American Journal of Environmental Science and Engineering
2022; 6(1): 16-21
http://www.sciencepublishinggroup.com/j/ajese
doi: 10.11648/j.ajese.20220601.13
ISSN: 2578-7985 (Print); ISSN: 2578-7993 (Online)

Application of Formaldehyde Free Adhesive in Composite Floor

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To cite this article:

Zhiyong Zheng, Yongqiang Jiang, Kaixuan Zheng, Qi Li, An Mao. Application of Formaldehyde Free Adhesive in Composite Floor. *American Journal of Environmental Science and Engineering*. Vol. 6, No. 1, 2022, pp. 16-21. doi: 10.11648/j.ajese.20220601.13

Received: December 30, 2021; **Accepted**: January 14, 2022; **Published**: January 24, 2022

Abstract: With the enhancement of consumers' concept of "health and environmental protection", the requirements for the living environment are higher and higher, and the quality of home decoration materials has attracted much attention. The green adhesive without formaldehyde has become a research and application hotspot in recent years, and has been more and more widely used in the composite floor industry. Composite floor is an indispensable building material with large application area in residential decoration. The selection and use of adhesives directly determine the environmental protection grade of composite floor. Biomass adhesives, polyurethane adhesives and thermoplastic resin adhesives represented by soybean adhesives are the three types of aldehyde free adhesives with the greatest development potential in composite floor industry at present. This paper reviews the application of aldehyde free adhesives such as polyurethane (including isocyanate) adhesives, waterborne polymer isocyanate adhesives, polyethylene films, soybean protein adhesives and polyvinyl acetate adhesives in solid wood composite floors and paper impregnated laminated wood floors (laminate floor), bamboo floor and other common composite floors, discusses the existing problems, and looks forward to the main research and development direction in the future.

Keywords: Composite Floor, Formaldehyde Free Adhesive, Bio Based, Protein Adhesive, Isocyanate

1. Introduction

With the enhancement of consumers' concept of "health and environmental protection", the requirements for the living environment are higher and higher, and the quality of home decoration materials has attracted much attention. Since 2017, the introduction of fine decoration policies of local real estate has opened the era of "hardbound house". The quality of wood forest products used for interior decoration has become a key factor affecting the health quality of China's living environment, and the formaldehyde emission has therefore become the most important environmental protection index for consumers. In recent years, China has formulated a series of standards for formaldehyde free or low formaldehyde wood-based panels, such as the national standard evaluation of green products, wood-based panels and wooden floors, the industrial standard technical requirements for green wood-based panels and their products, the group standard formaldehyde free wood-based panels and their products, and the newly implemented national standard classification of formaldehyde emission from wood-based panels and their products, The implementation of these standards is of great significance to standardize the production of low aldehyde / non aldehyde additive products and promote the green development of wood-based panel and its products industry in China [1-3].

Composite floor is an indispensable building material with large application area in residential decoration. Environmental regulation: it can partially regulate the indoor

