

Effect of Post-Added Water Amount on Pre-Concentrated Bark Foaming Materials by Mechanical Stirring

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Abstract: In this study, pre-concentrated bark, furfuryl alcohol and other biomass raw materials were used to prepare foaming materials by high-speed mechanical stirring without using a foaming agent. We investigated the effect of the post-added water amount on the properties of foaming materials. In particular, we determined basic physical properties of these materials, including the limiting oxygen index (LOI), porosity, thermal conductivity, thermogravimetric analysis, pore size distribution, and microstructure. The results of scanning electron microscopy (SEM) indicated that the pore size distribution was uniform and the pore size increased with increasing water volume. Thermogravimetric analysis (TG/DTG) showed that when the temperature reached 410°C, the foam was easily decomposed, the final residual mass was only 2.8%, and water addition had little effect on it. Moreover, the amount of post-added water is 5–30 g, the density and compression strength of the foamed materials gradually decreased, while the degree of pulverization increased. LOI ranged from 26.1% to 30.79%, and porosity ranged from 81% to 83%. The change in water volume greatly affected the foam's performance, the performance of foamed material deteriorated as the amount of added water increased, but the effect on thermal conductivity was not very obvious. The highest thermal conductivity was only 0.0179 W/(m·K), still providing excellent thermal insulation.

Keywords: Pre-concentrated bark; mechanical whipping; foamed material; performance characterization

1 Introduction

Tannin-based foam is mainly used as a kind of biomass tannin with polyphenol structure [1,2]. The material has good thermal insulation [3–5], is fire retardant [6], and exhibit high sound absorption [7] and corrosion resistance [8]. Therefore, it has broad application prospects in many fields, such as architecture, packaging, furniture, medical treatment, and aviation [9–12], as well as high research value.



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In the last century, there has been significant research interest in tannin/furan foam materials [1,13], mostly focusing on the preparation and modification of the foam, while new foaming methods were rarely explored [14]. The research on tannin foam materials started late in China. The main process route was concentrated on the use of tannin as an additive in phenolic resin foam and polyurethane foam materials to improve their mechanical, flame resistance, and anticorrosive properties [15]. In recent years, our research team has gradually begun to explore new foaming processes and methods [9,16].

Foam preparation is possible through a physical foaming method, such as the inert-gas foaming method, where inert gas is pressured into molten polymer or paste material, then pressurized and heated, so that the gas expands and produces bubbles. This method requires complex high-pressure equipment. Alternatively, the low boiling point liquid foaming method uses a low boiling point liquid to vaporize and generate bubbles; however, the foaming temperature is difficult to control with this method. The thermal-decomposition foaming-agent method is a chemical foaming method, where a heating thermal-decomposition foaming agent is used for the decomposition, to produce gas and foam; the benefit of this method is that it is easy to control. In this method, inert gas is produced through the chemical reaction between two or more polymer components of the foaming system [17–19]. At present, the low boiling point liquid foaming method is used for the preparation of tannin foam.

In this study, we add an emulsifier to change the interfacial tension of molten polymer or paste material without using a foaming agent, in order to produce wrapping gas. We then make it wrap air through strong mechanical stirring to form bubbles of uniform size, and then form the foaming material after heating, curing, and drying. By adding different water volumes to control the foam density, foam materials with different properties are formed. The advantage of this process is that the density of the foam material is controlled before the chemical reaction, in a simple, accurate, and effective way, which is not easily affected by the volatilization of the foaming agent due to the different ambient temperatures.

2 Experimental

2.1 Experimental Materials

Industrial Bayberry bark pre-concentrated by a liquefaction process was used in this study. The water-solution concentration was 32%, and the tannin content was about 65%–70%, provided by Guangxi Wuming tannin extract factory. Furfuryl alcohol, para-toluene-4-sulfonic acid (pTSA), formaldehyde, all of analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd. Tween-80 of chemical purity was provided by Guangdong Guanghua Technology Co., Ltd. Distilled water was made in the laboratory.

