THE USE OF P-MDI RESIN IN MDF MANUFACTURE

Rynehvee Tan

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ABSTRACT

"The Use of p-MDI Resin in MDF Manufacture"

By Rynehvee Tan

Traditional manufacture of medium density fibreboard (MDF) involves the use of urea-formaldehyde (UF) resin as binder. After much study, formaldehyde emissions from this resin are found to cause negative health effects, that is, cancer, for humans and animals. Because of this, the Composite Panel Association recently published new lower limit on formaldehyde emissions, which made the use of UF resin costly from increasing the scavengers that minimize formaldehyde emissions from finished boards. MDF mills are now facing increased competitive pressure in keeping their emissions below the CARB Phase 2 limit and since then, different formaldehyde-free resins, may it be organic or synthetic, have been tried in place of UF resin.

The use of polymeric methylene diphenyl diisocyanate (p-MDI) as binder for wood composite panels is not new. It is widely known as a binder for oriented strand board (OSB). MDF mills in Europe and North America are now converting their systems to use p-MDI to alleviate pressure from the new emission limit. p-MDI has a lot of benefits in the production process, and even though it is more expensive, its benefits have proven to outweigh the cost. Improvements on the product such as high internal bond strength, better MOE and MOR, additional moisture resistance, and less formaldehyde testing and monitoring are just some of the advantages in using p-MDI.

This report concludes that despite these advantages, it is still important to understand how the resin reacts and cures when integrating this resin into a production process. It is necessary to have a gradual transition through multiple trials and document press settings and process modifications that produce on-spec MDF boards. When this is understood, the addition of catalyst and other additives that will improve the process can then be experimented on.

LIST OF KEY WORDS: p-MDI, Isocyanates, MDF, medium density fibreboard, Resin, UF, formaldehyde, Soyad, eMDI, PF

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INTRODUCTION

Medium density fibreboard (MDF) is defined as a “composite panel product typically consisting of cellulosic fibres combined with a synthetic resin or other suitable bonding system and joined together under heat and pressure” (Composite Panel Association, n.d.). Traditional manufacture of medium density fibreboard (MDF) involves the use of urea formaldehyde (UF) resin as binder. In recent years, the Composite Panel Association (CPA) published a limit on formaldehyde emissions of panel products to a maximum of 0.21 ppm. This limit required MDF mills to regulate their emissions to a level lower than 0.21ppm. Compliance to these limits could be achieved by increasing their additives, which incurs more costs, or by completely switching to formaldehyde-free synthetic or organic resins.

Recently, MDF mills in Europe and North America are now looking at possibilities of changing over to p-MDI to satisfy the formaldehyde emission limit on panel products. The use of polymeric methylene diphenol diisocyanate (p-MDI) in wood composite manufacturing is not new. p-MDI, a synthetic isocyanate resin, is already widely used for OSB manufacture.

AN OVERVIEW OF MDF MANUFACTURE

MDF is a homogenous material composed of refined wood fibre. The furnish for MDF is created by refining sawdust and shavings into wood fibre. The wood fibre is then resinated. Traditional MDF mills have a blowline blending system where resin, wax, and other additives are injected into wet fibre passing through a blowline, a 5" diameter pipe, to the dryers. The resin, wax, and other additives are added to wet fibre because dry fibre tends to form bundles due to hydrogen bonding, and will not be as consistent when sprayed (Beutel, 1996). When wood fibres, composed mainly of cellulose chains, are wet, the –OH groups in the polymer chain are attached to water molecules and are not free to attach to other wood fibres. However, hydrogen bonding can occur when the –OH groups in the cellulose chains free to bond with other chains, which only happens when the wood fibre is dry, thus creating clumps of wood fibre. The fibre inside the blowline is traveling at high velocity, and as the fibre exits the tip of the blowline, the fibre explodes when exposed to atmospheric pressure inside the dryers. The system is known as the "black box" (Chapman, 2004)because it is difficult to ascertain how the wood fibre behaves and how the resin is distributed in a completely closed system.

