Biobased Resins – Towards a Sustainable and Healthier Future

Aik Fei Ang[1] and Rasmina Halis[1,2]*

[1]Department of Forest Production, Faculty of Forestry,
[2]Institute of Tropical Forestry and Forest Products,
Universiti Putra Malaysia, 43400, Serdang,Selangor, Malaysia.

**Corresponding author's email : angaikfei@upm.edu.my*

Introduction

Biobased resins are a term devised to describe a resin or resin formulation derived from biorenewable resources. Thus, many traditional resins such as protein-based soybean, blood, collagen or casein, or carbohydrate-derivatives from cellulose or starch, natural rubber based adhesives and natural phenolic adhesives such as tannin or lignin may all be classed as biobased resins. The existence of biobased resins is, therefore, not a recent phenomenon and man has been using these adhesives for millennia, long before the advent of MDI [4,4'-methylenebis (phenyl isocyanate)], phenol-formaldehyde (PF), melamine-urea formaldehyde (MUF) or other synthetic systems. Though, with the exponential development of petroleum industry and low in price, synthetic petroleum-based resins rapidly occupied the entire composite wood panels industry.

Nevertheless, there is a dramatic shift in the development of novel materials derived from biorenewable resources in the past few years due to rising environmental awareness, depletion of petroleum resources, and health concerns (Fernandes et al., 2013). Apart from this, biobased materials produced from feedstock that derived from different natural and biorenewable resources have been applied in several end applications such as in the automotive and biomedical fields (Ojijo et al., 2013). Some desire properties of natural and biorenewable materials such as biodegradability, acceptable specific strength, low density, recyclability, ease of separation, high toughness, good thermal properties, no health risk, reduced tool wear, non-irritation to the skin, and enhanced energy recovery have made them a material of choice (Dobos et al., 2012). The availability of biobased materials is abundant and readily available at very low cost as they are derived from natural and renewable feedstock that emerged naturally (Dhakal et al., 2012).

Synthetic Adhesives

Synthetic adhesives that depend on feedstock derived from petrochemicals are threatened from the instability of the price of the raw materials and the chemical persistence. In addition, adhesives as an important component in engineered wooden products should be separated for life cycle costs and must not impart undesirable effects on building occupants or the environment. Due to these reasons, it can be foreseen that the importance of biobased adhesives especially in the wood manufacturing and construction industries will be increasing soon.

Market Drivers

Nowadays, synthetic adhesives industry is facing several issues such as increment in raw material costs as well as health and environmental concerns attributed to the utilization of synthetic adhesives. Increasing costs of raw materials, oil price fluctuation and higher costs incurred in the modifications of synthetic resins to comply with environmental and safety regulation had threaten the utilization of synthetic adhesives. The increment in costs will be absorbed by purchasers as sellers would like to maintain their profits and public awareness on the health, safety and environment concerns are the primary market constraints to synthetic adhesives

i. Health, Safety and Environment Concerns with the Resins:
There is health risk could be generated from particular raw material (chemicals) of such synthetic resins. For example, the most well-known chemical used is formaldehyde in the production of formaldehyde-based adhesives such as urea formaldehyde (UF) and phenol formaldehyde (PF). Excessive exposure of human and environmental to carcinogenic formaldehyde is concerns and risky.

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ii. Health, Safety and Environment Concerns with Other Adhesive Components:
Additionally, other components in the adhesives may also generate some issues. Resins in synthetic adhesives are dissolved in organic solvents which served as carrier so that the resins can be applied easily. Such organic solvents can comprise up to 80% of the final weight of the product and this is the main issue. Volatile organic solvents that emit harmful gases are bad to air quality and legislation in this area is becoming increasingly stringent.

iii. End of Life Concerns and Recycling
Adhesives are one of the considered contaminants besides paint and wood preservatives which would disturb on the ability to reuse, recycle or in some cases energy recovery from the reclaimed wood resource. If engineered wooden products are bonded with bioresins, it is an attractive way where the used wooden products could be sent for composting, reuse or recovery of energy without any compromising to the environmental or health and safety issues.

iv. Standards and Best Practice
Many standards and regulations have been devised for assessment of performance for adhesives and adhesives bonded products. New products must pass through the rigor of this process.

