The effect of walnut processing by-product filler on properties of plywood

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Abstract. In this study, walnut processing by-product was served as filler to make three-layer plywood, and the physical-mechanical properties were also discussed. The results showed that the formaldehyde emission of plywood corresponding to walnut shell and walnut dregs decreased by 0.0542 mg/L and 0.066 mg/L, respectively. The properties of plywood filled with walnut dregs are better than that of walnut shell filler, and the formaldehyde emission of the corresponding plate is lower. At the same time, compared with flour, the wet bond strength of walnut shell plywood increased by 0.0332 MPa, and that of walnut dregs plywood decreased by 0.123 MPa, but they all met the national standards.

1. Introduction

Urea-formaldehyde resin is an amino-based thermosetting resin synthesized from urea and formaldehyde. It is widely used in the bonding of various kinds of artificial boards due to its synthetic raw materials are simple and easy to obtain; the color of adhesive layer is colorless and transparent. However, it also has poor mechanical properties. Disadvantages such as poor water resistance and high formaldehyde emission[1], usually modified by adding modifiers during resin synthesis, melamine was usually used as modifier to enhance the properties( melamine- urea formaldehyde resin, MUF for short) [2].

Filler is a substance which is added in the resin during the preparation of plywood to improve the initial viscosity of the adhesive and improve the processability and pre-compression performance. Coconut shell powder, bark powder, mineral powder, soy flour, etc. are widely used as fillers for urea-formaldehyde glue. Domestically, flour is the main filler and the consumption is nearly 300,000 tons per year [3].

Walnut has the largest planting area and annual output in China. It produces a large number of processing by-products such as walnut shell and walnut dregs. After the oil extraction finished, the walnut shells are generally discarded or incinerated, while the walnut core are used as feed. The value of processed by-products of walnuts has not been fully utilized, resulting in great waste of resources. With the rapidly development of the walnut industry, walnuts have been mainly sold as dried fruits in the past, and gradually changed into centralized processing and oil production. The recycling of walnut processing by-products is possible [4, 5].
In this paper, the walnut processing by-product walnut shell (WS for short) and walnut dregs (WD for short) were used as filler for plywood preparation after smashing, and the influence of the by-product filler on the performance of plywood was also discussed.

2. Materials and methods

2.1. Resin preparation
Adding the first batch of formaldehyde to the reaction kettle, adjusting the pH to 7.5-8.0, adding the first batch of urea and melamine, raising the temperature to 90°C for 40 min, adjusting the pH to 4.5-5.0, and reacting to the desired viscosity. Adjust the pH to 8.0-8.5 and add the second batch of formaldehyde and urea, reaction for 25 min. slowly adjust the pH to 5.0-5.5 and react to the desired viscosity. The pH was adjusted to 7.5-8.0, the by-product of walnut processing was added, and the reaction was carried out for 30 minutes, after which the mixture was cooled to room temperature to obtain a MUF resin. The F/U is 1.37. The final pH of the resin was 8.5, the solids content was 52.3%, and the initial viscosity was 35 mPa.s.

2.2. Sample Preparation
Weigh 3 parts of MUF resin, add 20% resin curing agent NH4Cl, and add 10% resin flour, 10% walnut shell powder and 10% walnut powder as filler, Stir well.

2.3. Preparation of plywood
Three-layer plywood: the amount of glue is 300g/m² (double-sided); the flour; walnut shell powder and walnut dregs are respectively fillers, and the added amount is 10% of the resin mass.

2.4. Performance test
PH test method: pH meter: Model PB-10, Sartorius, Germany, measured at room temperature at 25°C.
The formaldehyde emission of plywood board is carried out according to the provisions of the dryer method in GB/T17657-2013 "Test Methods for Physical and Chemical Properties of Artificial Panels and Finished Panels".

The wet bonding strength of plywood is carried out according to the provisions of Class II plywood in GB/T17657-2013 "Test Methods for Physical and Chemical Properties of Artificial Panels and Finished Panels". The number of test pieces for each set of plywood was 15. The pre-compression pressure is 0.8 MPa, the test piece is 1 h, the hot pressing temperature is 125°C, the hot pressing pressure is 1.2 MPa, and the hot-pressed test piece is 5 min. After boiled for 3 hours, it was taken out, and the mechanical properties were measured by a universal testing machine.

