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Application of Graphene Oxide in Composite Geothermal Floor

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Abstract: With the rapid development of China's solid wood composite flooring industry, the market of solid wood composite geothermal flooring is gradually huge. The adhesives used in traditional solid wood composite geothermal flooring are mainly urea formaldehyde resin and phenolic resin. Its bonded wood-based panel has the problems of formaldehyde emission and poor waterproof. With the enhancement of people's awareness of safety and environmental protection, the problem of formaldehyde has attracted more and more attention. Looking for various formaldehyde free adhesives that can replace urea formaldehyde resin has become a research hotspot. Graphene oxide is a new carbon material with excellent properties, which has high specific surface area and rich functional groups on the surface. In this study, powdered oxygraphene material and isocyanate resin were mixed in different proportions to press the three-layer solid wood composite floor substrate, and the bonding strength and thermal conductivity were tested to investigate the effect of graphene oxide powder on the bonding and thermal conductivity of isocyanate resin. The experimental results show that the viscosity of the resin system increases with the increase of the amount of graphene oxide powder; Graphene oxide powder with mesh number of 250 can significantly enhance the bonding strength of isocyanate, But when the amount is too large (10%) on the contrary, the bonding strength decreases. Graphene oxide powder with mesh number of 50 does not significantly enhance the bonding strength; adding graphene oxide powder can improve the thermal conductivity of the floor. With the increase of the proportion of graphene oxide, the thermal conductivity, thermal conductivity and electrothermal conversion rate of the floor are significantly improved, but graphene oxide with mesh number of 50 is not as good as graphite oxide with mesh number of 250 Alkene increased significantly. The addition of an appropriate amount of graphene oxide fine powder reduces the infiltration of resin into wood, enhances the bonding performance and thermal conductivity, provides a new possible way for the application of graphene oxide material and isocyanate in the substrate of solid wood composite floor, and provides a certain practical basis for the manufacturing process and application technology development of thermal conductive floor and geothermal floor.

Keywords: Graphene Oxide, Isocyanate, Three Layer Solid Wood Composite Floor, Base Panel, Bonding Strength

1. Introduction

Graphene oxide is the oxide of graphene, which is generally represented by go. Its color is brown yellow. The common products on the market are powder, flake and solution. Due to the increase of oxygen-containing functional groups on graphene after oxidation, its properties are more active than graphene, and its properties can be improved through various reactions with oxygen-containing functional groups. Graphene oxide can be regarded as a non-traditional soft material with the characteristics of polymer, colloid, film and amphoteric molecules. Graphene oxide has long been regarded as a hydrophilic substance because of its superior dispersion in water. However, the relevant experimental results show that graphene oxide is actually amphiphilic, showing the distribution of hydrophilic to hydrophobic properties from the edge to the center of graphene sheet.

Therefore, graphene oxide can exist at the interface as an interfacial surfactant and reduce the energy between the interfaces. Its hydrophilicity is widely recognized [1-3].

After oxidation treatment, graphite oxide still maintains the layered structure of graphite, but many oxygen functional groups are introduced into each layer of graphene. The introduction of these oxygen functional groups makes the single graphene structure very complex. Many scientists try to describe the structure of graphene oxide in detail and accurately in order to facilitate the further study of graphene materials. Although the structure of graphene oxide has been analyzed by means of computer simulation, Raman spectroscopy and nuclear magnetic resonance, the precise structure of graphene oxide cannot be determined for various reasons. Recent theoretical analysis shows that the surface functional groups of graphene oxide are not randomly distributed, but highly correlated [4].

At present, there are three main methods for preparing graphite oxide: Brodie method, staudenmaier method and Hummers method. Hummers method is the most commonly used one because of its relatively good timeliness and relatively safe preparation process. After the oxidation reaction between potassium permanganate in concentrated sulfuric acid and graphite powder, a brown graphite sheet with derived carboxylic acid groups on the edge and mainly phenolic hydroxyl and epoxy groups on the plane is obtained. The graphite sheet layer can be stripped into graphene oxide by ultrasonic or high shear vigorous stirring, and a stable, light brown yellow single-layer graphene oxide suspension is formed in water. Although the final graphene product or reduced graphene oxide has many defects, resulting in its conductivity not as good as the original graphene, this oxidation − stripping − reduction process can effectively make the insoluble graphite powder processable in water and provide a way to make reduced graphene oxide. Moreover, due to its simple process and solution processability, considering the industrial process of mass production, the above process has become a very attractive process for manufacturing graphene related materials and components. Graphene oxide also shows its excellent physical, chemical, optical and electrical properties. Due to the coexistence of a variety of oxygen-containing functional groups on the base and edge of graphene lamellar skeleton, graphene oxide can modulate its conductivity and band gap by adjusting the type and number of oxygen-containing functional groups. The material has a wide range of applications. Graphene oxide is a new carbon material with excellent properties, which has high specific surface area and rich functional groups on the surface. Graphene oxide composites, including polymer composites and inorganic composites, have a wide range of applications [5].

