Alcohol Modifiers and Mechanism of Animal Glue Binder

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ABSTRACT

Animal glue exhibits excellent properties that are non-toxic and unharmful, easy to collapse and degrade, but the compression strength of sand mold is low, easy to coacervate at room temperature, in order to solve the problem, which needs to be modified. Animal glue can be modified to the binder in the foundry by esterification crosslinking and grafting copolymerization. Coacervation of animal glue is modified by esterification crosslinking of alcohol modifiers and its result structure is characterized by FT-IR in this paper, in which its mechanism is analyzed. The experimental results show that Gel state of animal glue is made better in which improved sand compressive strength obviously. The initial compressive strength could be achieved 0.42 MPa and the final strength reached 3.30 MPa. Its mechanism is an esterification reaction, which happens between the carboxyl (-COOH) of animal glue and the Hydroxyl (-OH) of alcohol modifiers mainly, which improves adhesion; In addition, the strength of binder and bonding mechanism is analyzed by fracture methods of molding sand.

INTRODUCTION

The animal glue is non-toxic, which can be biodegradable aqueous natural rubber. It has abundant raw materials and low costs, and it is a kind of environmentally friendly material\textsuperscript{[1,2]}. Its main components belong to the amino acid polymer compound, having good mechanical properties such as strength and toughness\textsuperscript{[3]}. It can provide a kind of ideal green casting binder. In 1996, the United States, J.S. Siak and others according to the principle that it is environmental friendly and its intensity is above commonly used binder, animal protein has been putforward as the binder, which was called GMBOND, plus it also was applied for a patent\textsuperscript{[4,5]}. The binder was used in automobile’s cylinder head and cylinder block of aluminum casting, achieving good results. Characteristics of the patented product are that is subsequently to model after using special equipment hot-melt, the process was relative complex. In addition, the use of methods like physical

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heating of dehydration, curing methods, the curing speed was slow, which was not applicable to the needs of mass core production efficiently. In China, Jingyu Shi and others who are from Jilin University of Technology, applying protein binder [6] directly as sand core binder. However, the use of protein glue without modification, it is difficult to realize the industrial production of sand mixing. In 1991, Indian scholar B. Ramatai and other [7] people researched the system of bone glue modification scientifically, and pointed out that the modification can be obtained by synergism function and addition reaction. Shenyang institute of foundry Lv Dezhi and other [8] people also studied the modification mechanism of animal glue, but which failed to release the potential high bond strength, meanwhile its reactivity also was low. Xiuxia Su and others [9,10] studied the synthesis and performance that is a new type of liquid bone glue binder, using epichlorohydrin as the crosslinking agent, using the method of acid solution and copolymerization crosslinking, modification the traditional bone glue, gaining a new type of adhesive liquid binder at room temperature. They acquired optimum process conditions of binder synthesis.

Animal glue exists in nature and as a renewable resource; it is significant to replace the current widely used in foundry industry of petroleum base synthetic polymer binder with animal glue. This paper is mainly through alcohol amending animal glue binder, by means of infrared spectrum to analyze modified animal binder of modification mechanism.

EXPERIMENTAL METHOD

The Manufacturing Process of Modified Animal Binder

A certain amount of water and animal glue were added into a 500 ml three-necked flask, then swelled for 30 minutes, catalyst NAOH was been added to alkaline hydrolysis, they were heated by the furnace at room temperature bathroom water while mixed with the power of electric mixer. In the next step, the heating temperature should be controlled and put appropriate modifier, it can form stable good fluid liquid under the sufficient stirring. Finally, anticoagulant should be added and it would be cool to generate brown viscous liquid until reaching the room temperature.

Alkaline hydrolysis process: the quality of water-binder ratio is 4:4; and NAOH will be as the catalyst, its dosage is 6% of animal glue quality, alkaline hydrolysis time is 35 min, alkaline hydrolysis temperature is 55℃.

The manufacture of animal glue binder process is shown in figure 1.