3. Results and discussion

3.1. The effect of walnut processing by-product filler on the pH of MUF resin
The variation of pH values of the mixture in 8 min was shown in Fig.1. The initial pH of MUF resin was 8.5. The initial pH of the resin MUF+flour, MUF+WS, MUF+WD was decreased to 7.19, 6.69 and 6.38, respectively. The pH value decreased after adding walnut processing by-products, because Walnut shell powder and walnut powder are all weakly acidic, and the acidity is greater after mixing. After 8 min, the change became stable, and the pH values were 6.51, 6.31, and 6.15, respectively.
3.2. The effect of walnut processing by-product filler on formaldehyde emission from resin plywood

As shown in Fig. 2, the formaldehyde emission of the plywood obtained by using the dryer method to detect of the MUF+F, MUF+WS, MUF+WD was 0.3902 mg/L, 0.3260 mg/L and 0.3242 mg/L, respectively, meet the national standard E0 grade. Among them, the formaldehyde emission of the plywood board produced by the processing of by-products of walnut processing is significantly lower than that of the flour, indicating that the by-product of walnut processing is effective in reducing the formaldehyde emission of the plywood. The reason is that some organic acids and phenolic substances contained in the walnut shell would chemically react with formaldehyde, meanwhile, the walnut dregs contains various amino acids, and the formaldehyde in the MUF resin can chemically react with the amino group of the amino acid to form a methylol derivative. At the same time, because the ingredients in the walnut stalk can react with formaldehyde more than in the walnut shell, the corresponding plywood sheet has a lower formaldehyde emission.

3.3. The effect of walnut processing by-product filler on wet bonding strength of plywood

As shown in Fig.3, the wet bonding strength of the plywood obtained of MUF+F, MUF+WS, MUF+WD is 0.9877 MPa, 1.0209 MPa and 0.8647 MPa, respectively. Compared with MUF+F, the wet bonding strength of MUF+WS has increased, and MUF+WD has been weakened, which meet national standards.
The curing agent ammonium chloride added in the resin can react with free formaldehyde to form an acidic substance which is promote the resin to cure. The content of free formaldehyde in the resin is different, and the curing rate is also different. If the amount of acid formed by the reaction between ammonium chloride and free formaldehyde is insufficient, the curing of the resin may be incomplete, resulting in low bonding strength and poor water resistance of the bonded product [1]. The cellulose in the walnut shell accounts for 22.06%, and the lignin accounts for 56.65% [6]. It belongs to the high reaction capacity of the guaiac wood-syringyl-based (GS type) lignin, which contains more guaiac wood-based structural units and phenolic groups which was easily to react with formaldehyde.

The MUF resin is acidic after adding the curing agent. The main component of the walnut shell powder does not react with formaldehyde. Only a small amount of organic acid and phenolic substances react with formaldehyde, which does not affect the full reaction of ammonium chloride with free formaldehyde. The powder significantly increased the viscosity of the glue and reduced the internal stress in the adhesive layer, which is better than the water resistance of the flour, and significantly improves the wet bonding strength of the plywood. The protein content of walnut dregs is above 43% [7]. Free formaldehyde can chemically react with the amino group of the amino acid to affect its full reaction with ammonium chloride, which ultimately affects the curing of the resin and reduces the wet bonding strength of the sheet.

4. Conclusion
The walnut processing by-products replaced the flour as a filler, and the release amount of formaldehyde in the plywood obtained from walnut shell and walnut dregs was reduced by 0.0542 mg/L and 0.066 mg/L, respectively, and the effect of the filler of walnut dregs was better than that of the walnut shell, and the corresponding formaldehyde emission of the sheet is lower. All values meet the E0 grade values of national standards.

The processing of walnut by-products as a filler has a certain influence on the wet bonding strength of the plywood. Compared with flour, the wet bond strength of walnut shell plywood increased by 0.0332 MPa, and that of walnut dregs plywood decreased by 0.123 MPa, but they meet the national standards.

As a substitute for flour, the processing by-product of walnut is used as a plywood filler. While reducing the amount of formaldehyde released from the board, its wet bonding strength are also in line with national standards, laying a foundation for further in-depth research.

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