temperature and humidity. Strong sense of natural vision: the surface of solid wood composite floor has beautiful natural texture, fine structure, rich in change, beautiful and generous color. Comfortable foot feeling: the solid wood composite floor has appropriate elasticity and moderate friction coefficient, which is easy to use. Good material, easy to process and recyclable: wood is a renewable natural material, It is one of the four major materials in the world today (steel, wood, plastic, cement) is the most sustainable green material. Among them, the three-layer solid wood composite floor can be renovated after shaving and paint removal. With good geothermal adaptability, multi-layer solid wood composite floor can be used in geothermal heating environment, which solves the problem of solid wood floor in geothermal heating environment. Strong stability: due to solid wood, the excellent structural characteristics of wood composite floor ensure the stability of the floor technically. Easier construction and installation: solid wood composite floor usually has a large format size, and can be installed directly by suspension method without keel, so as to make the installation faster. The installation cost and time are greatly reduced, and the product quality accidents caused by poor keel are avoided. Excellent environmental protection performance: the solid wood and environmental protection adhesive used in the solid wood composite floor are processed through advanced production technology, so the environmental protection performance is good and meets the national mandatory environmental protection standards. Create a comfortable environment: good thermal insulation, heat insulation, sound insulation, sound absorption, insulation performance, etc. Richer decorative performance: the surface layer of solid wood composite floor is colorful. It is made of precious natural wood with unique color and pattern. In addition, the design of surface structure and the introduction of dyeing technology make the decorative performance of solid wood composite floor more colorful. The comprehensive utilization rate of wood has been greatly improved, which has greatly improved the comprehensive utilization rate of wood, especially saving a large number of high-quality wood, which is in line with the industrial policies of the state and the industry, and is conducive to the sustainable development of the country. The wear resistance of solid wood composite floor is more than 10-30 times stronger than that of ordinary floor. In addition, it also has the functions of anti impact, anti-static, pollution resistance, light resistance and so on. The selection and use of adhesive directly determines the environmental protection grade of composite floor [4-6].

This paper reviews the application of aldehyde free adhesives such as polyurethane (including isocyanate) adhesives, waterborne polymer isocyanate adhesives, polyethylene films, soybean protein adhesives and polyvinyl acetate adhesives in solid wood composite floors and paper impregnated laminated wood floors (laminate floor) and bamboo floor, discusses the existing problems, and looks forward to the main research and development direction in the future [7].

2. Application of Aldehyde Free Adhesive in Composite Floor

Solid wood composite floor is made of solid wood panels or veneers (including reconstituted decorative veneer). At present, three-layer solid wood composite floor and multi-layer solid wood composite floor are mostly used in the market. The solid wood composite floor retains the natural texture and comfortable foot feeling of the solid wood floor, and the dimensional stability is higher than that of the solid wood floor. The base material of multi layer solid wood composite floor is usually multi-layer plywood, so the varieties and requirements of adhesives used are the same as those used for plywood.

2.1. Biomass Adhesive

In recent years, biomass adhesives represented by soybean protein have developed rapidly. The traditional soybean protein adhesive generally has the problems of low water resistance and short storage life. After years of practice and improvement, the synthetic modification methods of soybean gum have been continuously improved, In solid wood composite floor (including multi-layer solid wood composite flooring and composite wood flooring with thick core board substrate and solid wood panel substrate) the application process is gradually mature, the gap between the physical and chemical properties of its products and aldehyde glue is narrowing, the products have been industrialized, and the consumption is increasing. The consumption of soybean protein based adhesive is about 40000 tons in 2019, with a year-on-year increase of 58%, mainly used for bonding At present, there are 4-5 typical enterprises producing soybean protein glue on a large scale in China [8].

Other biomass adhesives can also be used in solid wood composite floor substrates, but most of them are still in the R & D and experimental stage, which is still a certain distance from industrial production. Starch is a natural polymer material with high yield, wide source and low price. It has gel, thickening and film forming properties. Starch based adhesive has better initial viscosity than soybean adhesive, but its wet bonding strength is low and easy to mildew in the process of use. At present, starch glue still has some practical problems in plywood production. The process conditions need to be further studied and explored. It often needs to be combined with other adhesives in practical application. Lignin is the second abundant renewable resource in the world. The sewage of paper industry contains a large amount of industrial lignin. The effective utilization of waste lignin resources has become the research goal. At present, lignin containing active functional groups such as alcohol hydroxyl and phenol hydroxyl is mainly used to replace phenol to prepare low toxicity lignin modified phenolic resin. After modification, lignin can also be directly used as adhesive in plywood production.

