



ARTICLE

## Optimization of Animal-Glue Binders for Casting Applications

Tianshu Wang<sup>1</sup>, Guoqing Sun<sup>1</sup>, Shaojun Zhang<sup>1</sup>, Mingyu Wang<sup>1</sup>, Jixin Wang<sup>2</sup> and Yunwu Han<sup>3,\*</sup>

<sup>1</sup>Mechanical and Electronic Engineering, Shandong Jiaotong University, Jinan, 250357, China

<sup>2</sup>Chongqing Research Institute, Jilin University, Chongqing, 401123, China

<sup>3</sup>School of Intelligent Transportation, Jiangsu Vocational College of Electronics and Information, Huai'an, 223003, China

\*Corresponding Author: Yunwu Han. Email: hangyunwu@jsei.edu.cn

Received: 05 January 2023 Accepted: 14 March 2023 Published: 18 September 2023

### ABSTRACT

In typical metal foundry applications, sand casting is still the most used technology. The related binder plays a very important role as its performances can directly influence the quality of castings. Among many binders, glues of animal origin have attracted much attention in recent years due to their reduced environmental impact. However, they display some drawbacks such as the tendency to coagulate easily at room temperature and a relatively low strength. In this study, a novel gas-hardening casting binder was prepared using an animal glue and anhydrous potassium carbonate as a hydrolyzing agent to avoid undesired agglomeration. Moreover, sodium pyrophosphate and furfuryl alcohol were exploited as modifiers to obtain a binder with a high compressive strength. The best modification conditions, determined by means of an orthogonal design matrix approach, were 4 g of Na<sub>2</sub>CO<sub>3</sub>, sodium pyrophosphate, furfuryl alcohol and animal glue with a ratio of 4:12:100, at 85°C and with a duration of 115 min, respectively. The viscosity of the mixture obtained under these optimized conditions was 1250 mPa·s. The compressive strength of the binder, hardened by CO<sub>2</sub> gas, was 4.00 MPa. Its gas evolution at 850°C was 15 ml·g<sup>-1</sup>, and its residual strength after 10 min calculation at 800°C was 0.01 MPa, which is high enough to meet the requirement of core-making in foundry. Moreover, after hydrolysis and further modification, animal glue and modifiers displayed a grafting reaction and an esterification reaction, respectively, which made the adhesive network denser and improved its thermal stability.

### KEYWORDS

Animal glue binder; phosphate; CO<sub>2</sub> gas; casting sand

## 1 Introduction

As we all know, many kinds of organic binders, such as epoxy resin [1,2] phenolic resin [3,4], furan resin [5,6], are used in casting industry every year. Some components of organic adhesives do great harm to the environment and workers, so a variety of pollution-free binder is needed for casting. Therefore, binders obtained from natural materials attract a lot of attention. Clay, montmorillonoid and starch have the advantages of low cost and short molding cycle. However, their castings are prone to sand washing, sand inclusion, porosity and other defects, which restrict their application [7,8].

Animal glue is a kind of non-toxic, ecologically clean, and biodegradable natural polymer material, which is also abundant and inexpensive [9,10]. Nevertheless, animal glue binder applications are limited.



Most of the research involving binders based on animal glue focused on preventing or eliminating its room temperature aggregation. One of the ways is to combine animal glue with other polymeric binders. Thus, Mohammad Sadeghi et al. developed a new super absorbent adhesive with animal glue and MMA as the main raw materials, which has good thermal stability [11]. Weihua et al. used acrylic acid and glucose to prepare an animal glue binder with high tensile strength and apply it to aluminum alloy castings [12]. Ren Yuyan et al. a new type of animal bone glue adhesive was synthesized by using ethanol and glycerol as composite modifiers. The modified adhesive molecules had a network space structure [13]. Miao et al. developed a liquid bone glue adhesive using epichlorohydrin [14]. Guo et al. proposed to chemically cross-link  $Al^{3+}$  with the bone glue. The surface of the resulting CA membrane was smoother and denser than of the original bone glue membrane [15]. Khatua et al. developed an amino-plastic based thermosetting resin adhesives using animal glue and melamine, the adhesive is cost effective, eco-friendly and enhance the fire retardant property [16]. Krishnanand et al. graft-cured polycaprolactone acrylate on the surface of animal glue can improve the biological inclusiveness of the adhesive and has good hydrophilicity [17]. Fan Chenchen et al. used water-based polyurethane blends to modify animal glue and quickly cured it with compressed air [18]. The tensile strength of the molding sand could reach 2.60 MPa.

