Walnut Meal as Formaldehyde-free Adhesive for Plywood Panels

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Walnut meal and polyethyleneimine (PEI) were used as raw materials for producing an environmentally friendly adhesive to bond plywood, and the shear strength was investigated. The results showed that the walnut meal-based mixture adhesive can successfully be used for the production of plywood. However, the shear strength of plywood clearly changed with different raw materials ratios. Both the wet and hot water strength were improved with increasing polyethyleneimine (PEI) content. This indicated that PEI had an important contribution to the water-resistance of the mixture system, and considering the cost of PEI, a walnut meal powder and PEI weight ratio of 70:30 was recommended. The effects of walnut protein solution thermal processing time and temperature were also studied. It was beneficial to enhance the wet and hot water shear strength of plywood to increase the thermal processing time and temperature. The investigation of curing characteristic of mixture system and monomer ingredient *via* differential scanning calorimetry (DSC) revealed that the curing peak temperature of the mixture system was similar to PEI, and that a chemical reaction should be made between them during the heating process. Lastly, the thermal characteristic of the mixture system was investigated *via* thermogravimetric (TG) analysis, where good thermal resistance was displayed.

Keywords: Walnut meal; Polyethyleneimine; Bonding strength; Curing characteristics

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INTRODUCTION

Today, wood adhesives are mainly chemical synthetic polymers, especially formaldehyde-based resins such as: urea-formaldehyde (UF), melamine-formaldehyde (MF), and melamine-urea-formaldehyde (MUF). Together they comprise up to 90% of the weight ratio in the wood industry. These types of resins have excellent characteristics, such as stronger bonding strength, relatively low cost, abundant raw material, *etc.*, but the formaldehyde release is their critical defect (Lee and Kim 2013; Ye *et al.* 2013). Meanwhile, the limits of formaldehyde-based adhesives are gradually focused with the growing societal demand for green and ecological processes. Therefore, to decrease the negative effects of formaldehyde on people's health and the environment, numerous methods have been reported in literature (Dunky 1998; Boran *et al.* 2011; Nuryawan *et al.* 2014), such as lowering the resin final mole ratio, adding a formaldehyde scavenger, *etc.* Although great progress has been made, the potential harm of formaldehyde has not been completely eliminated.

Due to the potential harm of formaldehyde-based resins, bio-based adhesives, including protein, starch, tannin, carbohydrate, and so on, have attracted increased attention in the wood panel industry. Today, research on soy-based adhesives has been a hot topic in the field of wood adhesives (Chen *et al.* 2014; Jang and Li 2015). However, it is worth noting that soybeans, as one of the sources of human edible raw materials, will compete with industrial materials as an adhesive. Therefore, it is of great importance to find more protein-containing raw materials for further sustainable development of protein-based adhesives.

According to the Food and Agriculture Organization in China, China's annual walnut production was 50% higher than that of the rest of the world's (FAO 2014). The walnut seed is rich in protein and oil, and a lot of protein resides in walnut meal after oil extraction (Savage 2001; Prasad 2003). Thus, the extracted meal has a promising future as the raw material of bio-based wood adhesive development.

Poor water-resistance has been a barrier for the application of bio-based adhesives. At present, in order to improve bio-based adhesive's water-resistance, formaldehyde or formaldehyde-based resin have been usually used as modifiers. Although some progress has been made, in fact, because of these modifiers used, the environment-friendly character of bio-based adhesives has been lost.

PEI has high chemical reactive ability with many functional groups, especially ethylene and amino groups. It is possible to improve the properties and water-resistance of protein-based adhesive through the chemical reaction between protein molecular and functional groups of PEI. At present, the open literature on PEI used as modifier of bio-based adhesive is very limited.

Therefore, walnut meal powder was used to produce a wood adhesive for plywood panels, and polyethyleneimine (PEI) was selected as modifier or cross-linking agent to prepared an environment-friendly wood adhesive in this work. Meanwhile, the effect of different material weight ratio on bonding strength was also evaluated. And the curing characteristics and thermal resistance were estimated *via* differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis, respectively.