2.2. Aqueous Isocyanate

Waterborne isocyanate adhesive is a kind of two component adhesive composed of main agent and crosslinking agent. The main component is polymer aqueous solution, water emulsion, water dispersions or their mixture. The main component of isocyanate compound is a crosslinking agent. When in use, the main agent and crosslinking agent react to form a three-dimensional crosslinking structure, so as to obtain better water resistance and heat resistance. Under the conditions of cold pressing, hot pressing and high-frequency heating, the aqueous isocyanate adhesive can cure and has stable performance. The water resistance and bonding strength of its floor substrate are generally better than those of soybean adhesive and ordinary aldehyde adhesive. The application mode of waterborne isocyanate adhesive is flexible. By changing the addition amount of crosslinking agent, it can not only be used for bonding of solid wood composite floor, but also for secondary processing of laminated wood, hollow board and blockboard [9].

The release and implementation of the industry standard water-based polymer isocyanate wood adhesive has promoted the rapid development of water-based isocyanate adhesive. At present, water-based isocyanate adhesive products have been industrialized. The formaldehyde emission of the bonded solid wood composite floor substrate fully meets the requirements of the group standard of aldehyde free wood-based panel and its products, and all physical and chemical properties are good. At present, the cost of aqueous isocyanate adhesive still needs to be further reduced. Wang Shumin and others prepared starch solution by oxidative acidolysis of starch, then added polyvinyl alcohol and emulsifier to synthesize starch based main agent, and finally added isocyanate to prepare starch based aqueous isocyanate adhesive. The introduction of starch reduced the cost of aqueous isocyanate adhesive [10].

2.3. Non Aldehyde Thermoplastic Resin

Thermoplastic resin has been gradually used in the production of wood composite board in recent years. In 2009, the State Forestry Administration issued and implemented the industry standard non formaldehyde thermoplastic resin plywood, which defined and standardized the ordinary plywood prepared with wood veneer as raw material and non aldehyde thermoplastic resins such as polyethylene and polypropylene as adhesive. At present, the most commonly used thermoplastic resin is high-density polyethylene. Polyethylene is a thermoplastic resin material with good performance and suitable for plywood production [11].

Polyethylene can be modified and grafted with polar groups, so as to produce a strengthening bond force with hydroxyl groups on the wood surface, so as to obtain sufficient bonding strength under the condition of small sizing amount. Chang Liang et al. Concluded by comparing the properties of polyethylene adhesive film plywood and urea formaldehyde resin plywood commonly used in the market that under normal use environment, the bonding properties of polyethylene adhesive film plywood and urea formaldehyde resin plywood are equivalent, and polyethylene adhesive film plywood is significantly better than urea formaldehyde resin plywood in water resistance, stability and environmental protection. The solid wood composite floor prepared with polyethylene adhesive film plywood can meet the requirements of the standard of solid wood composite floor for floor heating for dimensional stability, surface cracking resistance, surface moisture and heat resistance and so on.

Liu Jiankai and others melt grafted maleic anhydride into low-density polyethylene. The obtained graft copolymer takes polyethylene macromolecular chain as the skeleton and maleic anhydride as the side group. Through extrusion blow molding, a high-performance adhesive film without formaldehyde and volatile toxic substances is prepared, which has been well used in plywood. At present, polyethylene adhesive film plywood has started industrial production in Fujian and is gradually being popularized and applied in the fields of furniture plate, floor substrate, building formwork and so on.

Polyvinyl acetate emulsion, also known as "white latex", "white glue" and "woodworking glue", is a thermoplastic adhesive prepared by emulsion polymerization of vinyl acetate as a reaction monomer in the dispersion medium. It has the advantages of fast curing speed, strong adhesion, low price, non-toxic and no pollution, but because of its poor heat and water resistance, It can be mixed with isocyanate in an appropriate proportion into two-component isocyanate white emulsion for use, or it can be used directly after modifying the white emulsion. Khan et al. Strengthened polyvinyl acetate with graphene, and the bonding strength and toughness of its adhesive were increased by 4 times and 7 times respectively. Chaabouni et al. Used nano cellulose to strengthen polyvinyl acetate, which increased its shear strength by about 2 times and improved its water resistance [12].