This paper reports synthesis method of a modified animal glue binder with high compressive strength and low viscosity prepared using sodium pyrophosphate and furfuryl alcohol. A thorough analysis of the resulting material by using Fourier transform infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC), provides insights into its formation, modification, and performance mechanism, which is discussed in details in this paper.

## 2 Materials and Methods

### 2.1 Materials

All initial materials (animal bone glue, anhydrous potassium carbonate, sodium pyrophosphate and furfuryl alcohol) were analytically pure. The sand ZGS-50/100(60) was purchased from Dalin Co. (China).

### 2.2 Binder Preparation

120 g water and 100 g animal glue were mixed at room temperature, for 30 min. Then, 1, 2, 3, 4, 5, 6 g  $Na_2CO_3$  as the catalyst was added, respectively, after sodium pyrophosphate and furfuryl alcohol were added. The resulting mixture was heated under constant stirring, after 5 g anticoagulant was added. The mixture was stirred for another 30 min and then cooled down naturally to room temperature. The resulting brown liquid was a modified animal glue binder. The binder has a shelf life of 90 days at room temperature.

An orthogonal experimentation was used to determine the best modification conditions. Compressive strength and viscosity were tested as the important performance indicators of the binder. The orthogonal experiment of  $L_9(4^3)$ , which contains factors with three levels of sodium pyrophosphate, furfuryl alcohol, modification time and modification temperature, was designed as Table 1, and the test scheme was arranged as Table 2.

**Table 1:** Design of orthogonal factors and levels

Level	Sodium pyrophosphate (g)	Furfuryl alcohol (g)	Modification time (min)	Modification temperature (°C)
1	2	10	100	65
2	4	12	115	75
3	6	14	130	85

**Table 2:** Test scheme

Level	Sodium pyrophosphate (g)	Furfuryl alcohol (g)	Modification time (min)	Modification temperature (°C)
1	A1	B1	C1	D1
2	A1	B2	C2	D2
3	A1	B3	C3	D3
4	A2	B1	C2	D3
5	A2	B2	C3	D1
6	A2	B3	C1	D2
7	A3	B1	C3	D2
8	A3	B2	C1	D3
9	A3	B3	C2	D1

### 2.3 Sand Sample Preparation

1000 g of sand, 30 g of the binder, and 12.5 g of  $\text{Ca}(\text{OH})_2$  (used as a hardening accelerator) were mixed in casting sand mixer (120 r/min) for 2 min, and then it was made a standard “ $\Phi 50 \text{ mm} \times \Phi 50 \text{ mm}$ ” sample, and hardened under a constant  $\text{CO}_2$  flow (0.6  $\text{m}^3/\text{h}$  air blowing amount and 60 s air blowing time). Then, the samples were taken out and cooled to room temperature for next testing. The compressive strength of the prepared samples was the average of the 5 samples.

### 2.4 Sand Sample Characterization

A scanning electron microscope (SEM) was used to characterize the bonding bridge and fracture morphology of the molding sand sample. Cut a 10 mm  $\times$  10 mm  $\times$  10 mm cube test block along the section of the molding sand sample, and place it on the gold spraying station to spray gold.

Collapsibility of sand: Heat the sand sample to different temperatures for 10 min, then cool it to room temperature, and test its strength. The test result is the average of 3 samples.

Gas emission: Use SFL gas emission tester to test the gas emission at 850°C with (1  $\pm$  0.01) g sand sample.

### 2.5 Measurement of Binder Viscosity

The viscosity of binder was measured by a “NDJ-1” rotary bond meter. The 200 g binder sample, which was cooled to room temperature, was placed in a beaker, and after rotating 120 s at the 3<sup>#</sup> rotor (30 r/min speed) read value, this experiment repeated 5 times, the data averaged.