EXPERIMENTAL

Materials

Walnut meal with a composition of: protein (35% to 40%), carbohydrates (10% to 14%), and fibre (1.5% to 2%), was obtained from the Yunnan Academy of Forestry (Kunming, China). By using an automatic grinder, the walnut meal was made into a powder and then sieved by using a 180-mesh screen. The retained fraction was used in subsequent experiments. Poplar veneer with a thickness of 1.5 mm and moisture content of 8.3% was purchased from Zhi Wei Veneer Factory (Hebei, China) for the preparation of plywood. Polyethyleneimine (PEI) was a commercial product with a molecular weight of 70,000 (Li Chuang Environmental Technology Co., Ltd., Tianjin, China).

Preparation of protein solution of walnut meal powder

First, a mixture of the sieved walnut meal powder and water was prepared with a mass ratio of 1:8, and placed into a three-neck flask with a mechanical stirrer, thermometer, and condenser.

Then, the mixture pH value was adjusted to 9 with a 40% sodium hydroxide solution (note hazard due to high concentration), and kept for 1 h under each temperature of 60 °C, 67 °C, 75 °C, 85 °C, and 95 °C, and namely, five protein solution samples were obtained, respectively. After cooling, the five groups of samples were separated using a centrifuge with a velocity of 4800 r/min for 10 min. The top liquid of each sample of material was gathered to produce the adhesives.

Preparation of walnut meal powder adhesive

The process of producing adhesives was simple. At room temperature, 20 parts (based on mass) of the sieved walnut meal powder was placed into a glass beaker, then 60 parts of protein solution and different ratio PEI were added. The mixture was blended by hand until a uniform solution was made. In this work, by changing the PEI mass ratio (based on the amount of walnut meal powder used), different groups of adhesives were obtained.

Preparation of three-layer plywood panels bonded with walnut meal-based adhesives

The plywood was produced with dimensions of 400 mm × 200 mm × 4 mm. The single side glue loading was 200 g/m^2. After gluing, the veneers were assembled and allowed to rest at room temperature for approximately 5 min. The plywood was pressed under pressure at 1.5 MPa and 160 °C for 4 min.

Methods

Evaluation of shear strength of plywood panels

According to the Chinese national standard GB/T 17657 (2013), the plywood panels were cut into shear specimens with dimensions of 100 mm × 25 mm to determine their shear strength and water resistance after conditioning for 24 h at room temperature. The bonded areas of each specimen were 25 mm × 25 mm. The shear strength of plywood specimens was tested on a WDS-50KN mechanical testing machine (Shenzhen Suns Technology Stock Co., Ltd., Shenzhen, China). The average of the six specimens strength was taken as the final strength result. In this work, three kinds of strength were determined: dry strength, wet strength, and hot water strength. To determine the wet strength, the specimens were soaked in 20 °C ± 3 °C water for 2 h. For hot water strength, the specimens were soaked in 63 °C ± 3 °C water for 2 h and then dried for 1 h using a convection drying oven.

Differential scanning calorimetry (DSC) and TG analysis

The DSC and TG analyses were performed on each sample using a NETZSCH DSC 204 analyzer (NETZSCH-Gerätebau GmbH, Selb, Germany) and a TG 209F3 (NETZSCH-Gerätebau GmbH, Selb, Germany), respectively. For DSC, approximately 5 mg of liquid resin was weighed on an aluminum pan and sealed with another aluminum cover.

The prepared sample was heated from 25 °C to 200 °C with a heating rate of 10 °C/min under a nitrogen flow of 20 mL/min. The oven-dried sample was weighed to approximately 10 mg and placed into an alumina crucible; it was then tested in the range from 35 °C to 600 °C with the same heating rate as DSC under a nitrogen flow 20 mL/min.