3. Laminate Floor

Laminate floor is a floor impregnated with thermosetting amino resin with one or more layers of special paper, paved on the surface of wood-based panel substrate such as particleboard and high-density fiberboard, with balance layer on the back and wear-resistant layer on the front, and hot pressed and formed. At present, the laminate floor produced is mostly laminated from top to bottom by wear-resistant layer, decorative layer, base material layer and balance layer. The base material layer generally adopts high / medium density fiberboard or particleboard. Laminate flooring has the advantages of good surface wear resistance and high dimensional stability. At present, urea formaldehyde resin is still used in the bonding of fiberboard for most substrates, resulting in a certain formaldehyde pollution. In recent years, aldehyde free adhesives have been widely used in fiberboard.

3.1. Isocyanate Adhesive

In 2019, the consumption of isocyanate for wood-based panel was about 70000 tons, with a year-on-year increase of 36%. At present, polydiphenylmethane diisocyanate is the

most widely used isocyanate (PMDI). Compared with formaldehyde resin, isocyanate has the advantages of strong reactivity, fast curing, good water resistance of adhesive layer and no formaldehyde release from bonded wood-based panels. However, due to its small molecular weight, the monomer in isocyanate is easy to penetrate into wood pores and cause glue shortage on the surface of veneer. Therefore, isocyanate is generally not directly used for bonding plywood. In North America, isocyanate is mainly used for bonding plywood It is used for bonding oriented particleboard and medium density fiberboard, and gradually applied to various wood composite boards and surface decorative boards such as particleboard (particleboard, oriented particleboard), medium / high density fiberboard in China.

Isocyanate can be used alone for bonding of fiberboard substrate. However, due to the high price and frequent change of isocyanate, the stable use of isocyanate is affected to some extent. Moreover, the strong reaction ability of isocyanate is easy to cause the problem of adhesion between steel strip and pressing plate. Release agent needs to be used continuously, which affects the continuity of production and leads to the decline of production efficiency. In addition, isocyanate bonded fiberboard can basically meet the requirements of laminate substrate in terms of various physical and chemical properties. Isocyanate can also be used in combination with urea formaldehyde resin and polyurethane, which can not only reduce the cost, but also solve some defects of these resins when used alone.

At present, dozens of large-scale wood-based panel enterprises in China have successively used isocyanate to produce fiberboard, and isocyanate has been used more and more. However, due to its strong reactivity and high cost, some enterprises began to try to use aqueous isocyanate adhesive to produce fiberboard, but it is still in the production test stage and has not really started mass and stable production [13].

3.2. Soy Protein Adhesive

The process parameters of modified soybean protein adhesive in fiberboard production were studied by orthogonal analysis. The results show that the performance index of fiberboard can meet the requirements of national standard by using reasonable process parameters; Under the conditions of hot pressing temperature 180°C, hot pressing time 25 s / mm, sizing amount 12-15% and moisture content 15-17%, the best performance of fiberboard can be obtained: the static bending strength is more than 29 MPa and the internal bonding strength is close to 0.8 MPa. GUI Chengsheng and others initially produced samples of 12mm thick high-density fiberboard on the continuous flat pressing production line. They found that the high-density fiberboard pressed with soybean glue can meet the strength requirements of the standard fiberboard for floor substrate, but the subsequent processing performance needs to be further evaluated. In general, the application of soybean protein adhesive in fiberboard has not been fully industrialized. There are mainly problems of high viscosity and low initial viscosity, and the strength of pressed fiberboard decreases rapidly and is easy to mildew.

4. Bamboo Floor

Facing the shortage of wood raw materials, domestic wood-based panel enterprises began to seek bamboo as an alternative raw material for wood, and formed two representative products: Bamboo laminated flooring and bamboo cement formwork. Bamboo floor is one of the mainstream products of bamboo wood-based panel, which is mainly used for indoor and outdoor floor decoration [14].