Although the blowline blending process works well with MDF manufacture, other blending systems are now being developed to reduce the problems associated with blowline blending such as frequent plugging of the blowline and build up in the dryers—which in turn affects resin distribution and is believed to be a big cause in sudden blows and delaminations in an otherwise smooth process. Flakeboard's MDF plant in St. Stephen, New Brunswick believes that the addition of resin further in the process can decrease resin pre-cure and avoid a lot of buildup in the blowline, therefore saving the company resin and maintenance costs, as well as decrease the production of rejected panels when the blowline is plugged. Together with Sunds MDF Technologies (Dieffenbacher division), they developed a post-dryer resination system, the EVOjet™, and have already been consistently successful in using the system and realizing resin savings of about 40% (Tice, 2011).

The dryers dry the resinated fibre at 150°C from 50%MC to around 10%MC. The fibre is blown to dryer cyclones and then transported to the weigh scales using screw conveyors. As the fibre fall from the screw conveyors to the weigh scales, an in-line moisture meter measures the fibre's moisture content. The weigh scales then measure the weight of the fibre, and with this data, the resin loading can be accurately monitored. After being weighed, fibre is then transported to a dry storage bin and from this bin, exact amounts of fibre go through ducts to the formers that form the mat. The mat is pre-pressed to remove excess air and then the pre-pressed mat is hot pressed.

Pressed boards are then sent to cooling racks. After cooling, rough boards are sent to the finishing area where boards are sanded, trimmed to dimensions, and stacked into units. Units are sent to the packaging area where they are packaged and staged for shipping.

Traditional MDF mills commonly use urea formaldehyde (UF) resin as binder which had been adopted from particle board manufacture. Other MDF mills use alternative resins such as phenol formaldehyde (PF) resin and polymeric methylene diphenol diisocyanates (p-MDI) to minimize the product's formaldehyde emissions when in use (Value+Created Review, 2006). As of 2006, the first emergence of binders from renewable resources is announced; Columbia Forest Products developed its new soy-based resin technology (Healthy Building Network, 2008), however, its performance with MDF and its effect on the board's physical properties has not yet been published.

UF RESIN VS P-MDI

In MDF manufacturing, it is important to understand what these resins are capable of so that a manufacturing plant can evaluate the resin's fit in the manufacturing process, how the resins' strengths can benefit the manufacturing process, and if its weaknesses can be offset by its benefits.

UREA FORMALDEHYDE

UF resin is traditionally used in MDF and particleboard production. The resin provides a tacky consistency to wood fibre that helps maintain the form of the mat when forming. UF is also a desirable binder because it provides finished boards with a resiliency (Wise Geek, 2012) that enables its core to be routed smoothly. This is an important property needed in MDF boards used for mouldings. Traditional MDF manufacturing plants are built to have processes that use UF resin. UF had been the first choice for fibreboard manufacture due to its relatively low cost when compared to other resins (Figure 1).

	name	abrev	cost* US$/lb.	use	durability
interior	poly-vinyl-acetate	PVA	0.10	finger jointing	interior
	urea-formaldehyde	UF	0.30 – 0.37	PB/MDF	interior
	melamine-formaldehyde	MF	0.69 – 0.78	MDF/PB	lim. ext.
structural	phenol-formaldehyde	PF	0.32–0.52	LVL/OSB/MDF	exterior
	methylene-diphenol-diisocyanate	pMDI	0.93–1.06	OSB/MDF	exterior

* Jan22, 2010 james.taylor@hexion.com

FIGURE 1. RESIN TYPES AND ASSOCIATED COST FOR EACH RESIN (SMITH, 2012)