Adhesives are an important raw material used in the manufacturing of many kinds of consumer product. Due to the reasons mentioned above, the development of environmentally friendly biobased adhesives is noteworthy and numerous researches in this area indeed have been conducted in the past few decades.

Types of Biobased Adheisves

As mentioned in the previous section, there are several examples of natural and biorenewable compounds that may offer commercialization prospects for new adhesive systems, these include: tannins, lignin, cashew nut shell liquid (CNSL), carbohydrates, triglycerides and proteins.

Tannin-Based Adhesives
The primary precursor to form tannins is gallic acid residues that are linked to glucose via glycosidic bonds, as shown in Figure. 1.

Tannins are natural and renewable phenolic chemical compounds. They are classified into two different classes namely hydrolysable tannins and condensed

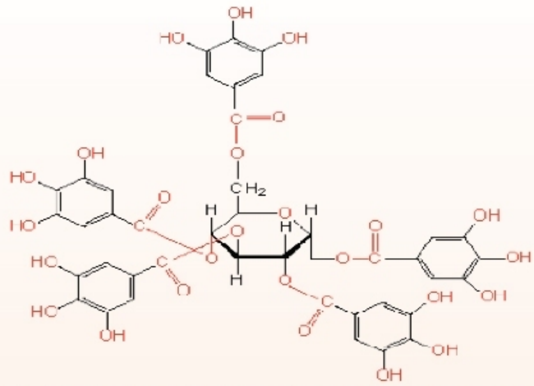

Fig. 1. Basic chemical structure of tannin compounds

Hydrolysable tannins are not commercial feasible to use as feedstock for production of biobased resins and adhesives as their structure is naturally less reactive and limited availability worldwide. Contrary, condensed tannins which are presently constituting majority of the total world production of commercial tannins are more feasible to use as feedstock for the preparation of adhesives and resins when both chemical reactivity and economic factors are come into consideration. Tannin oligomers and polymers occurred in nature through the polymerization of the simplest units known as galloyl. Duplicating similar chemical linkages in adhesive systems could be achieved, for example through Ullmann reactions for the preparation of biphenyls or biaryl ethers.

Condensed tannins are the formation cursors for flavonoids, and are abundantly be found in nature. Beside the presence of tannin in red wine and tea, tannins are able found naturally and abundantly in bark of various trees that could be fulfilled the needs for commercial extraction purpose. This expands the opportunities for timber bark which generated as waste for primary processing procedures for value added end-uses.

Lignin
Originating from plants, lignin exists in large quantity in plants after cellulose and mainly served as mechanical support and binder to the plant fibers. The polyphenolic in nature of lignin is attributed to its constituents which are comprise of three types of monolignols (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) and those monolignols have an unsubstituted C_3 or C_5 position on the aromatic ring. Moreover, owing to its possession of phenolic and aliphatic hydroxyl groups that can create quinone methide intermediates which are able to react with an aldehyde, tannin, phenol and isocyanate by heating under alkaline condition, lignin is suitable to be utilized as chemical for polymerization reactions in wood adhesives (Abdelwahab and Nassar, 2011; El

Mansouri et al., 2011). As a polyphenol, lignin should behave like phenol in phenol formaldehyde (PF) resins which reacts and crosslinks with formaldehyde to yield hydrophobic and water insoluble adduct. Lignins (lignosulfonate and kraft) which its structure have been modified during the acid and alkaline pulping processes require further crosslinking so that they could be transferred into insoluble resins.

Cashew Nut Shell Liquid (CNSL)
The cashew tree is originally native to Brazil but it is widely planted in more than 30 countries worldwide due to the popularity of cashew nuts. The nut crop is estimated of around 2.3 million tons per annum. The function of CNSL is to act as a deterrent to prevent animals eating the exposed kernel and the nut inside. As shown in Figure. 2, the chemical structure of CNSL may differ due to the substitution of 4 different main groups of compounds in the aromatic phenolic ring.

The taste of CNSL is extremely bitter and this is attributed to the phenolic compounds present in CNSL. The phenolic in nature of CNSL makes it a possible feedstock for biobased resins production. However, some factors such as region of production as well as different in seasons would affect the composition of CNSL. This variability may limit the commercial application since the chemical properties may vary from batch to batch.