2.2 Experimental Instruments

Electronic balance: JJ200, precision 0.0001 g, Changzhou Aohua Instrument Co., Ltd.; universal mechanical testing machine: AG-50 kg, Shimadzu, Japan; eggbeater: HM-955, maximum speed: 2500 r/min; Mitsubishi Electric; oxygen index tester: XWR-2046, Cangzhou Jilu Test Instrument Co., Ltd.; automatic double pure water distiller: SZ-93, Shanghai Yarong biochemical instrument equipment Co., Ltd.; scanning electric Mirror: 300, Carl Zeiss (Shanghai) Management Co., Ltd.; thermogravimetric analysis: TGA5500, American TA instrument; thermal conductivity tester: YBF-2, Hangzhou Dahua Instrument Manufacturing Co., Ltd.; desktop drying oven: 202-0, Beijing Yongguangming Medical Instrument Co., Ltd.

2.3 Preparation of Foaming Materials

Before the preparation of foaming materials, we prepared 65%-pTSA and 32%-Tween-80 aqueous solutions as shown in Tab. 1. In a 500-ml plastic beaker, we added pre-concentrated bark, water, furfuryl alcohol, and formaldehyde according to the formula, and stirred the mixture with an egg beater at 500 r/min for 2 min to obtain a uniform foam resin precursor (Fig. 1A). Then, we added Tween-80 and

p-toluene sulphonic acid solutions (pTSA), and stirred for 8 min at 2000–2500 r/min, so that the air was wrapped in the mixture to form a stable and uniform foam (Fig. 1C). In order to avoid foaming non-uniformity in the immediate heating, the solution was placed for 2 h to make it firm. The pre-cured solution was heated in an oven at 75°C for about 12 h to make it completely solidified. The sample was then taken out of the oven and left to stand for 1 week under natural conditions to fully cure and dry. The foaming material was prepared without a foaming agent, which can be obtained by adding an emulsifier with strong mechanical stirring.

Table 1: The formulation of pre-concentrated bark foams

Component	Furfuryl alcohol (99%)/g	Formaldehyde (37%)/g	Bark pre-concentration (32%)/g	pTSA (65%)/g	Tween 80 (32%)/g	Post-added water/g
W10	13	7.4	30	15	3	10
W15	13	7.4	30	15	3	15
W20	13	7.4	30	15	3	20
W25	13	7.4	30	15	3	25
W30	13	7.4	30	15	3	30

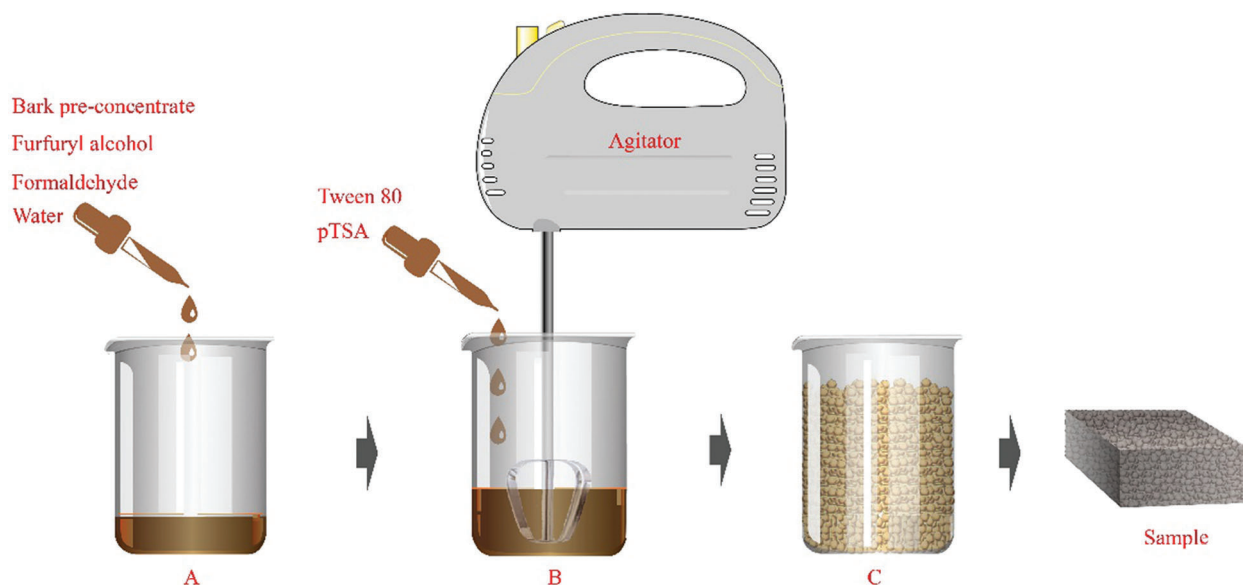


Figure 1: Schematic diagram for tannin foam preparation in the lab-scale

The foam formulation and process plan are shown in Tab. 1 and Fig. 1, respectively. In Tab. 1, W10–W30 represent the mass of post-added water in the formula, which is 10–30 g, respectively. The additional amount of other foaming raw materials refers to previous research results [16].

