walt McGuire, Jim Copsom, Chris Watt, Christel Van Den Bosch, Katia Smeets and Gitta Van Hemel. And for background information on plywood, Risto Seppela.

I would like to thank the following people with whom Huntsman collaborated in the fundamental studies of the interaction of wood with isocyanates. Chris Buckley (formerly King's College, London) and his team, who conducted all the studies on x-ray microscopy. Peter Rinaldi (Akron University, Ohio) for his support and efforts in solid state NMR studies. Dave Sykes and Ann Waddilove (ISST, University of Loughborough) and Alison Chew (Loughborough Surface Analysis) for the surface analytical studies. And finally M.M. Mahandru (ICI India R&D) for his investigation into biological resistance of isocyanate-bonded wood.

Special mention should go to Sophie Poelmans for the complete WFIB section of this monograph and to Bart Michielsen and Jan Stroobants for their updated contribution on accelerated cure resins and to Paul Coleman, Bart Singulé and Bill H Voll for some of the historical information.

I would like to thank de Gruyter publishers for permission to reproduce some of the figures from their publications and Chris Pearson for editorial advice and configurations.

Finally, I would like to thank Simon Baker, Michael Scharf, Ilse Vanden Brande, Natalie Yates, Bart Singulé, John Hobdell and Niek van Wiechen for their corrections, proof-reading and challenging comments. And last but by no means least, I would like to thank Elise Verdeyen and Iain Stanton for the coordinating, managing and editing and significant suggestions for improvements for this second edition.

Chris Phanopoulos

References

1. Wilkinson, J. G. The manners and customs of the ancient Egyptians. Publ. John Murray (London) 1872
2. Dahlquist, C. A. An overview of Adhesive technology. *Kautsch. Gummi, Kunststoffe* 38(7), 617-620 (1985)
3. Dinwoodie, J. M. Properties and performance of wood adhesives. Chapter 1 in *Wood Adhesives: Chemistry and Technology*, Dekker, New York, NY Ed. A. Pizzi (1983)
4. Skeist, I. (ed.) *Handbook of Adhesives*, 2nd edn., Van Nostrand Reinhold Co., New York (1983)
5. Phanopoulos, C. The Nature of Bond Formation and Failure in Wood-Adhesive Systems. PhD thesis (1986)
6. Randall, D. and Lee, S. (eds). *The Polyurethanes Book*. J. Wiley & Sons Ltd. (2002)
7. Marcinko, J. J.; Teachey, P. and Phanopoulos, C. Why does chewing gum stick to hair and what does this have to do with lignocellulosic structural composite adhesion? *Wood Adhesives 2000*, pages 111- 121, Lake Tahoe, Nevada (2000)
8. Buckley, C.; Phanopoulos, C.; Khaleque, N.; Engelen, A.; Holwill, M. E. J. and Michette, A. G. Examination of the penetration of polymeric methylene di-phenyl-di-isocyanate (pMDI) into wood structure using chemical-state x-ray microscopy. *Holzforstung* 56(2), 215 (2002)
9. Desch. H.E. *Timber, its structure, properties and utilisation*. 6th edition. Rev. by Dinwoodie, J.M. MacMillan Press, London (1981)
10. Bao, S.; Daunch, W. A.; Sun, Y.; Rinaldi, P. L.; Marcinko, J. J. and Phanopoulos, C. Solid state NMR studies of pMDI derived species in wood. *J. Adhesion* 71(4), 377 (1999)
11. Bao, S.; Daunch, W. A.; Sun, Y.; Rinaldi, P. L.; Marcinko, J. J. and Phanopoulos, C. Solid state two-dimensional ¹⁵N-¹H correlation (HETCOR) NMR studies of polymeric diphenylmethane diisocyanate (pMDI) reaction in wood. *Forest Products Journal* 53(6), 63 (2003)
12. Waddilove, A. Characterisation of the wood-adhesive interface in an isocyanate based adhesive system using laser microprobe mass spectrometry. ICI Polyurethanes' funded LIMS investigation at The Institute of Surface Science and Technology, Loughborough University (1994)
13. Pizzi, A. and Walton, T. Non-emulsifiable, water based, mixed di-isocyanate adhesive systems for exterior plywood. Pt 1. Novel reaction mechanisms and their chemical evidence. *Holzforschung* 46, 541-7 (1992)
14. Rowell, R. M. 211th Presentation given at ACS National Meeting New Orleans (1996)
15. Chapman, K. M. and Jordan, P. J. Resin-Fibre mixing in high velocity blowline in MDF manufacture. Proceedings of the 9th Asian Pacific confederation of chemical engineering congress. 883, (2002)
16. Dunky, M. (ed.) COST Action E13 Report: Wood adhesion and glued products. Working group 1: Wood adhesives. State of the art report. (2001)

Norm and standards listed:

- EN 302-2 Adhesives for load bearing timber structures, test methods Part 2. determination of resistance to delamination. (2004)
- EN 310 Wood-based panels. Determination of modulus of elasticity in bending and of bending strength. (1993)
- EN 312 Particleboards – specifications. (2003)
- EN 317 Particleboards and fibreboards. Determination of swelling in thickness after immersion in water. (1993)
- EN 319 Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board. (1993)
- EN 323 Wood-based panels. Determination of density. (1993)
- EN 1087-1 Particle boards. Determination of moisture resistance. Particle boards. Determination of moisture resistance. Boil test. (1995)
- EN ISO 9664 Adhesives. Test methods for fatigue properties of structural adhesives in tensile shear. (1995)
- ASTM D-2559 Standard specification for adhesives for structural laminated wood products for use under exterior (wet use) exposure conditions. (2004)
- ASTM D-3434 Standard test method for multiple-cycle accelerated aging test (automatic boil test) for exterior wet use wood adhesives. (2006)
- ASTM D-4300 Standard test methods for ability of adhesive films to support or resist the growth of fungi. (2001)
- ASTM D-4680 Standard test method for creep and time of failure of adhesives in static shear by compression loading (wood-to-wood). (2004)
- ASTM D-4783 Standard test methods for resistance of adhesive preparations in container to attack by bacteria, yeast and fungi. (2007)

Glossary of Abbreviations

%	percent
μ	unit of vapour diffusion factor
ASTM	American standard
BC	before Christ
ca.	circa
cm	centimetre
cm^{-1}	per centimetre/wave number
eMDI	emulsified or emulsifiable MDI
EN	European standard
etc.	et cetera
FTIR	Fourier transform infrared
gcm^{-2}	grams per centimetre square
gcm^{-3}	grams per cubic centimetre
hr	hours
IB	internal bond
J	joule
K	kelvin
kg	kilogram
LVL	laminated veneer lumber
m^2	square meter
m^3	cubic meter
MDF	medium density fibreboard
MDI	methylene diphenyl diisocyanate
MF	melamine formaldehyde
mm	millimetre

Glossary of Abbreviations (continued)

MOE	modulus of elasticity
MOR	modulus of rupture
MPa	megapascals
ms	milliseconds
MUF	melamine urea formaldehyde
MUPF	melamine urea phenol formaldehyde
N	newtons
Nm ⁻²	newtons per metre square
oC	degrees centigrade
OSB	orientated strand board
OSL	orientated strand lumber
Pa	Pascal
PB	particle board
PF	phenol formaldehyde
pMDI	polymeric MDI
PRF	phenol resorcinol formaldehyde
PSL	parallel strand board
R	generic alkyl group
s ^{1/2}	square root seconds
s/mm	seconds per millimetre
UF	urea formaldehyde
US	United States
W	watts



European headquarters

Huntsman
Everslaan 45
B-3078 Everberg
Belgium
Telephone +32 2 758 9952

American headquarters

Huntsman
10003 Woodloch Forest Drive
The Woodlands
Texas 77380
USA
Telephone +1 281 719 4916

Asian headquarters

Huntsman
No 452 Wen jing Road
Minhang Development Zone
Shanghai China 200245
Telephone +86 21 2403 7288

HUNTSMAN

Enriching lives through innovation

www.ibondwood.com
ibondwood@huntsman.com

Huntsman Polyurethanes warrants only that its products meet the specifications agreed with the buyer. Typical properties, where stated, are to be considered as representative of current production and should not be treated as specifications.

While all the information and recommendations in this publication are to the best of our knowledge, information and belief accurate at the date of publication, NO GUARANTY, WARRANTY OR REPRESENTATION IS MADE, INTENDED OR IMPLIED AS TO THE CORRECTNESS OR SUFFICIENCY OF ANY INFORMATION OR RECOMMENDATION OR AS TO THE MERCHANTABILITY, SUITABILITY OR FITNESS OF ANY PRODUCTS FOR ANY PARTICULAR USE OR PURPOSE.

IN ALL CASES, IT IS THE RESPONSIBILITY OF THE USER TO DETERMINE THE APPLICABILITY OF SUCH INFORMATION AND RECOMMENDATIONS AND THE SUITABILITY OF ANY PRODUCT FOR ITS OWN PARTICULAR PURPOSE. NOTHING IN THIS PUBLICATION IS TO BE CONSTRUED AS RECOMMENDING THE INFRINGEMENT OF ANY PATENT OR OTHER INTELLECTUAL PROPERTY RIGHT AND NO LIABILITY ARISING FROM ANY SUCH INFRINGEMENT IS ASSUMED. NOTHING IN THIS PUBLICATION IS TO BE VIEWED AS A LICENCE UNDER ANY INTELLECTUAL PROPERTY RIGHT.

Products may be toxic and require special precautions in handling. The user should obtain Safety Data Sheets from Huntsman Polyurethanes containing detailed information

on toxicity, together with proper shipping, handling and storage procedures, and should comply with all applicable safety and environmental standards.

Hazards, toxicity and behavior of the products may differ when used with other materials and are dependent on the manufacturing circumstances or other processes. Such hazards, toxicity and behavior should be determined by the user and made known to handlers, processors and end users.

Huntsman Polyurethanes is an international business unit of Huntsman International LLC. Huntsman Polyurethanes trades through Huntsman affiliated companies in different countries such as Huntsman International LLC in the USA and Huntsman Holland BV in Western Europe.

Except where explicitly agreed otherwise, the sale of products referred to in this publication is subject to the general terms and conditions of sale of Huntsman International LLC or of its affiliated companies.

I-Bond®, I-Release®, Ruminant® are registered trademarks of Huntsman Corporation or an affiliate thereof, in one or more countries, but not all countries.

Copyright © 2010 Huntsman Corporation or an affiliate thereof.
All rights reserved.