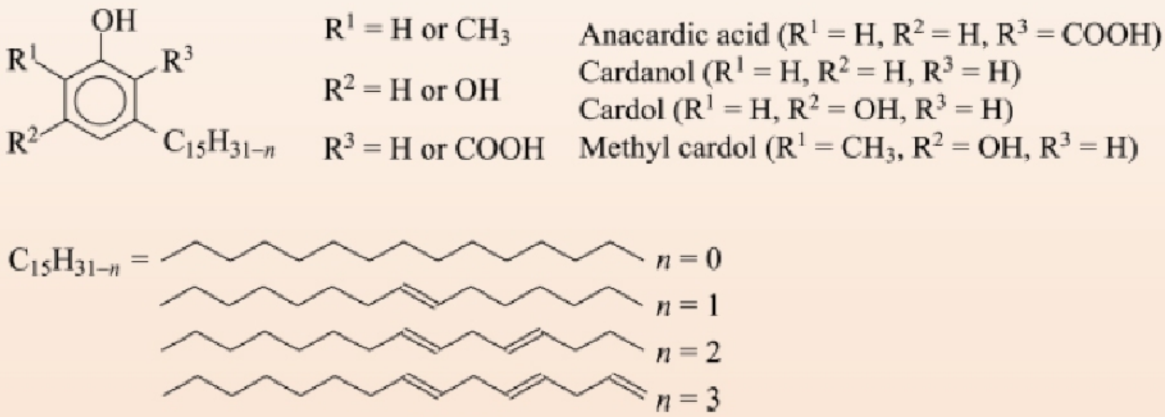

Fig. 2. Components of CNSL.

Carbohydrates
Gums, polysaccharides (cellulose, starch and hemicellulose) and sugars are example of carbohydrates that can be used to produce adhesives. Carbohydrates-based adhesives are readily available and very cost effective but they unable to serve as binder in engineered wooden products. Narayan et al. (1989) revealed that cellulose-polystyrene graft polymer had been successfully used as binder to produce wood-plastic composite (WPC).

Partly carbohydrates substituted PF resins have been tested to bond wood veneers (Conner and Lorenz, 1986). The authors found that the modified PF resins did not negatively affect the dry or wet shear strength of 2-ply softwood panels.

Triglyceride
Plant based triglyceride oils can be used to synthesize several different monomers for use in structural applications. These monomers have been used to produce polymers with a wide range of properties. These resins are capable to serve as binder to bond glass fibers and natural fibers such as flax and hemp to produce composite materials. These resins are also capable to use as binder to produce hybrid composites from the low cost natural fibers and high performance synthetic fibers. Their properties lie between those displayed by the all-glass and all-natural composites.

Plant-Based Protein
Soya, either the soybean meal or a protein isolated from the soybean is the most studied plant protein adhesive. The water resistance of this resin is low and the bonding strength is also inferior. It can be hot pressed and has been used as binder to fabricate interior softwood plywood in the past.

The utilization history of soy-protein-based wood adhesives can be traced back to centuries ago. However, these adhesives have been extensively replaced by high performance and cheaper petroleum-based adhesives. Adekunle et al. (2011) reported that soybean oil thermosetting polymer had been successfully used as binder to fabricate composites and hybrid composites using jute fabrics and carded lyocell fiber.

Animal-Based Adhesives

Casein from milk curds has been used as wood adhesive for bonding and lamination of timbers for interior applications. However, its disadvantage is such wood adhesives are very expensive as the raw material is costly. Such animal protein-based wood adhesive is chosen as they possess superior moisture resistance compared to other animal and plant protein glues.

Glues made from blood albumin are water resistance and they were important class of moisture resistant glue for softwood plywood manufacturer before the existence of the synthetic resins. Such wood adhesives exhibited some temperature resistance and are more resistance to the deterioration by mold and fungi than the traditional animal glues and casein glues.

Conclusions

Biobased resins have been used for centuries in wood industries. Resins or resin formulations derived from natural and biorenewable resources are virtuous for environmental and health aspects. However, due to some technical limitations such as low water resistance, low bonding strength and higher cost, biobased resins have been rapidly replace by high performance and lower price petroleum based synthetic resins in manufacturing of wooden products. Though, petroleum based synthetic resins are now coming under increasing restrictions due to tightening environmental exposure regulations. Hence, biobased resins should be revived to substitute synthetic resins as a sustainable manner, provided the performance of biobased resins can be improved through robust of researches.

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