Despite these product performance and financial benefits, UF resin also has its challenges. Although UF is a thermosetting polymer, its cure (i.e. its condensation reaction) is reversible through the addition of water (Smith, 2012). Therefore, the board will not perform well in the presence of water and the manufacturing process will need to add sufficient wax to the furnish in order to meet the manufacturer's thickness swell specifications. UF resin also gained a bad reputation due to its formaldehyde emissions when in use, which are determined to be carcinogenic to humans and can cause irritation in various parts of the body (Green Seal, 2001). Although formaldehyde is released in small amounts, the US Environmental Protection Agency argues that "in homes, the most significant sources of formaldehyde are likely to be pressed wood products made using adhesives that contain urea-formaldehyde (UF) resins" (EPA, n.d.). This assessment continues on to say that among all UF resinated engineered wood panels, MDF has the highest resin add-on % and is therefore the product that emits the most formaldehyde when in use. MDF manufactures who still use UF resin use scavengers to minimize their product's formaldehyde emissions to meet the California Air Resources Board Phase 2 limit. Scavengers are additives that bind the formaldehyde and therefore, minimize emissions (Healthy Building Network, 2008). However, scavengers can only minimize, not eliminate formaldehyde emissions. Rigorous testing of boards for emissions is still needed to make sure that the emissions meet the limit. Continuous use of scavengers can also be costly and can affect the performance of the resin and the resulting physical properties of the board (Breyer, et al., 1997). This makes the use of UF resin not very cost effective despite its low cost.

It is also known that UF resin has a short shelf life. The UF resin used for industrial fibreboard manufacture has a shelf life of approximately 4 months (Glues Direct, 2007). This makes the resin a variable in the production process and may have a negative effect on the boards. A "stale" resin may result in resin pre-cure and therefore, in higher rates of blown and rejected boards. UF resin is also sensitive to pH changes in the fibre raw material. A study conducted suggests that UF resin's gel time decreases as its pH becomes more acidic (Xing, et al., 2007). The effect can be synonymous to the result of adding a catalyst. Because of this, it is a standard operating procedure to have a scheduled buffer capacity test for raw materials coming in. This test makes sure that the pH of the raw material is still within the operating window of the UF resin. If the pH is too low, it may result in resin pre-cure and low face densities.

P-MDI

CHEMISTRY

Polymeric MDI is a pure organic brown liquid composed of polyaromatic isocyanates. The more 3-ring or higher molecular weight polymers exist, the more viscous the product is. Higher molecular weight also means higher functionality. Figure 1 shows the molecular composition of a monomeric MDI and a polymeric MDI.

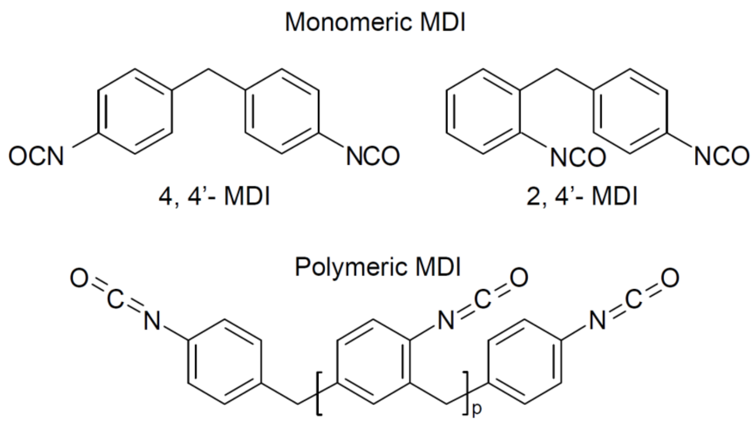

FIGURE 2. MOLECULAR STRUCTURE OF MONOMERIC AND POLYMERIC MDI (BASF, 2009)

p-MDI has a density of 1.23 g/cm^3 at 25°C. p-MDI can also tolerate high temperatures and is considered to have a low flammability risk due to its flash point of over 200°C. It will start to decompose at temperatures above 230°C.

p-MDI is made from a combination of crude oil, natural gas, and toluene. The BASF Group, the largest diversified chemical company in the world, is a producer of p-MDI. According to their process, these raw materials are distilled to get polyurethane feedstock, benzene. The compound then undergoes nitration with the addition of nitric acid (becomes nitrobenzene) and hydrogenation to become aniline. The aniline is condensed with formaldehyde to produce methylene dianiline (MDA) which is then reacted with phosgene to form MDI. Figure2 shows the process summary of the production of MDI.