RESULTS AND DISCUSSION

Effects of Protein Solution Processing Temperature on Plywood Bonding Strength

Different series of adhesives were prepared with walnut meal powder sieved with a 180-mesh screen and PEI (M_w = 70000) with a weight ratio of 50:50. Walnut meal protein solutions (with liquid portion three times the mass of walnut meal powder) with different processing temperatures were used. The results after testing the plywood panels for shear strength are shown in Fig. 1. It was apparent that the dry shear strength of plywood was universally higher than the standard value set forth (0.7 MPa) in GB/T 17657 (2013). Moreover, this trend also gradually increased with the walnut meal processing temperature after the temperature was raised from 75 ℃ to 95 °C; however, when the dry strength at 67 °C and 60 °C were compared, the dry shear strength at 60 °C was higher than that of 67 °C. Meanwhile, the wet shear strength and hot water shear strength had the same trend as the dry strength, except that the hot water shear strength of plywood at 67 °C was below the standard of 0.7 MPa. However, all the wet shear strengths were lower than the dry shear strengths, but higher than the hot water strength. This indicated that walnut meal can be used to produce plywood panel adhesives with good water-resistance characteristics. It is worth noting that the strengths showed various changes before and after 67 °C, most likely due to the change in the walnut protein structure and composition, because the walnut protein's degradation temperature is 67 °C (Guo *et al.* 2012), protein molecular was degraded, the structure superiority was decreasing. Therefore, it was understandable that the hot water strength was the lowest at 67 °C.

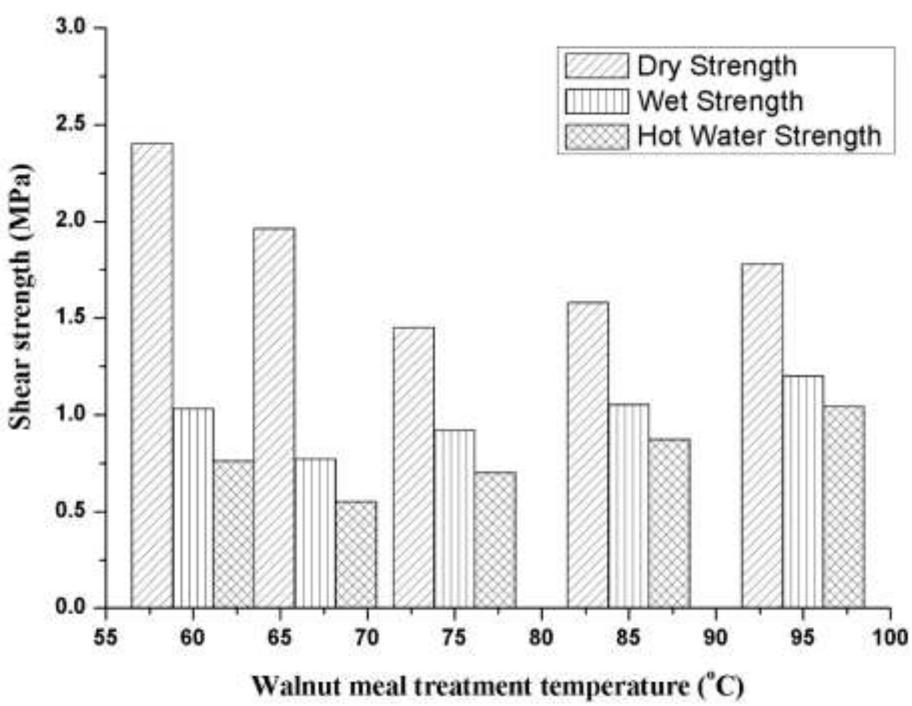

Fig. 1. Bonding strength of plywood panels with protein solution, using different thermal processing temperatures

When the thermal processing temperature was lower than 67 °C, the walnut protein structure was mostly unbroken, possibly allowing the large protein molecules to positively impact the bonding strength. Moreover, when the thermal processing temperature was higher than 67 °C, especially at 95 °C, the hot water strength was excellent. This may have been due to more reactive groups connecting with PEI, which increased the chemical bonding link. Therefore, higher thermal processing temperatures also contributed to a higher water-resistance property. However, considering both the cost of the adhesive and the performance, a thermal processing temperature of 85 °C was recommended.

Effects of PEI Use on Plywood Bonding Strength

Based on the results of the effects of protein solution processing temperature on plywood bonding strength, a thermal processing temperature of 85 °C was chosen. The walnut meal and PEI ratio was varied to study the bonding strength of the plywood panels. The final results are presented in Fig. 2. The bonding strength of plywood gradually decreased with increased walnut meal weight ratio. This was very noticeable for the wet and hot water strengths. This result signified that PEI was a key factor in creating good water-resistance walnut meal based adhesives for plywood. When the walnut meal and PEI weight ratio was higher than 70:30, both the wet and hot water strength were reduced to lower than 0.7 MPa, which did not satisfy the Chinese standard requirement. Additionally, the adhesive cost improved with increased PEI use, and thus a walnut meal and PEI weight ratio of at least 70:30 or lower is recommended.