The bonding effect of soybean protein adhesive on bamboo is better than that of urea formaldehyde resin, which is an advantage of soybean adhesive in bamboo bonding. Studies have shown that the performance indexes of bamboo flooring prepared with modified soybean protein adhesive can meet and exceed the relevant national standards. At present, the dry shear strength of modified soybean glue can reach about 3.0MPa, and the wet shear strength can also reach 1.5MPa. This modified soybean glue has begun industrial production [15]. It is mainly used in plywood and particleboard bonding, food label bonding and papermaking industry, but there is little research on its application in bamboo cutting board and bamboo flooring. The impregnation peel strength of a bamboo floor with three-layer structure bonded by bean glue in a bamboo floor enterprise in South China is better than that of E_1 urea formaldehyde resin.

Shi Junyou and others conducted a production test of starch based aqueous isocyanate adhesive for bamboo flooring. It is found that the physical and chemical properties of bamboo floor adhesive products made of starch based aqueous isocyanate adhesive fully meet the requirements of relevant standards, and there is no release of formaldehyde and other harmful substances. This adhesive has certain advantages in process operability, raw material cost, social environment and economic benefits. It has the advantages of long activity period, good preloading and simple hot pressing process, and has a good development prospect.

5. Conclusion

Generally speaking, after the rapid development in recent years, aldehyde free adhesives have been more and more used in the production of composite flooring, but there are still some common problems: protein adhesives still have the problems of low preloading, insufficient initial adhesion and weak bonding durability, and 30% of domestic soybean consumption is imported from the United States, Sino US trade friction affects the supply-demand relationship and price of soybean, which is bound to cause some unstable factors for downstream products; The cost of water-based isocyanate adhesive is still high, and the requirements for process parameters such as temperature, humidity and opening time are high. When applied to plywood, the previous process of urea formaldehyde resin needs to be greatly adjusted, and the blank assembly time is long;

Isocyanate is easy to stick to the plate during hot pressing, so it is necessary to spray release agent on the surface of the hot plate in industrial production. In addition, the frequent fluctuation of isocyanate price has hindered its wide application in wood-based panel industry; the price of thermoplastic film products is high and the process conditions are complex. Although the use of thermoplastic adhesive film greatly simplifies the gluing or mixing process of wood-based panel, the hot pressed panel needs to be naturally cooled by cold pressing, which affects the production efficiency to a certain extent.

Biomass adhesive, polyurethane adhesive and thermoplastic resin adhesive represented by soybean adhesive are the three types of aldehyde free adhesive with the greatest development potential in the composite floor industry. To promote the rapid development of aldehyde free adhesives in the flooring industry, in addition to solving the above-mentioned problems such as the defects and application process of adhesives, the following work should also be done:

Increase the research investment of aldehyde free adhesive, improve the existing adhesive species, design and develop new adhesive species, and improve some properties according to the product use requirements on the premise of ensuring its bonding strength and durability, so as to better adapt to different types of floor substrates; Research and develop technologies matching the production of composite floor substrate, such as aldehyde free veneer technology of laminate floor, and abandon the traditional melamine formaldehyde resin, so that laminate floor is not only aldehyde free, but also aldehyde free veneer materials; Establish a stable market supply expectation and price system, and expand the application scope of aldehyde free adhesive; Actively promote the specialization of adhesive supply and the production of environmental protection and intelligence, and produce stable and high-quality environmental protection flooring products.

Author Contributions

The Manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Zhiyong Zheng and Yongqiang Jiang contributed equally and should be considered as co-first authors.

Conflicts of Interest

The authors declare that they have no competing interests.

Acknowledgements

The authors are grateful for the supports of the Agricultural Science and Technology Fund Project of Shandong Province (Forestry Science and Technology Innovation) (Project No. 2019LY008) and the "Youth Innovation Science and Technology Plan" of Colleges and Universities in Shandong Province (project no. 2020KJF012).

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