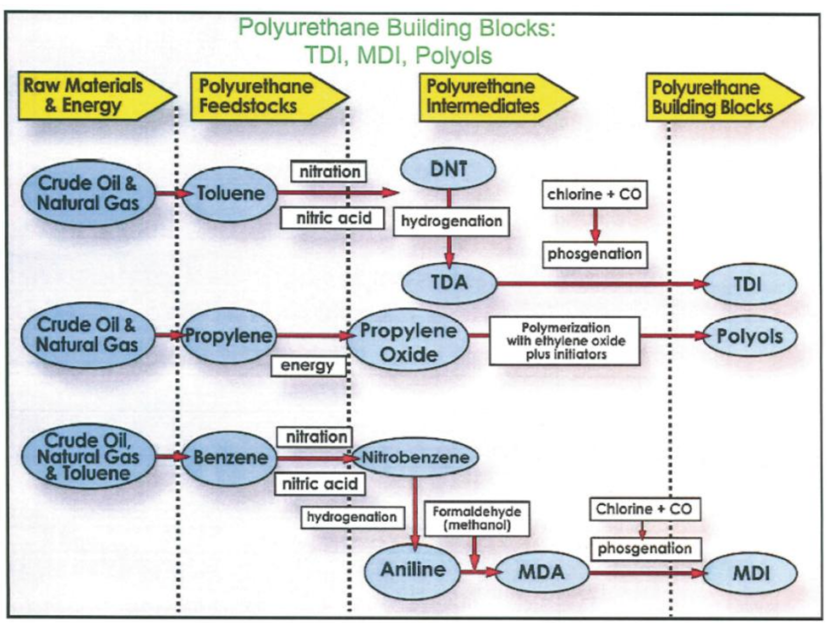

FIGURE 3. BASF'S PRODUCTION PROCESS OF MDI (BASF, 2009)

p-MDI is mostly used in the production of rigid polyurethane foams. These rigid foams are very good thermal insulators and are widely used in freezers, refrigerators, and even buildings. Polyurethane is also used as an industrial strength adhesive, available to consumers in bottled glue such as Gorilla Glue (Gorilla Glue, 2011).

P-MDI AND WOOD

p-MDI was first used in the Germany particleboard market in the early 1970s. Since then, it is widely used in the OSB worldwide and MDF mills in Europe and a few MDF mills in North America (Papadopoulos, et al., 2002). Understanding how p-MDI reacts with wood furnish is important to be able to know if the urethane linkage will strengthen the board to be more durable in different environmental conditions. Theoretically, p-MDI's isocyanate groups can react with hydroxyl groups in wood furnish and moisture to form irreversible urethane linkages. Figure 3 shows how the urethane linkage is formed.

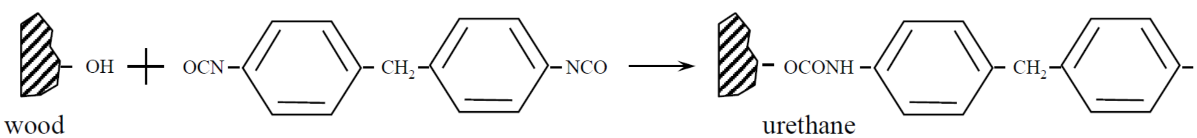

FIGURE 4. THEORETICAL P-MDI RESIN REACTION (SMITH, 2012)

However, there is still uncertainty about the significance of this reaction to how strong the bonding is. p-MDI resin wets easily and penetrates deeply into wood furnish, as it is a low viscosity, low surface tension (contact surface angle of < 90°) organic liquid (Smith, 2012). The resin is even considered to be overpenetrating, yet it is documented to be performing as well as (or even better than) other synthetic resins. This is because p-MDI penetrates into the amorphous regions of the wood furnish cell walls, interweaving on the molecular level until it "plasticizes" the wood cell wall itself (Pizzi & Mittal, 2003).