## 3 Results

### 3.1 Hydrolysis Catalyst Optimization

The peptide groups (-NH-CO-) presence is the main reason for the animal glue aggregation at room temperature [19,20]. However, accumulations can be prevented by introducing hydrolysis catalysts such as acids, bases, and enzymes into the system during its synthesis process. These liquid additives do not affect the chemical reaction [21,22].

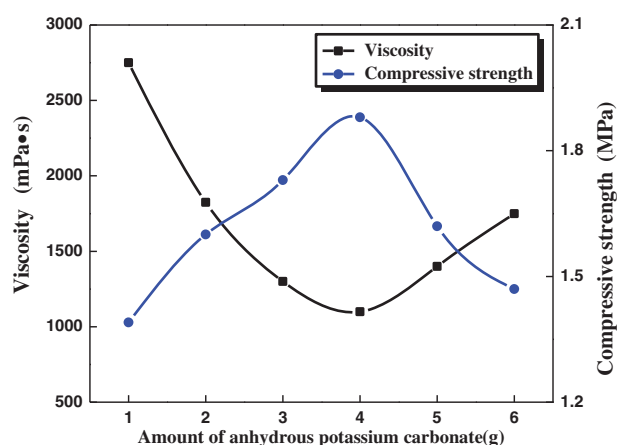
We used HCl,  $\text{Na}_2\text{CO}_3$ , and KOH as anticoagulants to study how they affected the final animal glue binder properties.

As seen in Table 3, the best combination of the binder viscosity and compressive strength of the hardened cast was obtained when  $\text{Na}_2\text{CO}_3$  was used as the anticoagulating agen. Therefore, it was used for all further experiments as a hydrolysis catalyst.

**Table 3:** Viscosity of the animal glue binder and the compressive strength of the final cast prepared using various hydrolysis catalysts

Catalyst	Binder viscosity (mPa·s)	Compressive strength (MPa)
NONE	2800	1.08
HCl	1550	1.57
Na <sub>2</sub> CO <sub>3</sub>	1100	1.88
KOH	1250	1.79

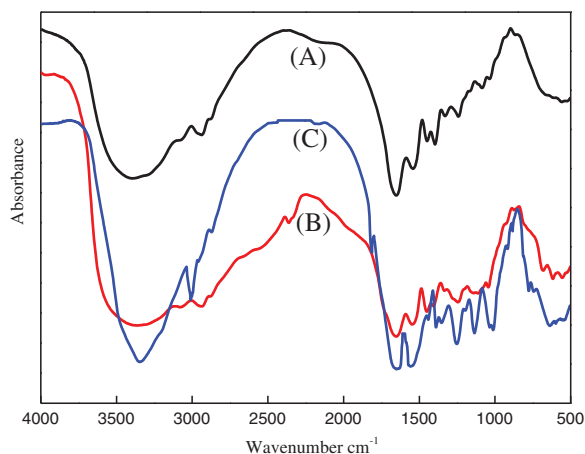
We also performed experiments to optimize Na<sub>2</sub>CO<sub>3</sub> quantity. When 1–3 g Na<sub>2</sub>CO<sub>3</sub> was added, the viscosity of the binder decreased rapidly, and the compressive strength of the molding sand increased as the Na<sub>2</sub>CO<sub>3</sub> amount increased (see Fig. 1). When over 4 g of Na<sub>2</sub>CO<sub>3</sub> was added, the compressive strength of the molding sand decreased, and the viscosity increased proportionally. The lowest viscosity and the highest compressive strength were obtained when 4 g of Na<sub>2</sub>CO<sub>3</sub> was used. This level was used in all further experiments.

**Figure 1:** Effect of anhydrous sodium carbonate content on properties of binders

### 3.2 Characterization

The comparison of the FTIR spectrum of the hydrolyzed (by Na<sub>2</sub>CO<sub>3</sub>) animal glue with the unmodified sample (shown in Fig. 2A) showed that there is a wider absorption band at 3500–3200 cm<sup>-1</sup> (which was attributed to the increased amount of OH groups), peaks at 1658, 1456, and 930 cm<sup>-1</sup> (which were attributed to the carboxylic -COOH and -COO groups) and signals at 1558, 1147, and 3340.71 cm<sup>-1</sup> (which were ascribed to the amino NH<sub>2</sub> groups) (see Fig. 2B). Thus, peptide bonds of the animal glue were broken by Na<sub>2</sub>CO<sub>3</sub> into hydroxyl, amino and carboxylic groups.

