Hydrolysis optimization and application of animal glue binder for casting

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Abstract. With the animal glue binder as raw material, the optimal hydrolysis process of anhydrous sodium carbonate is determined by single factor. The results show that the optimum hydrolysis process is as following. The hydrolysis time is 30 min for a reaction temperature of 60°C, and the mass ratio of water to animal glue is 120:100. The amount of anhydrous sodium carbonate is 4wt.% to binder. Under these conditions, the compression strength of binder reaches 2.50MPa, and the surface tension of binder is 33.236 mN/m. The molecular weight of hydrolyzed binder is greatly reduced, and the binder contains hydrophilic molecular groups such as amino and hydroxyl, which improves the hydrophilicity and thermal stability of the animal glue binder.

1. Introduction
Animal glue is one of the earliest natural glue materials used by human beings, which is non-toxic and harmless, biocompatible and biodegradable[1-3]. In 1994, J.S Siak et al. first applied animal glue in foundry industry to prepare sand cores for automobile cylinder blocks and applied for relevant patents[4]. Subsequently, the considerable research to animal glue from casting industries and institutions[5-7]. However, animal glue is easy to agglomerate at room temperature, low strength of sand, so it is necessary to add other reagents to endow the binder with some characteristics. The research shows that the macromolecular chain of animal glue can be destroyed by using hydrolysis catalyst before the reaction between animal glue and other reagents. The research from Shaanxi university of science and technology showed animal glue can be hydrolyzed by hydrochloric acid and citric acid (citric acid is 0.06 wt%). After hydrolysis, the binder has a lower freezing point (the value is -2°C), and it has good thermal stability[8]. Moreover, Liu et al. prepared a new modified animal glue casting binder with sodium hydroxide as hydrolysis agent, which has good fluidity and high tensile strength[9].

Studies have shown that strong base weak acid salt can be used as catalyst to hydrolyze animal glue, but there is little research in this area. In this paper, the hydrolysis of animal glue with anhydrous sodium carbonate was taken as the main research object, and the optimum hydrolysis process was determined by single factor experiment. Fourier-transform infrared (FT-IR) spectra and Gel permeation chromatography (GPC) were used to characterize and analyze the binder.

2. Experimental procedures
A certain amount of water and animal bone glue are poured into a three-necked round-bottom flask, and then mechanically stirred and mixed. Then, anhydrous sodium carbonate catalyst was added to the mixture. Thereafter, 10g of mixed alcohol (m (glycerin) /m (fururyl alcohol) = 2: 3) was added. After reaction for a certain time, a brown liquid binder was finally obtained.
Sand sample preparation: 1000g of sand was mixed with 30 g binder and 12.5g Ca (OH)₂ (as a curing-promoter) for 2min. This mixture was used to create the standard Ф50mm×50mm sand samples by a hammer machine. After then the samples were hardened in a sample barrel by blowing 1.0m³.h⁻¹ CO₂ gas for 100s, the sand samples were removed for subsequent testing.

3. Results and discussion
Under the same addition amount, the influence of different hydrolysis catalysts on the compressive strength and surface tension are shown in Table 1.

| Hydrolysis catalyst     | Surface tension (mN/m) | Initial strength (MPa) | Final strength (MPa) |
|-------------------------|------------------------|------------------------|----------------------|
| No catalyst             | 72.842                 | 0.33                   | 1.21                 |
| Hydrochloric acid       | 47.879                 | 0.45                   | 1.83                 |
| Anhydrous sodium carbonate | 33.236                | 0.55                   | 2.50                 |
| Sodium hydroxide        | 36.451                 | 0.51                   | 2.27                 |

As presented in Table 1, the samples hydrolyzed by anhydrous sodium carbonate have the highest compressive strength, while the adhesive surface tension is the lowest. Due to the carbonate ions is easy to ionize in aqueous solution, which leads to the pH value of solution is shown weak alkaline. Furthermore, it is conducive to promote the hydrolysis and cleavage of peptide chain structure in animal glue molecules into short molecular chain active groups. Surface tension is one of the important parameters to describe the wettability of liquid. After hydrolysis, the surface tension of binder decreases, which is mainly due to the good wettability between binder with sand.