STRENGTHS AND OPPORTUNITIES

It is documented that p-MDI resin gives dimensional stability and a degree of moisture resistance to the pressed board (Geimer, et al., 1992). Because water is needed to start the crosslinking, p-MDI can then be applied to furnish with higher moisture content, which then reduces the energy needed to dry the fibre raw material (Conner, 2001). This also means that the board will be pressed closer to the equilibrium moisture content of the environment the board will be used in, thereby minimizing the internal stresses in the board. As opposed to UF resin, p-MDI's thermosetting linkage is irreversible, giving the board a degree of moisture resistance. This irreversible urethane linkage is also what makes the MDF board perform really well in both interior and exterior uses.

In the manufacturing end, it is observed that p-MDI dosing is significantly less compared to other synthetic resins to achieve the same (if not better) MDF board physical properties such as internal bond strength and face density. Despite its cost, Huntsman, one of the world's major suppliers of p-MDI, claims that this resin is the key for a more cost effective fibreboard manufacturing process. UF and p-MDI should not be compared in a cost-to-cost basis because UF resin loadings are significantly higher than p-MDI. For a 3mm thin board, UF resin loadings are up to approximately 11% while p-MDI resin loadings are just around 2-3%, both achieving the same physical properties (Huntsman, 2009). Huntsman's Iain Stanton has stated in an interview the benefits of p-MDI that justify the cost.

> *"In order to draw a direct comparison between MDI and other resins, it is fundamentally important to understand that you do not need to use the same quantity of MDI as you do with more conventional products. MDI is far more efficient and highly effective in lower doses, so a little can go a really long way when binding wood… The correct comparison to use is on a cost per m^3 of panel basis where the price, coupled with the increased performance of the panels, looks much more attractive" (Huntsman, 2009).*

There is also an observed improvement on the fibreboard's internal bond strength, modulus of rupture (MOR), and for operators running the press, a more steady processing window (Huntsman, 2009). p-MDI also cures at low temperatures (Smith, 2012), which can lower the production facility's energy consumption and enables the plant to have high production line speeds. The isocyanate's lack of cold tack, that is, a pre-cure stickiness, also minimizes resin-fibre buildup in the blenders and therefore minimizes maintenance and cleaning costs (Pizzi & Mittal, 2003). The higher price is compensated with this these production gains and can be considered a more cost-effective and efficient option as opposed to the other traditional synthetic resins. Also, due to p-MDI's bonding not primarily coming from chemical reaction to the wood but its ability to penetrate and plasticize the wood furnish cell walls, the resin can tolerate a wider variety of wood species with different chemical compositions (Wood Based Panels International, 2009). Also, p-MDI also has a longer shelf life of at least 6 months, provided that the resin is stored at the recommended temperature range and without any contact with water or condensation (BASF, 2009). In an industrial setting, however, p-MDI resin can reportedly be stored up to almost a year.

p-MDI is not sensitive to pH changes in raw material. This can effectively cut down on buffer capacity testing on raw materials. p-MDI is also a certified no-added-formaldehyde resin which makes the p-MDI – resinated boards CARB Phase 2 compliant. These two characteristics represent huge cost savings to the manufacturer in reduced testing, less rejected boards, and less claims from formaldehyde emissions.

Using p-MDI as binder will then give a manufacturer competitive advantage in the MDF market. Boards made with p-MDI have the opportunity to capture a larger market share over the competition. By manufacturing MDF that does not emit formaldehyde, companies are able to set a new industry standard. Competitors that are unable to produce a formaldehyde free product will be at a disadvantage if regulation gets tighter.

An additional benefit is the ability to differentiate the product in the market place. Consumers are leaning on safer alternatives in panel products where end users are not subjected to exposure to VOCs. A niche market can be created for consumers who are aware of the health risks associated with exposure to formaldehyde. As awareness grows, formaldehyde-free boards can be priced at a premium. p-MDI also produces a colorless bond that makes the panel look more natural. The natural colour is more appealing to customers (Wood Based Panels International, 2009) than the dark bondlines produced by other synthetic resins. Isocyanate resins are still not very much optimized due to lack of technology but it has a lot of potential in this industry.