2.4 Performance Test

We tested the foam apparent density, compression strength, pulverization degree, foam water absorption, limiting oxygen index (LOI), external appearance (using SEM), and thermal conductivity, as indicated in previous research [16]. The thermal stability of the foam was measured by TGA5500 analyzer (TA).

Specifically, the 5–8 mg sample powder was transferred to the platinum tray and heated from 30°C to 790°C at 10°C/min. Foam porosity is estimated by the ratio of the foam bulk density to the bulk density, as shown in Formula (1).

$$\phi = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \quad (1)$$

ϕ is the porosity, ρ_b is the bulk density, and ρ_s is the solid density of the specimen.

3 Results and Discussion

Apparent density indirectly reflects the pore size of the foam, which determines the range of its uses. The relationship between the amount of post-added water and the density of the foaming material made from pre-concentrated bark is shown in Fig. 2. When the post-added water mass increased from 10 g to 30 g, the density of the foaming material decreased from 57.46 kg/m³ to 47.64 kg/m³. The material exhibits medium low density. The results show that the amount of post-added water can effectively control the density of the foaming material. In Fig. 3, we observe that the solution volume inside the beaker increases significantly with the addition of water. The reasons for this result are as follows: first, stable bubbles can be produced in the mixture after adding the emulsifier; second, formaldehyde, pre-concentrated bark, and p-toluenesulfonic acid are all water-soluble substances. With increasing water content, the viscosity of the mixture decreases in turn, and its ability to wrap air is also enhanced.

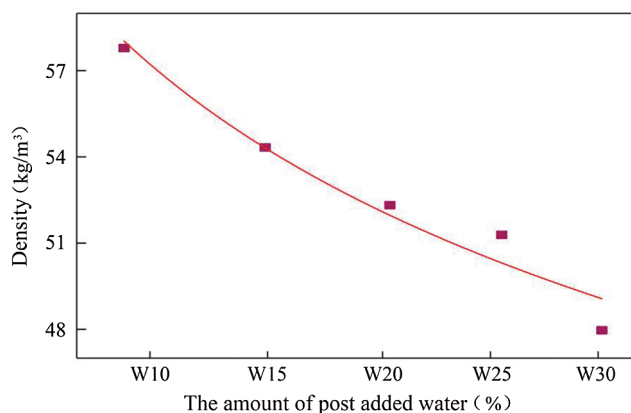


Figure 2: Relationship between the amount of post-added water and density

Fig. 4 is the SEM and pore size distribution of the pre-concentrated bark foaming material. It can be clearly seen from the left column of the figure that the pore size of the foamed material is evenly distributed in the form of open holes, and there are cracks between the holes (such as the red circle area in the figure). The entire wall can be clearly seen from the triangle cross area marked with a yellow circle in the figure. After measurement, the wall thickness under this process condition is about 2–3 μm, and the wall thickness does not change with the amount of post-added water.

The porosity of the foam material reflects the shape of the foam cell to a certain extent. As seen in Fig. 5, with increasing water content, the porosity of the foam material gradually increases, and the maximum porosity is about 83%. Density is inversely correlated with porosity, which is consistent with the conclusion shown in Fig. 2. When the water content is small, the viscosity of the mixture is high. During the stirring process, air is not easily wrapped in the resin solution, and the foam porosity is relatively low, which leads to a relatively large density of the foamed materials. In Tab. 2, mechanical beating cannot

produce foam with a large diameter. Even if the post-added water volume is increased to 30 g, the pore size of the foam remains about 300 μm .



Figure 3: Relationship between the amount of post-added water and the volume of the foam materials after stirring

Fig. 6 shows the stress–strain diagram of the foaming materials. The first stage is the linear elastic stage at the beginning. The strength of the foam materials often depends on this stage. The second stage is the longer yielding platform stage, where the stress–strain curve is gentle, and the third stage is the foam compaction stage. At this stage, the cell walls and internal fillers of all foamed materials collapse. Under the solid foam part, the slope of the stress–strain curve of the material rapidly increases [16]. The compression strength of the foaming material gradually decreases with increasing water content (Fig. 6). When the post-added water content is 10 g, the compression strength is 0.15 MPa. When the post-added water content increases to 30 g, the compression strength is only 0.05 MPa, which is only one third of that at 10 g.