After modifying the binder with sodium phosphate and furfuryl alcohol, a band at 3500–3000 cm<sup>-1</sup> became weaker because of the decreased amount of the OH groups in the binder (see Fig. 2C). The peaks at ~640 and 1025 cm<sup>-1</sup> were assigned to the O-P-O bond bending and stretching, respectively. An absorption peak near 1250 cm<sup>-1</sup> was interpreted as a P-O-C bond stretching, while the one at 1344 cm<sup>-1</sup> was P=O stretching. No peaks attributable to the P-O-P bending vibrations were detected (typically located around 800–750 cm<sup>-1</sup>). These results indicate a cross-linking reaction completion between pyrophosphate and the -OH groups of the binder. The peaks at 1600–1500 cm<sup>-1</sup> belonged to the C=O stretching vibrations, while a band at 1045 cm<sup>-1</sup> belonged to a C-O-C. These bands indicate a fatty anhydride formation during animal glue binder and furfuryl esterification reaction.



**Figure 2:** FT-IR spectra of (A) unmodified, (B)  $\text{Na}_2\text{CO}_3$ -treated, and (C) modified animal glue binder

As can be seen from Table 4, GPC data indicated that the average molecular weight of the untreated animal gum was 268160, the polydispersity was 2.73, and the molecular distribution was wide. Animal glue binder treated by  $\text{Na}_2\text{CO}_3$  had a lower molecular weight, and its molecular weight distribution was relatively narrow. Moreover, the modified animal glue binder was higher than the unmodified binder, but the distribution was narrower. After modification, the molecular weight of the binder was increased, indicating that the molecules of the animal glue and the modifiers are grafted and cross-linked to form a larger molecule, and the smaller molecular component in the binder made the molecular weight distribution narrower.

**Table 4:** Distribution of molecular weight of binders

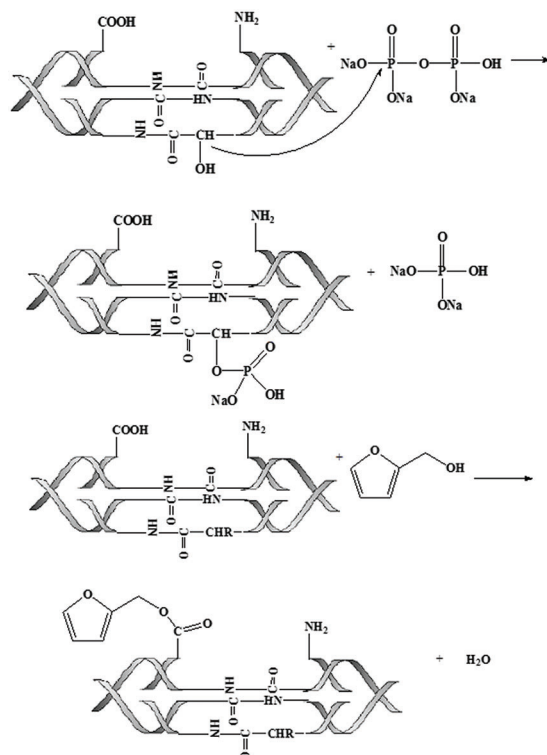
	Mw	Mn	Polydispersity
Untreated animal glue binder	731109	268160	2.73
Animal glue binder treated by $\text{Na}_2\text{CO}_3$	95910	43795	2.19
Modified animal glue	398341	295067	1.35

The modified mechanism can be expressed by the reactions shown below (see Fig. 3).