Because traditional MDF manufacturing plants are built for UF resin, integrating p-MDI into their production process requires multiple trials and process adjustments to figure out the optimum press heats, line speeds, and other process variable settings. Switching over to p-MDI using their existing blowline blending system is possible, as had been demonstrated by a few MDF manufacturers worldwide. However, it is believed that the blowline blending system is not the optimum blending system for this resin. p-MDI does not require any mechanical turbulence to improve resin distribution as opposed to UF resin. p-MDI has a wider operating window; the resin moves a lot through the fibres and can therefore distribute itself throughout the furnish. Therefore, the harsh conditions of the dryers can be avoided by resinating further on in the system, that is, applying the resin onto dry fibre, reducing resin pre-cure and reducing resin dosage, and consequently, produces resin savings of up to 50% (Tice, 2011). The biggest challenge of this resin is the availability of the right blending technology to further optimize the use of this resin and minimize maintenance costs and rejected boards. Flakeboard's EVOjet that allows the resin to be applied on dry wood furnish (Tice, 2011). This plant is currently successful in using this technology with UF resin and theoretically, this system would definitely work for p-MDI as well, realizing huge cost savings. Dieffenbacher Group also developed a better blending system (PROjet) in which resin droplet size is as small as possible to be able to have a more efficient resin application.

INTERNAL WEAKNESSES AND EXTERNAL THREATS

p-MDI's chemical structure makes it adhere to metal oxide surfaces (Smith, 2012). "A clear disadvantage of p-MDI wood binders is that they adhere strongly to nearly all surfaces, including steel" (Pizzi & Mittal, 2003). Unlike other resin binders, p-MDI resin cannot be used in the top and bottom face material without the use of release agents. Without release agents, the boards will stick on the press belt or platen and will have to be pried apart and scraped off from the press. The use of external release agents is widely used among MDF manufacturers, more so with manufacturers who use p-MDI resin. These external release agents are based on waxes or soaps. Successful MDF production using p-MDI resin is hugely dependent upon proper and complete application of release agents on press belts/platens.

Another disadvantage of p-MDI compared to other synthetic resins is its price. Figure 4 shows the price of synthetic resins used in the engineered wood products industry. p-MDI is one of the most expensive adhesives for composite wood panels and over three times as much as UF resin (Figure 4). It is not financially logical for a manufacturing plant to use p-MDI unless its process gains can account for it.

Isocyanates, in general, irritate the skin and can cause dermatitis and eczema. It is also irritates the eyes, mucous membranes, and respiratory tract. p-MDI also have high acute toxicity when inhaled (Healthy Building Network, 2008) . Chronic effects from long term exposure to isocyanates include asthma and sensitization in human's respiratory system. p-MDI is then in its most dangerous when being sprayed. In industrial use, p-MDI is sprayed in sealed ducts because most (if not all) MDF manufacturing plants are closed systems. Although most of the documented health risks associated with p-MDI is in its production, fibreboard manufacturing plants still need to take safety measures in using the resin because of the possible negative health effects the resin may have on workers who are exposed to the resin at work.

ADDITIVES AND ALTERNATIVES

p-MDI resin is combined with other additives to further increase its performance such as catalysts and proteins. Catalysts may be an attractive solution when the production process needs the p-MDI resin to cure faster, especially with thin board (< 6mm). Soy proteins may also be added to p-MDI to achieve better plasticity in the board and provide the resiliency it needs to have a smooth core when routered. There are also some alternatives that can be used in place of p-MDI in the fibreboard industry. Some of them are Soyad™ adhesive systems developed by Ashland Inc., emulsified MDI, and PF resin.

SOYAD™

This new technology provides a natural renewable solution to the strict CARB Phase 2 limits on formaldehyde emissions. The Soyad adhesive is made from soy flour and a proprietary cross-linking resin that reacts with the protein to form a durable adhesive with a degree of water-resistance (Ashland, n.d.). It is composed of 50% solids and has a low viscosity (1500cps at 70-80°C).