The force structure of foam mainly results from the internal filling of the triangular cross area between the foam wall and the foam wall. From our SEM observations, the thickness of the bubble wall remains unchanged. With increasing the water content, the change of the strength of the foam material is not directly related to the cell wall, but to the density. When the amount of post-added water is more than 30 g, the strength of the foamed material is very low, which limits its application. Therefore, the amount of post-added water is also limited, and must be controlled within a reasonable range.

The thermal conductivity of foaming materials is an important indicator of their thermal insulation performance. Regardless of the amount of post-added water, the thermal conductivity of the material is generally low under the process conditions, showing excellent thermal insulation (Tab. 2). With increasing water content, thermal conductivity decreases from 0.0179 to 0.015 W/(m·K). This can be explained by the fact that the density of the material decreases gradually due to the increase of the water content, resulting in an increase in the proportion of air in the same volume of foam material and a very

low thermal conductivity of the air. The thermal conductivity of polyurethane foam is generally 0.017–0.023 W/(m·K), and that of polystyrene is generally 0.03–0.04 W/(m·K). The thermal conductivity of phenolic foam is about 0.023 W/(m·K). The thermal conductivity of other types of tannin foam is generally 0.02–0.035 W/(m·K). Therefore, the foam material prepared by mechanical stirring is superior to other foam materials in terms of thermal insulation performance [19–21].