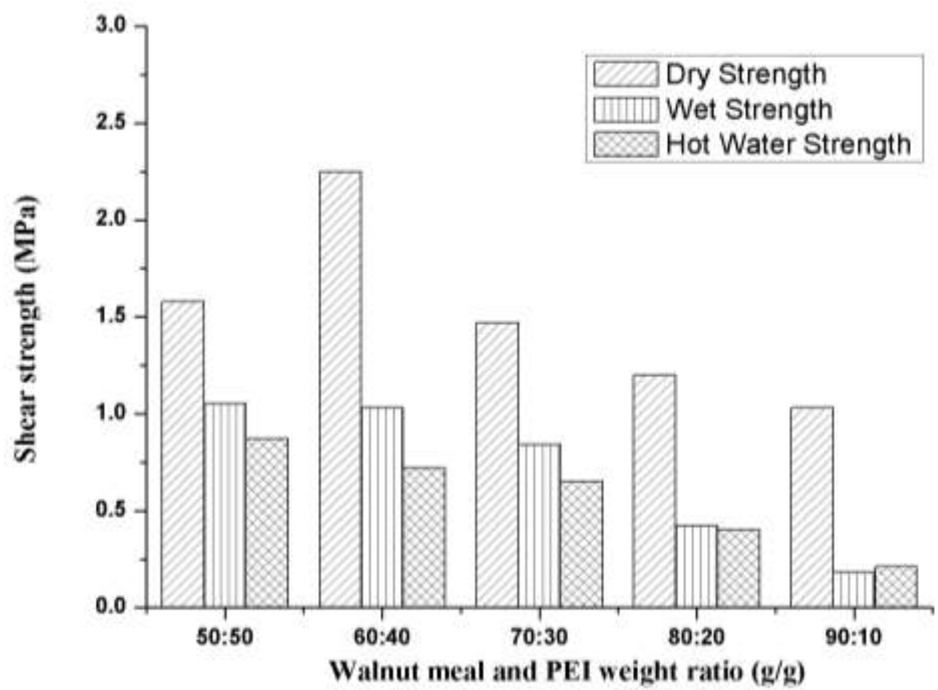

Fig. 2. Bonding strength of plywood panels with different walnut meal and PEI weight ratios

Effects of Walnut Meal Processing Time on Bonding Strength

To further explore the walnut meal protein solution processing time on the bonding strength of walnut meal-based adhesives, three levels of processing time were investigated; the relationship of processing time and bonding strength is shown in Fig. 3. The effects of processing time on the bonding strength was distinct. The averages of the dry and wet shear strengths were the best and far higher than the others when the processing time was 1 h. However, the strength did not decrease with increased processing time, thus the best processing time cannot be made. However, the hot water strength was the highest at 3 h among the three levels of processing time, and the strength change from dry strength to wet strength then to hot water strength was the smallest. Based on this finding, a processing time of 3 h was best. At the same time, it was very obvious that the change range from dry to hot water strength gradually decreased with increased processing time. Hence, the processing time was selected on the basis of actual application.