The solid wood composite floor is made of staggered lamination of plates of different tree species, which overcomes the shortcomings of wet expansion and dry shrinkage of solid wood floor to a certain extent. The dry shrinkage and wet expansion rate is small, has good dimensional stability, and retains the natural wood grain and comfortable foot feeling of solid wood floor. Solid wood composite floor not only has the stability of laminate floor and the beauty of solid wood floor, but also has the advantage of environmental protection. In recent years, China's solid wood composite flooring industry has developed rapidly, in which the market of solid wood composite geothermal flooring is gradually huge. The adhesives used in traditional solid wood composite geothermal flooring are mainly urea formaldehyde resin and phenolic resin. Its bonded wood-based panel has the problems of formaldehyde release and poor waterproof. With the enhancement of people's awareness of safety and environmental protection, the problem of formaldehyde has attracted more and more attention. Looking for various formaldehyde free adhesives that can replace urea formaldehyde resin has become a research hotspot. Isocyanate is an ideal alternative glue at present [6]. In North America, isocyanates are mainly used for bonding oriented particleboard and medium density fiberboard, and are gradually widely used in China. Compared with formaldehyde thermosetting synthetic resin, isocyanate has the advantages of strong reactivity, fast curing, good water resistance of adhesive layer and no formaldehyde release from bonded wood-based panel; but the high cost limits its wide application. In addition, the monomer component in isocyanate is easy to penetrate into the wood pores due to its small molecular weight, resulting in lack of glue on the veneer surface. Therefore, it is generally not directly used to glue the substrate of solid wood composite floor [7-10].

In view of the above problems, the author tried to mix powdered oxygraphene with isocyanate resin and press solid wood composite floor substrate, and study the effect of graphene oxide powder on isocyanate bonding and thermal conductivity. The experimental results can provide a new possible way for the application of graphene oxide and isocyanate in the substrate of solid wood composite floor, and provide a certain practical basis for the manufacturing process and application technology development of thermal conductive floor and geothermal floor. In addition, the addition of graphene oxide powder increases the viscosity of the adhesive system, which can effectively reduce the excessive penetration of adhesive into wood, which provides a new possible way for the application of isocyanate in the production of solid wood composite flooring.

2. Materials and Methods

2.1. Materials

Graphene oxide powder, mesh 50 and 250, provided by angstron materials; Isocyanate (PMDI), lupranate m20fb, supplied by BASF, USA; poplar veneer, width 300 mm × 300 mm, thickness 1.6-1.7 mm, moisture content 10-12%.

2.2. Instrument

Digital display rotary viscometer, bolefield, USA; Hot press, Suzhou XinXieLi company; Universal mechanical testing machine, Instron, USA.

2.3. Preparation of Solid Wood Composite Floor Substrate

According to isocyanate (mass):graphene oxide powder (mass) = 100:0, 97.5:2.5, 95:5, 92.5:7.5, 90:10, mix isocyanate with two different mesh graphene oxide powders respectively, fully stir and apply it on the veneer surface within 30 minutes, with the glue amount of $150g/m^2$. Hot pressing conditions: temperature 135°C, pressure 1.2 MPa, time 1.1 min/mm. After hot pressing, cool to room temperature, sawing and grooving according to the specified size, Then put it into a constant temperature and humidity box with a temperature of 25°C and a relative humidity of 50% for 24 hours to obtain a three-layer graphene heat-conducting solid wood composite floor.

2.4. Performance Test and Characterization

The resin viscosity shall be determined according to GB/T 14076-2004. After the hot pressed solid wood composite floor substrate is aged for 24 hours, the test specimen shall be prepared according to GB/T 9846.4-2004, and the bonding strength shall be measured according to the requirements of class I plywood in GB/T 17957-2013 and GB/T 9846-2004 standards. In the above test, four composite floor substrates are pressed in each group, and 6 specimens are taken from each plate, and the average value is taken as the result.

The thermal conductivity is measured according to GB/T 7287-2008 test method for infrared radiation heater, which mainly tests the thermal conductivity, thermal conductivity and electrothermal conversion rate of solid wood composite floor substrate.