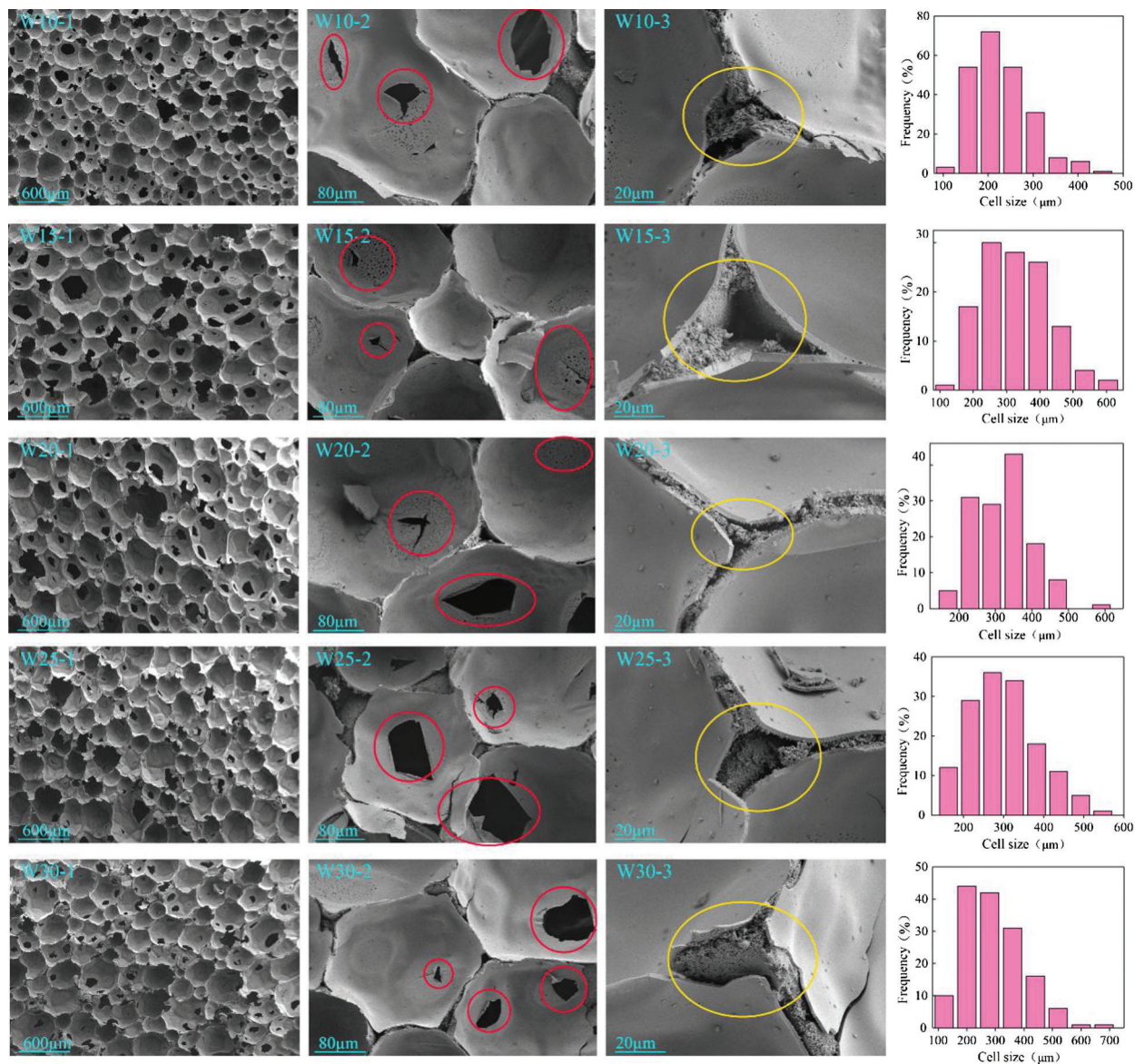


Figure 4: SEM and cell size distribution images for pre-concentrated bark foams

Table 2: Basic properties of pre-concentrated bark foams corresponding to different amount of post-added water

	W10	W15	W20	W25	W30
The average cell size (µm)	227.51	327.44	300.23	301.33	292.89
The maximum thermal conductivity W/(m·K)	0.0179	0.0157	0.0161	0.0157	0.015

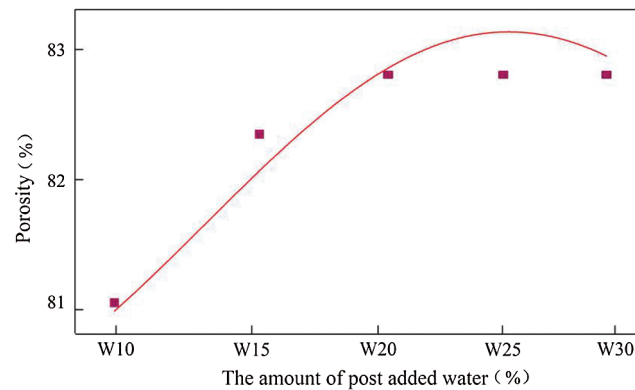


Figure 5: Post-added water mass as a function of the porosity of the foams

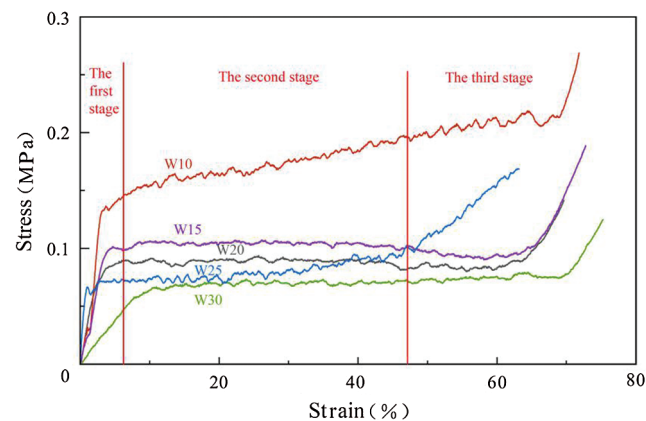


Figure 6: Stress–strain relationship for pre-concentrated bark foams

The degree of pulverization can reflect the soft hardness of foam and whether it is easy to drop slag, which will have a great influence on its production and application in the future. Fig. 7 shows the relationship between the amount of post-added water and the degree of pulverization. The diagram shows that when the amount of water added is relatively low, the degree of pulverization is only 8.95%, which does not produce dregs. With increasing water volume, the degree of pulverization of the foamed materials increases significantly, up to 28.26%, and drop slag is obvious. This may be due to the insufficient chemical reaction caused by excessive water, as mentioned earlier. Dregs are a common problem when using tannin/furan foams. Unfortunately, the mechanical stirring used here as well to prepare the foam material creates the same problem, which has not been solved.

Fig. 8 shows the results of our thermogravimetric analysis. For temperatures between room temperature and 400°C, the quality of the foaming material remains good, and the foam performance is stable. Within this temperature range, the foaming material has certain high temperature resistance and flame resistance. When the temperature reaches about 410°C, the material is decomposed by heat, and the final residual material is only about 2.8%, which indicates that the foaming material is easily decomposed thermally, and the residual material can be recycled, resulting in low environmental pollution. In addition, the amount of post-added water has little effect on the quality of the residual material after thermal decomposition.