It is currently being marketed as an adhesive on its own; however, it could also be a co-adhesive with p-MDI in fibreboard manufacture, acting as a p-MDI extender. According to a presentation conducted by Ashland representatives, the combination of both Soyad and p-MDI resins will result in approximately 30-60% increase in adhesive volume that can lead into improved distribution, coverage, and better fibreboard machinability (Dijkstra, et al., 2011). The Soyad adhesive will replace 40-60% of the volume of p-MDI and will easily emulsify (or disperse) p-MDI in water. This presents a big opportunity to reduce resin costs as Soyad costs about $0.80 per dry pound. Ashland has done pilot trials with OSB and Particleboard and found that mechanical properties (internal bond, MOR, and thickness swell) of the board made with 50%-50% Soyad-p-MDI fall between the mechanical properties of boards made with 2% p-MDI and 3% p-MDI. This means that manufacturing fibreboard with a regular 2% resin loadings of p-MDI may have higher mechanical properties when decreased to 1.5% p-MDI resin loading with 1.5% Soyad.

Despite these potential financial gains and product improvement, there are some issues that must be taken into account when using a natural organic resin. The shelf-life of an organic resin is usually short, and in this case, Soyad is claimed to have a shelf-life of 2 months to 8 months (with agitation). There is also the issue of mold build-up while in storage, in which Ashland claims that Soyad will not have any mold buildup.

This resin's performance and fit into the production process of MDF manufacture can only be fully realized by doing a trial. By doing a trial, the fibreboard's mechanical properties (IB, MOE / MOR, thickness swell, machinability, paintability, and screw withdrawal) can fully be tested as well as other production issues such as the amount of release aid needed (Ashland claims that release aid can also be reduced by using Soyad) and press temperatures.

E-MDI

p-MDI is a pure organic liquid that usually starts crosslinking when it reacts with the moisture in the furnish and in the release aid used. Therefore, unlike UF resin, its resin "solids" cannot be tweaked by adding water. It actually starts curing when combined with water. eMDI refers to p-MDI resin that is emulsified in water (Papadopoulos, et al., 2002). A thin film of polyuria coats around each p-MDI droplet, making p-MDI compatible with water. An experiment by Papadopoulos, et al. compared the performance of p-MDI and eMDI and concluded that the bonding mechanism achieved by eMDI is more efficient than the one achieved by p-MDI. Papadopoulos, et al. also discusses that the modifications required to make MDI compatible with water made the resin more reactive and that water may have contributed to improved resin distribution and uniform curing (Papadopoulos, et al., 2002).

PF

Phenol formaldehyde resin is also an alternative adhesive. It is a very durable resin and has an irreversible cure reaction. Unlike its formaldehyde counterparts, it does not emit formaldehyde after it cures. However, fibreboard manufacturers shy away from PF resin because it is as expensive as p-MDI and that it requires higher temperature to cure (Smith, 2012).

Despite the higher cost and higher press temperatures, PF can be integrated into a fibreboard manufacturing plant by changing the mat temperatures to achieve the speed required (Conner, 2001). Molecular weight and press parameters can also be changed to accommodate PF resin. Also, the resin add-on% with PF resin is probably the same as p-MDI. The only downside to this resin is that it will need higher temperatures to cure the resin. In contrast, p-MDI cures at lower temperatures and will therefore not need higher mat and press temperatures.

CONCLUSION

p-MDI gained a good reputation as the primary alternative to UF due to pressures from the stricter CARB Phase 2 limit on formaldehyde emissions. Besides having a no-added-formaldehyde status, it also has a lot of benefits in the production process and the product itself that can outweigh its high cost. Improvements in the performance of the product are apparent, such as higher internal bond, better MOE and MOR, and added moisture resistance. Manufacturing MDF with p-MDI also lessens the energy required to cure, has wider operating window, and is not sensitive to raw material moisture content and pH.

In integrating p-MDI into a fibreboard production process, it is important to have multiple trials to understand how to optimize the resin fully and take advantage of its capabilities to produce boards that will meet the manufacturer's published specifications. Also, this resin can be modified to suit the manufacturer's needs by adding catalysts, combining it with another resin, or emulsifying it in water. Different options can improve the production process and the final product's performance in use.

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