3. Results and Discussion

3.1. Effect of Graphene Oxide Powder Addition on Isocyanate Viscosity

After graphene oxide powder was added into the adhesive system, it absorbed some liquid isocyanate resin because of its powder structure, resulting in the change of system viscosity. Overall, the viscosity of the system increased rapidly with the increase of the amount of graphene oxide powder. Under the same addition amount, the viscosity of the system formed by 250 mesh powder is greater than that of the system formed by 50 mesh powder. Graphene oxide powder with smaller particle size has larger specific surface area, and there may be more physical and chemical interactions between it and isocyanate resin, such as the reaction between isocyanate and a small amount of water in graphene oxide powder; Isocyanate reacts with chemical groups in the powder; Agglomeration effect of graphene oxide powder itself. These effects may lead to the increase of viscosity [11].

When the content of graphene oxide powder is 10%, the viscosity of the system is too large, so it is difficult to test the viscosity, but the gluing operation can be carried out. When the addition amount is more than 10%, the system completely loses fluidity, and the resin is basically absorbed by graphene oxide powder, so the viscosity test and gluing operation cannot be carried out. Therefore, in the preparation of solid wood composite floor substrate, the plate with this ratio as adhesive is not pressed.

Table 1. Effect of addition amount of graphene oxide powder on viscosity of resin system.

Mesh	Addition ratio		Viscosity
	Isocyanate	Graphene oxide powder	(mPa·s)
250	100	0	235
	97.5	2.5	3054
	95	5	9785
	92.5	7.5	20123
	90	10	32144
50	100	0	235
	97.5	2.5	2971
	95	5	9700
	92.5	7.5	19887
	90	10	30121

3.2. Effect of Addition Amount of 250 Mesh Graphene Oxide Powder on Bonding Strength

The effect of the addition amount of 250 mesh graphene oxide powder on the bonding strength the reaction between isocyanate and wood is very complex. It is generally believed that in the process of bonding wood, isocyanate reacts with water in wood to form amines, and then reacts with excess free isocyanate group to form graphene oxide polyurea structure; At the same time, it can also self polymerize to form dimer and trimer, and form a ring structure. These reactions make the resin obtain cohesive strength. While the resin is crosslinked and cured, it reacts with hydroxyl groups in wood to form adhesive force. Isocyanate can form a stable network crosslinking structure after curing [12, 13].

By measuring the bonding strength of isocyanate resin bonded solid wood composite floor substrate, it can be seen from table 2 that with the increase of the addition amount of 250 mesh graphene oxide powder, the bonding strength increases, reaches the maximum value when the addition amount is 7.5%, and then the bonding strength begins to decrease. When pure isocyanate is used to glue the base material of solid wood composite floor, due to the relatively loose material of poplar veneer, isocyanate with low molecular weight is easy to penetrate into the wood pores, resulting in lack of glue on the veneer surface and affecting the bonding performance [14].

The viscosity of the adhesive system formed by adding a certain amount of graphene oxide powder increases, which can effectively reduce the excessive penetration of adhesive into wood. Isocyanate may also react with graphene oxide. However, since there is no large amount of residual isocyanate groups in graphene oxide powder and the moisture content is only 1% - 2%, the possible action relationship is that isocyanate reacts with a small amount of moisture in the powder; Isocyanate reacts with chemical groups in the powder; There are hydrogen bonds between polar groups and hydroxyl groups in graphene oxide powder. The first two reactions are beneficial to increase the crosslinking density and cohesion strength of isocyanate resin after curing; the occurrence of the latter is conducive to enhance the interaction between graphene oxide powder and wood, and the final results may be conducive to the improvement of bonding strength. At present, the research on the interaction relationship between graphene oxide and wood isocyanate bonding system is still very insufficient and needs to be further discussed. In addition, the addition of graphene oxide may increase the toughness of the brittle network crosslinking structure after isocyanate curing, so as to improve the aging resistance of the adhesive layer. Some graphene oxide powder may even enter the wood pores with isocyanate molecules to increase the crosslinking density, so as to enhance the adhesive force between wood and isocyanate.

Table 2. *Effect of addition amount of graphene oxide powder (250 mesh) on bonding strength.*

Addition ratio		bonding strength (MPa)		Wood failure (%)
Isocyanate	Graphene oxide powder	Mean	Standard deviation	
100	0	0.54	0.15	30-60
97.5	2.5	0.74	0.20	80-90
95	5	0.95	0.18	100
92.5	7.5	1.27	0.22	100
90	10	0.51	0.17	30-40

When the amount of 250 mesh graphene oxide powder is 10%, the bonding strength decreases. The reason may be that too much graphene oxide is added to absorb a large amount of resin, resulting in the rapid increase of system viscosity, affecting the wettability of the resin on the veneer surface, resulting in the difficulty of resin infiltration into the wood and the formation of network cross-linking structure between the wood pores; At the same time, too much graphene oxide powder in the resin will also make the cured adhesive layer lose continuity, thus affecting the bonding strength.