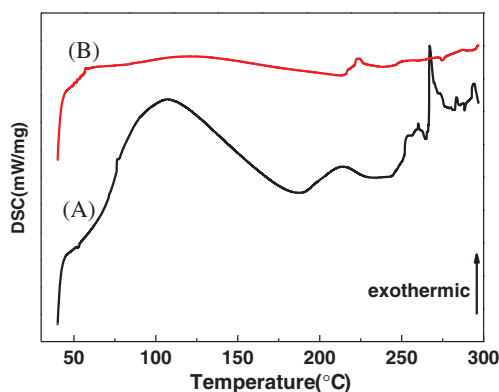
DSC curves of the unmodified and modified binder samples were significantly different (see Fig. 4). The shrinkage temperature of the unmodified binder was  $53^\circ\text{C}$  (curve A), the double endothermic peaks appear at  $180^\circ\text{C}$ – $200^\circ\text{C}$ , which indicates the unmodified animal glue has multiple thermal transitions. After the modification, the thermal denaturation peak of the binder basically disappeared (curve B), an exothermic plateau appeared when the temperature was raised to  $100^\circ\text{C}$ . The heat release of it accelerated when the temperature was higher than  $250^\circ\text{C}$ . The molecular chain of the modified binder becomes longer, hydrogen bonding increases, intermolecular bonding becomes stronger, and thermal stability increases.

### 3.3 Orthogonal Tests of the Best Parameters for the Binder Structure and Composition Optimization

To quantitatively evaluate how four factors affected final binder properties, and based on single factor test results. We designed an orthogonal experiment with four factors and three levels to analyze the corresponding data ranges (see Tables 4 and 5). All test results were the average of 5 samples.



**Figure 3:** The reaction equation of animal glue modification

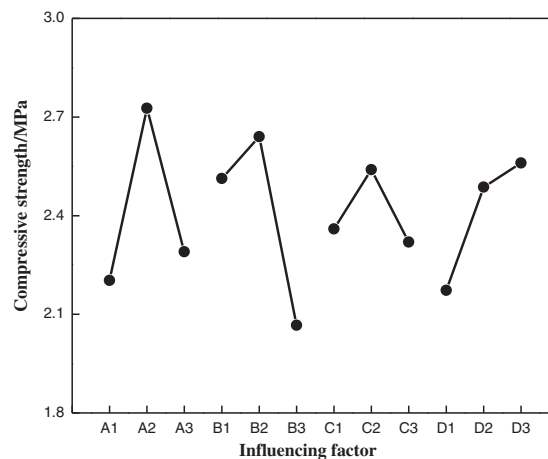


**Figure 4:** DSC curve of the (A) unmodified and (B) modified animal glue binder

Compressive strength was affected by these optimization factors in the following order: furfuryl alcohol > sodium pyrophosphate > modification temperature > modification time. Under T4 treatment (4 g sodium pyrophosphate, 10 g furfuryl alcohol, 115 min modification time and 85°C modification temperature), the highest tensile strength than other treatments were observed (see Fig. 5). However, according to the average value (k) of the compressive strength of each test factor, 4 g of sodium pyrophosphate, 12 g of furfuryl alcohol, a modification time of 115 min and a modification temperature of 85°C were selected for further testing (see Table 5). Under these conditions, it compared to T4, showed better effects not only on compressive strength (4.00 MPa) but also on viscosity (1250 mPa·s). Samples prepared under these conditions were used for the next round of tests.

