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The Forests, The Trees, The Fields, The Isocyanates

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The title of this article may have grabbed your attention and may seem ironic or out of context, but I hope to share with my readers how the use of isocyanate and polyurethane binders and adhesives allow for efficient, economic, green, and sustainable use of forest and agricultural resources. Starting with the forests, we know that forests provide beauty, habitat, biodiversity, climate control, economic and cultural benefits to our world. The forest products industry is a major contributor to the economies of many countries around the world. Wood based composites comprise the use of wood fiber, wood chips, and whole lumber adhered with a variety of adhesives types. One of the most efficient types of adhesives in use for these products are isocyanate binders and polyurethane adhesives.

Perhaps the first place to start is to understand the difference between a Binder and an Adhesive. In the literature, you may find these terms used interchangeable depending on the specific discipline being discussed. Both binders and adhesives hold together organic or inorganic materials via adhesive and cohesive mechanisms. The term binder, is typically used to refer to a resin used to hold fibers, or particles, or aggregates of some material together. They are commonly a liquid, but a binder can also be a waxy material. Binders are typically not highly formulated. An adhesive by contrast is typically thought of as a more highly formulated liquid polymeric material that binds or fastens two similar or different substrates. For the sake of wood composites, an isocyanate, like polymeric methylenediphenyl diisocyanate (PMDI), is considered a binder. PMDI binders may or may not contain other additives that are stable in the isocyanate, like a catalyst, or they may have been reacted with a small amount of polyol to impart a

degree of hydrophilicity, but in general they are high –NCO (isocyanate functional) containing liquids. In contrast, polyurethane adhesives are made by reacting some or all of the isocyanate functionality with hydroxyl or amine terminated polyols of different chemical functionality. They may also contain catalysts, surfactants, and organic or inorganic particulates. These materials can be found as one-component reactive or non-reactive adhesives, solvent borne one-component adhesives, or aqueous borne polyurethane dispersions. Polyurethane adhesives can also be two component materials in which the components react when they are mixed. These two component systems can be solventless or solvent borne materials. In addition, polyurethane adhesives can be solid or semi-solid, non-reactive or reactive hot-melts, which turn to liquids when heated and then solidify upon cooling. For wood composites like particleboard (PB) medium or high density fiberboard (MDF, HDF) or oriented strand board (OSB) PMDI is used as a high –NCO binder to hold these composites together.

Getting back to the forests, it is important to know that the forest resources available, in many parts of the world today are larger than they were decades ago. According to a 2015 United Nations Food and Agriculture Organization (FAO) report, the total forest area in Europe, North America, the Caucasus and Central Asia was reported to be over 1.6 billion hectares - half of which is in the Russian Federation, and 37% of which is in the United States and Canada. Altogether, these regions include 40% of the world's forests, and most of these forests are classified as boreal or temperate. South America contains about 27 % of the worlds forest defined as tropical and temperate.[1] The FAO report also states that the rate of forest loss globally has decreased by 50 percent. This is partially due to conservation efforts, partially due to reforestation efforts by governments and private corporations and partially due to a recognition of the economic value of maintaining and managing forest resources and forest sustainability.

The manufacturing of wood based composites has contributed to the trend of better use of forest resources. The reason for this, is that these composites are made from trees that have been reduced to some particle, fiber, or flake configuration. The particles, fibers or flakes are then reconstituted into structural and non-structural composites for industrial, construction and building, or furniture applications. The making of wood composites allows for the efficient use of almost the entire tree. In addition, a variety of wood species, which are not inherently strong enough for structural applications, or small trees from forest management practices can be broken down into particles, fibers, or flakes and reconstituted into strong composites. Recycled wood from various sources can also be used for this purpose. The global wood based composite panel market is reported to be in excess of $ 162 billion dollars with a predicted annual compound growth rate of over 7 percent for the period through 2026.[2] As such, renewable forest resources are valuable economically as well as biologically, ecologically and culturally.