Table 3. *Effect of addition amount of graphene oxide powder (50 mesh) on bonding strength.*

Addition ratio		bonding strength (MPa)		Wood failure (%)
Isocyanate	Graphene oxide powder	Mean	Standard deviation	
100	0	0.51	0.16	30-60
97.5	2.5	0.52	0.21	30-50
95	5	0.71	0.17	40-60
92.5	7.5	0.65	0.12	0-20
90	10	0.32	0.19	0

3.3. Effect of Addition Amount of 50 Mesh Graphene Oxide Powder on Bonding Strength

It can be seen from table 3 that the addition of graphene oxide powder with mesh number of 50 has no obvious effect on improving the bonding strength. After graphene oxide powder is mixed with isocyanate, a large amount of resin may be absorbed into the powder and wrapped, resulting in lack of glue on the surface of the veneer. After the resin with 50 mesh graphene oxide powder is cured, under the condition of boiling test, the graphene oxide component in the adhesive layer may absorb water and cause expansion, resulting in easier damage of the adhesive layer in the cyclic test and affecting the bonding strength and wood breaking rate [15].

3.4. Effect of Addition Amount of Graphene Oxide Powder on Thermal Conductivity

It can be seen from table 4 that adding graphene oxide powder with mesh number of 250 can significantly improve the thermal conductivity of the floor. With the increase of the addition proportion of graphene oxide, the thermal conductivity of the floor increases from 0.234 $w\cdot M^{-1}\cdot k^{-1}$ to 0.368 $w\cdot M^{-1}\cdot k^{-1}$, the thermal conductivity increases from 15.9°$C\cdot H^{-1}$ to 22.3°$C\cdot H^{-1}$, and the electrothermal conversion rate increases from 45.2% to 85.5%. Therefore, the addition of graphene can prepare a geothermal floor with good performance.

Table 4. *Effect of addition amount of graphene oxide powder (250 mesh) on thermal conductivity of floor.*

Addition ratio		Thermal conductivity coefficient ($w\cdot M^{-1}\cdot k^{-1}$)	Thermal conductivity (°$C\cdot H^{-1}$)	Electrothermal conversion rate (%)
Isocyanate	Graphene oxide powder			
100	0	0.234	15.9	45.2
97.5	2.5	0.256	16.8	52.9
95	5	0.298	18.8	68.7
92.5	7.5	0.352	19.8	79.8
90	10	0.368	22.3	85.8

Table 5. *Effect of addition amount of graphene oxide powder (50 mesh) on thermal conductivity of floor.*

Addition ratio		Thermal conductivity coefficient ($w \cdot M^{-1} \cdot k^{-1}$)	Thermal conductivity ($°C \cdot H^{-1}$)	Electrothermal conversion rate (%)
Isocyanate	Graphene oxide powder			
100	0	0.234	15.9	45.2
97.5	2.5	0.246	16.2	50.9
95	5	0.278	18.6	65.3
92.5	7.5	0.324	19.2	77.8
90	10	0.355	21.8	83.6

It can be seen from table 5 that adding graphene oxide powder with mesh number of 50 can also improve the thermal conductivity of the floor. With the increase of the proportion of graphene oxide, the thermal conductivity coefficient of the floor increases from 0.234 $w \cdot M^{-1} \cdot k^{-1}$ to 0.355 $w \cdot M^{-1} \cdot k^{-1}$, the thermal conductivity increases from 15.9$°C \cdot H^{-1}$ to 21.8$°C \cdot H^{-1}$, and the electrothermal conversion rate increases from 45.2% to 83.6%, but the improvement of thermal conductivity is not as obvious as that of graphene oxide powder with mesh number of 250.

4. Conclusions

The viscosity of the resin system increased with the increase of the amount of graphene oxide powder. When the addition amount is 10%, the resin viscosity is too large to be applied; Graphene oxide powder with mesh number of 500 can enhance the bonding strength of isocyanate, but when the amount is too large (10%) on the contrary, the bonding strength decreases. Graphene oxide powder with mesh number of 50 does not significantly enhance the bonding strength; adding graphene oxide powder can improve the thermal conductivity of the floor. With the increase of the proportion of graphene oxide, the thermal conductivity, thermal conductivity and electrothermal conversion rate of the floor are significantly improved, but graphene oxide with mesh number of 50 is not as good as graphite oxide with mesh number of 250 Alkene increased significantly. The addition of an appropriate amount of graphene oxide powder reduces the infiltration of resin into wood, enhances the bonding performance and thermal conductivity, provides a new possible way for the application of graphene material and isocyanate in solid wood composite floor substrate, and provides a certain practical basis for the process and application technology development of hard graphene oxide material.

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 Yuanting Zhu contributed equally and should be considered as co-first authors.

Conflicts of Interest

The authors declare that they have no competing interests.

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