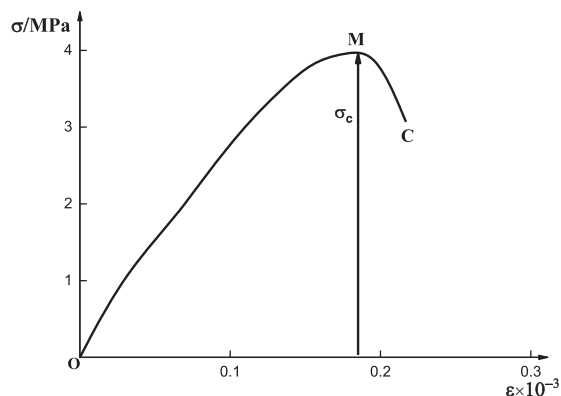
**Table 5:** Orthogonal experiment data

Test	Orthogonal test factors				Compressive Strength (MPa)	Viscosity (mPa·s)
	Sodium pyrophosphate (g)	Furfuryl alcohol (g)	Modification Time (min)	Modification Temperature (°C)		
T <sub>1</sub>	A1	B1	C1	D1	2.03	2000
T <sub>2</sub>	A1	B2	C2	D2	2.65	1625
T <sub>3</sub>	A1	B3	C3	D3	1.93	2050
T <sub>4</sub>	A2	B1	C2	D3	3.12	1350
T <sub>5</sub>	A2	B2	C3	D1	2.64	1500
T <sub>6</sub>	A2	B3	C1	D2	2.42	1550
T <sub>7</sub>	A3	B1	C3	D2	2.39	1650
T <sub>8</sub>	A3	B2	C1	D3	2.63	1550
T <sub>9</sub>	A3	B3	C2	D1	1.85	2200
k <sub>1</sub>	2.203	2.513	2.360	2.173		
k <sub>2</sub>	2.727	2.640	2.540	2.487		
k <sub>3</sub>	2.290	2.067	2.320	2.560		
R	0.524	0.573	0.220	0.387		

**Figure 5:** Analysis of the modifier addition ranges

### 3.4 Stress-Strain Curve of Compressive Process of Sand Sample

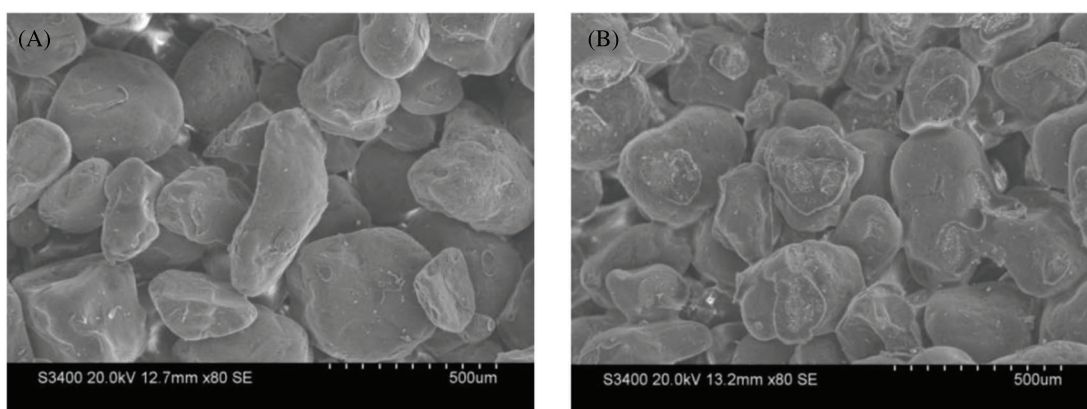
As can be seen from Fig. 6, it was found that the stress-strain curve of the sand sample was identified as two steps, the plastic deformation stage (O-M) and the rupture stage (M-C), and compressive strength of M point was the peak in the  $\sigma$ - $\epsilon$  curve. Under the action of compressive stress, the animal film between sand particles is squeezed to become smaller and undergoes irreversible viscoplastic deformation until the film reaches the stress level of resisting the compressive deformation of the bonding bridge. Moreover, when the stress reaches the ultimate compressive strength, the sample enters the stage of extrusion fracture, which lasts for a short time. When the stress exceeds the compressive strength of the sample, the sample will be crushed.



**Figure 6:** Stress-strain curve of compressive process of sand sample

### 3.5 Sand Characterization

Compared to the unmodified binder molding sand (shown in Fig. 7a), the surface of the modified sand possessed more bonding bridges and nets (see Fig. 7b). Additionally, the fracture areas of the bonding bridges in the sand sample prepared using the modified binder were larger, which indicates higher strength.