Figure 1 shows that the hydrolysis process parameters on its surface tension and compressive strength by anhydrous sodium carbonate.
As shown in Fig.1, the optimum hydrolysis conditions are as following. The amount of anhydrous sodium carbonate is 4wt.%, the water to binder ratio is 120:100, the hydrolysis time is 30 min, and the hydrolysis temperature is 60℃. Moreover, the compressive strength of sand sample can be reached 2.50 MPa, and the surface tension of binder is 33.236 mN/m.

In order to compare the effects of catalysts on the structure and properties of animal glue. The untreated binder and binders treated with three hydrolysis catalysts were analyzed by FT-IR. The results are shown in Figure 2.

![Fig.2 FT-IR results of animal glue binder treated by different hydrolysis catalysts](image)

As can be seen from Fig. 2, after hydrolysis, the molecular structure of animal glue has changed obviously. Compared with untreated binder (curve a), characteristic absorption peaks of O-H appeared at 3297cm⁻¹ of curve b-d. This is because the hydrolysis catalyst breaks the peptide chain in the binder molecule to produce hydrophilic functional groups -OH. Furthermore, the characteristic absorption peak of anhydrous sodium carbonate (curve b) is wider.

The bending vibration absorption peaks of O-H appeared at 1450cm⁻¹ and 950cm⁻¹, and the characteristic absorption peaks of -C=O appeared at 1650cm⁻¹, which proved that -COOH existed in the system. The obvious absorption peak near 1550cm⁻¹ is the primary amide bending vibration peak, and the absorption peak at 1165cm⁻¹ is the C-N tensile vibration peak. Moreover, the absorption peak of N-H is 3385cm⁻¹, which proves that-NH₂ exists in the binder. The FT-IR results showed that the peptide chain in the binder was broken into carboxyl, amino and hydroxyl groups by anhydrous sodium carbonate, and the binder was more hydrophilic. It is consistent with the surface tension values in Table 1.

Table 2 shows that the GPC (gel permeation chromatography) results of binders.

| Tab. 2 GPC analysis results of the binders |
|------------------------------------------|
| Number-average molecular weight (Mn)    | Weight-average molecular weight (Mw) | Polydispersity (α) |
|------------------------------------------|
| Untreated animal glue binder             | 124980Da                              | 383544Da          | 3.069       |
| Animal glue binder treated by anhydrous sodium carbonate | 46948Da                              | 101877Da          | 2.170       |
| Animal glue binder treated by NaOH       | 44968Da                              | 98480Da           | 2.192       |
| Animal glue binder treated by HCl        | 45239Da                              | 99526Da           | 2.200       |
It can be seen from Table 2, the number average molecular weight (Mn) of animal glue treated with Na$_2$CO$_3$ is lower than that of untreated, and its distribution is narrower. After hydrolysis, the molecular weight decreased, which indicated that the peptide bond of binder was broken, and smaller molecules formed. Moreover, the molecular weight of binder treated by anhydrous sodium carbonate is lower than that of untreated animal glue, and the binder is treated with sodium hydroxide and hydrochloric acid.

4. Conclusions
Animal glue binder treated by anhydrous sodium carbonate has better compressive strength and lower surface tension. Through single factor experiment, the optimum hydrolysis process was as follows. The appropriate amount of anhydrous sodium carbonate was 4wt.% of binder, the ratio of water to binder is 120:100, hydrolysis time is 30 min, and hydrolysis temperature is 60℃. Furthermore, the compression strength of casting sand could reach 2.50MPa, and the surface tension of the binder was 33.236mN/m. The analysis of FT-IR and GPC showed that the hydrophilic molecular groups such as -NH$_2$, -OH and -COOH were contained in the binder after hydrolysis with anhydrous sodium carbonate, which improves the hydrophilicity of the binder. Moreover, its molecular weight distribution was relatively narrower.

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