In addition to forest resources, agricultural waste from farm fields can also be used to make particleboards and fiberboards. Residues from rice production (rice straw), wheat and grain production (cereal straw), and sugar cane production (sugar cane bagasse) to

name a few, have been used to make non-structural composites for furniture and building applications. Many years ago, the United States Department of Agriculture Forest Products Laboratory conducted a literature survey to understand the number of agricultural sources of fiber used for composite building materials worldwide. The survey came up with over one thousand references.[3] That number has surely grown over the decades since the report.

The growing market for wood and agricultural composite panels leads to the demand for efficient binders for the manufacturing of these composites. PMDI is one of the efficient, cost effective binders which can be used. The molecular structures of the oligomeric species found in PMDI can be seen below in Figure-1.

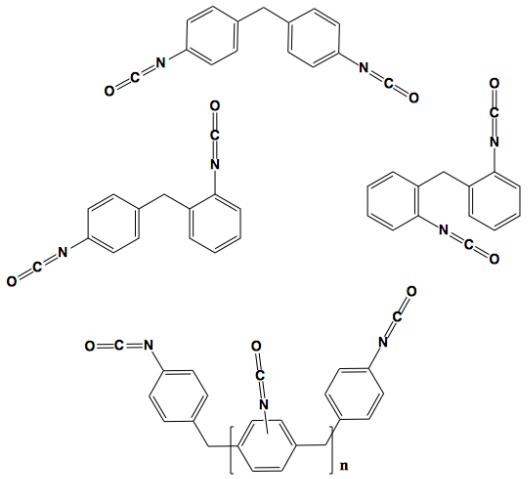

Figure-1. Illustrative structures of methylenediphenyl diisocyanate (MDI) and polymeric methylenediphenyl diisocyanate PMDI

PMDI is typically atomized onto wood or agricultural particles in large blending systems at the wood composite manufacturing plant. Engineering controls in the manufacturing plants are designed for safe and efficient atomization of the PMDI. The binding (adhesive) properties of PMDI result from the reactivity of the isocyanate groups. It is well known that isocyanates react with molecules and compounds that have active hydrogen moieties, such as water, alcohols, and amines. Wood is filled with many active hydrogen molecules from cellulose, hemicellulose, lignin, organic extractives, and of course water. Once the wood or agricultural fiber has been coated with PMDI the particles are formed into large matts and hot pressed at temperatures typically near or slightly above 200 ^{o}C. The addition of heat, via hot pressing, pushes the reaction of the PMDI with the active hydrogens in the wood and results in strong interpenetrating polymer networks. The primary reaction products, which are reported to occur in the wood composites made with PMDI, are the formation of urea and biuret polymer networks.[4, 5, 6] During hot pressing steam forms and the heat and pressure softens the

wood during consolidation of the wood composite. The urea and biuret molecules resulting from the reaction of the steam with the isocyanate molecules, grow and move within the wood due to the steam movement within the composite. This results in network polymers that are interpenetrating into the wood structure and form strong hydrogen bonding networks. It is also possible that some urethane bonding can occur by the isocyanates reacting directly with wood molecules, but urethanes are not reported to be the major reaction products formed.[4, 5, 6]

Let us ruminate back to the field and talk about another interesting technology which is derived from agricultural products and can be used in combination with MDI and PMDI. The ever-growing push toward greener chemistry has resulted in many new adhesive options based on proteins, lignin, and polysaccharides. All of these natural molecules contain active hydrogens which can be reacted with MDI and PMDI. Several companies are successfully exploiting these technologies commercially. The combination of these natural polymers with PMDI results in hybrid binder systems. These hybrid binders are reported to be able to allow the composite manufacturer to reduce the amount of PMDI used and still maintain or enhance the composite performance obtained when using neat PMDI binders. In addition, since most of these systems are aqueous dispersions of the natural product and the PMDI, the partial reaction of PMDI with these systems reduces the hygiene concerns associated with atomization and handling of neat PMDI. It is further reported, that these hybrid systems have a faster rate of cure of the binder within the composite, thus enhancing manufacturing productivity.[7, 8] The polymer synergies between these bio-based materials and PMDI result in a greener and more sustainable and economic binder option for wood composite manufacturers.

In closing, let us reflect that billions of people and countless species rely on the forests, the trees, and the fields for habitat, food, and survival. It is important that we use these resources responsibly and sustain these invaluable resources.

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