**Figure 7:** The morphology of the unmodified and modified animal glue sand

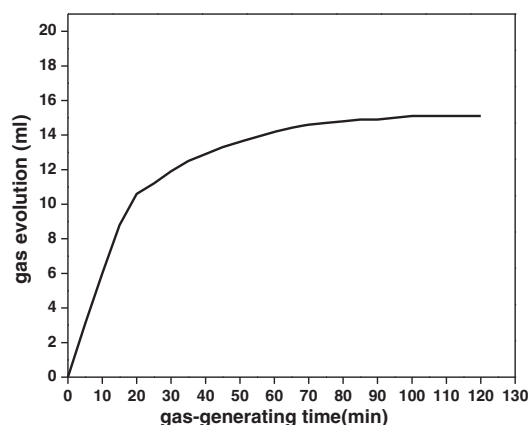
The addition of sodium pyrophosphate and furfuryl alcohol increased the amount of the active molecular groups and polarity of the binder. With the reaction, the binding force between the sand and the binder increases. The bond bridge network of molding sand increases, too. All these factors contributed to the enhanced strength of the molding sand.

We also tested the collapsibility and gas generation of the modified binder molding sand (see results in Table 6 and Fig. 8, respectively).

**Table 6:** Residual strength of sand as a function of the temperature treatment

Temperature/°C	400	500	600	700	800
Residual strength/MPa	1.75	0.64	0.35	0.14	0.01





**Figure 8:** Gas evolution from the sand used together with the modified binder as a function of time

Collapsibility means that sand is not easy to break after casting solidification. After touring at 800°C, the residual strength of the sample after annealing is only 0.01 MPa. Thus, the modified binder possessed excellent collapsibility, which is essential upon binder pouring into the molds. Gas evolution refers to the amount of gas emitted by the sand mold when encountering high-temperature metal solution during pouring. In this experiment, the gas evolution of the modified animal glue binder sand was 15 ml·g<sup>-1</sup>, which meets the casting requirements.

#### 4 Conclusions

A novel liquid animal glue binder was prepared by hydrolysis reaction and modification. It was used for core making based on CO<sub>2</sub> hardening. The samples prepared with this binder possesses high compressive strength (4.00 MPa) and suitable viscosity (1250 mPa·s). The main conclusions and results of this study are summarized as follows: Anhydrous potassium carbonate was the best hydrolysis catalyst. Its optimal level was 4 g per each 100 g of animal glue binder; The optimum sodium pyrophosphate/furfuryl alcohol/animal glue weight ratio was 4:12:100, while the best modification time and reaction temperature were 115 min and 85°C, respectively; FT-IR spectra confirmed that the chemical composition and structure of the binder has changed after the hydrolysis and further modification due to the cross-linking and esterification reactions. DSC analysis proved that the modified animal glue binder possessed remarkably high thermal stability; The modified binder sand possessed denser bonding networks.

Its gas evolution at 850°C was 15 ml·g<sup>-1</sup>. Its residual strength after 10 min calculation at 800°C was 0.01 MPa, which can meet the requirements of aluminum alloy sand castings. In this experiment, it is found that a large amount of waste sand produced during the experiment has caused waste of resources. Then, with the characteristics of good water solubility and biocompatibility of animal glue, we suggest that the waste sand can be regenerated by heating, water-machinery combination and other methods in the subsequent treatment of casting waste sand, and the regenerated sand can be used as new sand to realize waste recycling.

**Funding Statement:** This research was supported by the National Natural Science Foundation of China (51275313); Shandong Province Transportation Science and Technology Project (2021B115); Shandong Jiaotong University School Fund (Z2019036).