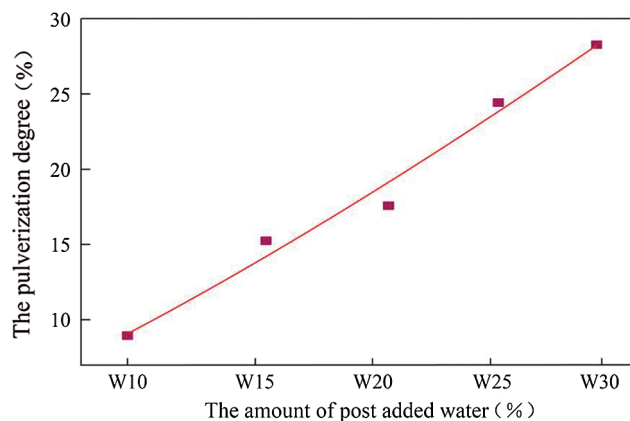


Figure 7: Relationship between the pulverization degree and the amount of post-added water

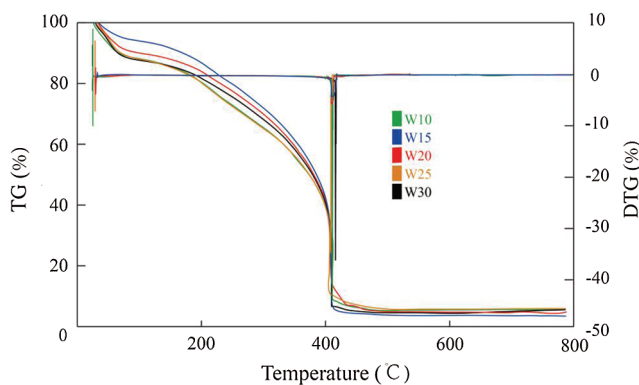


Figure 8: TG and DTG curves of foam materials with different amounts of post-added water

LOI is one of the main criteria for measuring the flame resistance of foaming materials. Fig. 9 shows the relationship between the water content and LOI. The diagram shows that the LOI of foaming materials increases with the post-added water content and the limiting oxygen index is improved from 26.1% to 30.79%. To sum up, the foaming material has good flame resistance and belongs to flame retardant materials.

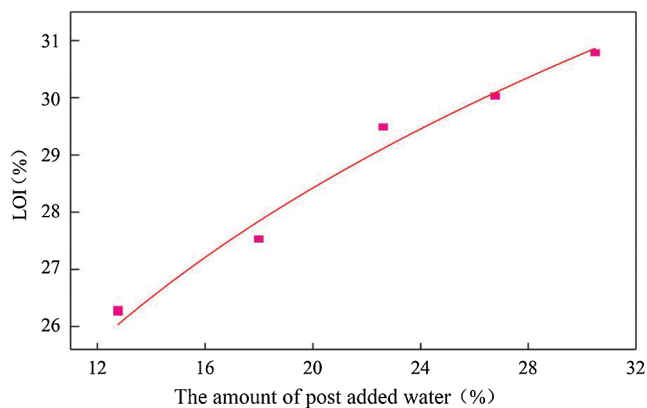


Figure 9: Relationship between the amount of post-added water and LOI

4 Conclusions

In this experiment, the mechanical stirring method was used to prepare the pre-concentrated bark rigid foam materials with density as low as 47.64 kg/m^3 , thermal conductivity as low as $0.015 \text{ W/(m}\cdot\text{K)}$, compression strength up to 0.121 MPa , and LOI of 26.1% . The foamed materials can be used as low-density and high-strength thermal insulation materials, which are expected to replace polyurethane foam that emits toxic gas during combustion.

By changing the amount of post-added water, the density, pulverization degree, and compression strength of the foaming materials can be effectively controlled, and pre-concentrated bark foaming materials with different properties can be prepared, which can expand the application of bark pre-concentration in the field of new foam materials.

Author contributions: Jinxing Li and Jingjing Liao performed the experiments; Jun Zhang gave some suggestions and performed the TG tests; Hisham Essawy and Guanben Du revised the manuscript; Xiaojian Zhou supervised this work. All authors have given the approval to the final version of the manuscript.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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