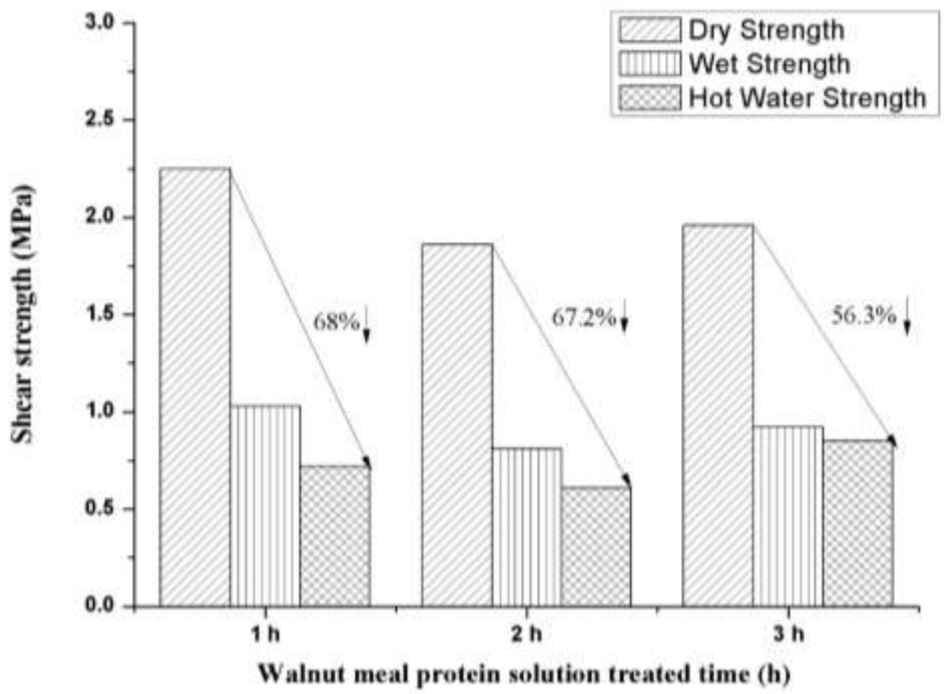

Fig. 3. The bonding strength of plywood panels with different walnut meal processing times

DSC Analysis of Walnut Meal-based Adhesive for Plywood Panels

The curing characteristics of the walnut meal-based adhesives and each monomer ingredient are shown in Fig. 4, in which the mixture system represented the walnut meal powder and PEI weight ratio 70:30 with walnut protein solution processing time of 3 h under 85 °C conditions. Comparing the four curves, there were obvious endothermic peaks, except for the walnut meal powder, and the curing peak temperature of the mixture system was nearly the same as that of PEI, at approximately 133 °C and 136 °C, respectively. The temperature of the mixture system was higher than that of walnut protein solution but lower than PEI, this meant that a higher curing temperature *versus* walnut protein solution was required to cure completely.

In contrast, the mixture system curing process indicated that chemical reactions could be conducted on walnut protein powder, protein solution, and PEI because no monomer ingredient curing feature was displayed. The curing end temperature was approximately 160 °C. This temperature meant that curing was finished, which corresponded to the hot press temperature during plywood production.

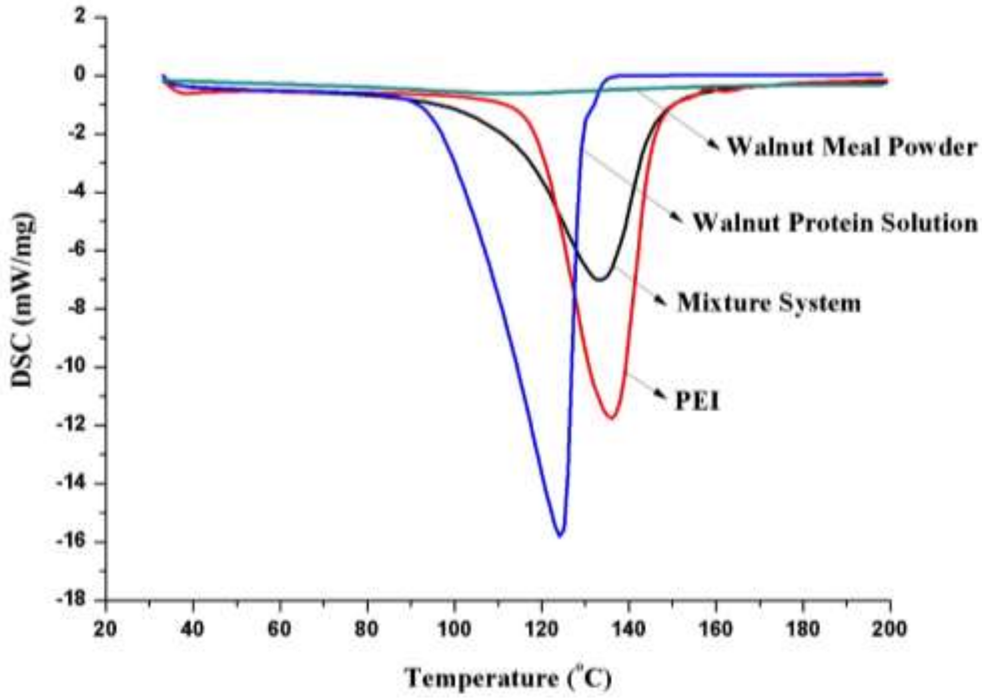

Fig. 4. The DSC curves of mixture system and each monomer ingredient

TG Analysis of Walnut Meal-based Adhesive for Plywood Panels

The thermal stability of the mixture systems of walnut meal and PEI was also investigated through TG and DTG analyses, the results are shown in Fig. 5.