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

## References

1. Knapíková, L., Behúnová, A. (2020). Research of casting moulding of epoxy resin composites reinforced with high-strength fibres during the manufacturing operations. *TEM Journal*, 9(4), 1488–1493.
2. Qian, X. W., Wan, P., Yin, Y. J., Qi, Y. Y., Ji, X. Y. et al. (2022). Gas evolution characteristics of three kinds of no-bake resin-bonded sands for foundry in production. *China Foundry*, 19(2), 140–148.
3. Kmita, A., Knauer, W., Holtzer, M., Holtzer, M., Hodor, K. et al. (2019). The decomposition process and kinetic analysis of commercial binder based on phenol-formaldehyde resin, using in metal casting. *Applied Thermal Engineering*, 156(25), 263–275.
4. Hu, T. T., Ren, Q. G. (2013). Research on synthesizing phenylic phenolic resin of foundry binder system. *Advanced Materials Research*, 2334(680), 15–19.
5. Kamińska, J., Puzio, S., Angrecki, M., Stachowicz, M., Los, A. K. (2019). Preliminary tests of innovative eco-friendly furfuryl resins and foundry sand mixtures based on these resins. *Journal of Ecological Engineering*, 20(9), 285–292.
6. Wen, H., Zhang, H. K. (2019). Synthesis process of a curing agent for low nitrogen furan resin bonded sand. *Foundry*, 68(9), 1009–1011.
7. Lachance, A. M., Hou, Z., Farooqui, M. M., Carr, S. A., Serrano, J. M. et al. (2022). Doctor-blade-assisted casting for forming thin composite coatings of montmorillonite and poly(vinyl alcohol). *Industrial & Engineering Chemistry Research*, 61(10), 3766–3774.
8. Giorleo, L., Bonaventini, M. (2021). Casting of complex structures in aluminum using gypsum molds produced via binder jetting. *Rapid Prototyping Journal*, 27(11), 13–23.
9. Wang, T. S., Zhang, Z., Zhang, S. J., Wang, M. Y. (2021). Hydrolysis optimization and application of animal glue binder for casting. *Journal of Physics: Conference Series*, 1948(1), 012217.
10. Fan, C. C., Tang, Q. (2020). Allyl glycidyl ether-modified animal glue binder for improved water resistance and bonding strength in sand casting. *Organic Polymer Material Research*, 2, 1–7.
11. Sadeghi, M., Heidari, B. (2011). Crosslinked graft copolymer of methacrylic acid and gelatin as a novel hydrogel with pH-responsiveness properties. *Materials*, 4(3), 543–552.
12. Liu, W. H., Zhang, Y. L., Li, Y. M. (2012). Process optimization of new air hardening animal glue for core sand binder. *Foundry*, 7, 718–721.
13. Ren, Y. Y., Wang, T. S., Ma, J. X., Liu, W. H., Li, Y. M. (2022). Alcohol modified animal glue binder and its modification mechanism. *Foundry*, 71(3), 351–356.
14. Miao, Z. C., Wang, F., Deng, D. (2012). Preparation of bone glue adhesives using epichlorohydrin modification. *Advanced Materials Research*, 6, 557–559.
15. Guo, M., Su, X., Zhou, L. (2015). Synthesis mechanism and water tolerance of bone glue adhesive material modified by  $Al^{3+}$ . *Journal of Functional Materials*, 12, 12039–12043.
16. Khatua, P. K., Dubey, R. K., Roymahapatra, G., Mishra, A., Shahoo, S. C. et al. (2017). Development of self fire retardant melamine-animal glue formaldehyde (MGF) resin for the manufacture of BWR ply board. *Journal of the Institution of Engineers (India): Series D*, 98, 195–202.
17. Kumar, K., Basanti, L. D., Abhishek, M., Bhuvanesh, G. (2013). Immobilization of gelatin onto acrylic acid grafted polycaprolactone monofilament. *Journal of Biomaterials and Tissue Engineering*, 3(2), 233–239.
18. Fan, C. C., Gong, C. B., Peng, J. D. (2020). Study on the preparation process of air hardening waterborne polyurethane modified animal adhesive. *Shandong Chemical Industry*, 49, 33–38.
19. Liu, W. H., Jin, Y., Li, Y. M. (2015). Research on preparation of a compound modification animal glue binder. *Foundry*, 64(2), 162–165.
20. Li, Y. M., Wang, T. S., Liu, W. H., Ren, Y. Y. (2016). Synthesis and properties of modified water soluble polymer adhesive. *Journal of Mechanical Engineering*, 52(14), 67–72.
21. Chen, X., Li, Y. M., Guan, J., Li, H. P., Zhou, J. Y. (2001). A study for developing the binder of modified gelatin. *Foundry*, 2, 88–91.
22. Liu, W. H., Wang, T. S., Li, Y. M., Ren, Y. Y., Huo, W. H. (2016). Preparation of a new animal glue binder for foundry use. *China Foundry*, 13, 238–242.