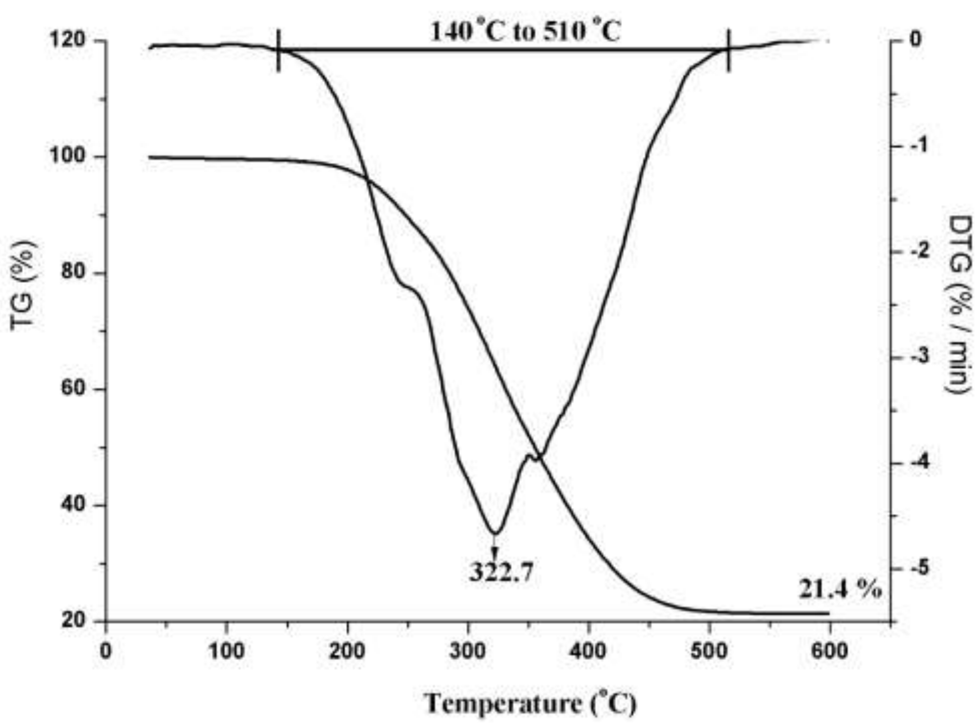

Fig. 5. The TG and Differential thermal gravity (DTG) curves of the mixture system

The DTG curve indicated that from 30 °C to 600 °C, the main thermal decomposition range was between 140 °C and 510 °C. At 140 °C, the weight of the sample tested began to decrease with increased temperature, and the weight also gradually decreased. When the temperature was 322.7 °C, the thermal decomposition rate reached its maximum. The sample weight also quickly decreased, which was primarily attributed to chemical bond degradation between the walnut protein and PEI. As the temperature was further increased, from 322.7 °C up to 600 °C, the DTG curve showed no peaks, and the TG curve slowly decreased. During the decomposition process, the sample mass loss reached 78.6%, and the rest mass ratio was 21.4%. The maximum thermal peak temperature of DTG for pure urea-formaldehyde resin usually used as plywood adhesive is 274.4 °C and the mass loss is approximately 22% (Suzana *et al.* 2011), this meant that the mixture system of walnut meal and PEI had an excellent thermal resistance property.

CONCLUSIONS

1. Walnut meal powder mixed with polyethyleneimine (PEI) and protein solution can be used as an adhesive for plywood panels. In the present work all dry shear strengths reached the Chinese standard requirement (≥ 0.7 MPa). The wet shear strength and hot water shear strength were heavily affected by the walnut meal and PEI weight ratio, protein solution thermal processing time, and temperature.
2. Considering the cost of adhesive, the walnut meal and PEI weight ratio 70:30 was recommended, and the thermal processing time could be decided by the plywood application, 1 h for good dry and wet shear strengths, then 3 h for hot water shear strength.
3. Through differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis, it was concluded that some chemical reaction took place between the walnut meal and PEI, which contributed to the mixture system's higher thermal resistance. Therefore, it has a promising future in wood-based production applications.

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