![Dissolution](https://via.placeholder.com/150)

*Figure 1. Glue bond process.*
Compressive Strength Test

In this test, universal hydraulic strength tester tested the compressive strength of the standard test specimen of animal glue bonded sand. 10 standard samples (ϕ50mm * 50mm) were manufactured. Five samples were as a group, measured its initial strength; final strength respectively after completing the specimens, and the result was got through averaged value.

The initial strength (σ0) was tested immediately after mixing the sand, it would be placed for 24 hours, and the final strength (σ24) can be taken.

RESULTS AND DISCUSSIONS

The Modified Effects of Alcohol to Animal Glue

After the animal glue has been modified by NAOH alkali solution, the selection of alcohol modifier was carried out in single factor modification experience respectively. The sand compressive strength of modified animal glue binder is measured. This experiment mainly inspected glycerol, alcohol, isopropanol, diethylene glycol.

| TABLE 1. COMPRESSIVE STRENGTH OF GLUE BOND BY ALCOHOL MODIFIED. |
|-----------------|---------------|---------------|
| Alcohols        | Initial Strength [MPa] | Final Strength [MPa] |
| No modifier     | 0.12           | 0.83          |
| Glycerol        | 0.42           | 3.6           |
| Ethanol         | 0.32           | 2.4           |
| Isopropanol     | 0.30           | 2.0           |
| Diethylene glycol| 0.28           | 1.7           |

Table 1 and Figure 2 are the organic alcohol solvent that was added the same quality percentage (accounted for 10% of animal glue), single solvent modified animal glue binder were used to acquire the molding sand’s initial strength and final strength. It can be seen from the figure, alcohol modification has more obvious modified effects, the glycerol and ethanol modifier have higher compressive strength. Therefore, these two modifiers were chosen as animal glue alcohol modifier.

Modification mechanism of alcohol to animal glue

![Figure 2. Compressive strength of glue bond by alcohol modified.](image)
Animal glue belongs to a kind of amino acid polymer; animal glue is actually composed of various alpha amino acids. The macromolecular structure of the animal glue is an amino group on one end, and the other end is a polypeptide chain which functional groups are carboxyl groups. In aqueous solution, the combination of amino (-NH2) and carboxyl (-COOH) make the gel group to be a mesh and insoluble one. Therefore, to ensure that the animal glue is liquid flow at room temperature, it is necessary to break down the association between molecular chains. Animal glue was resolved under alkaline conditions, through cutting the peptide bond; animal glue was released into appropriate-size molecules, and then reacted with alcohol \[^{11}\]. Currently, the majority of modification methods are addition reaction. Animal glue modification methods can be defined as esterification, enzyme addition, and aldehyde, but the application of esterification modification method is more popular. The esterification modification process is under the action of the catalyst, a certain amount of alcohol was added into the animal glue, the hydroxyl -OH from alcohol would have esterification cross-linking reaction with the side chains from animal glue’s carboxyl -COOH, to some degree, animal glue’s molecular chains have been extended. As the further reacting, three-dimensional network structure can be formed; animal glue binder will be improved greatly.

The infrared spectrum is a kind of light which wavelength is 1 ~ 15 rim leading molecular vibration and rotation, spectra were generated by absorbing light. When the molecules in a group or chemical bond vibrated or rotated requiring energy and infrared energy are equal (i.e. \( AE=Hv \)), it will absorb infrared ray. Every group in a Molecular, in the infrared spectrum with different compounds, enjoying the same absorption frequency, this is the basic reason for qualitative analysis. The second peak height and peak area are related to the concentration. This is the basis for quantitative analysis \[^{12}\].

Glycerol modified effect on animal glue

We through infrared spectrum study the mechanism of animal glue. Having infrared spectroscopy structure characterization on unmodified animal glue and modified animal glue adhesive by glycerol, we will obtain the infrared spectra, as shown in Figure 3.

**Figure 3.** FT-IR curves of unmodified and Glycerol-modified animal glue.
We can see from Figure 3, the area of stretching and vibrating peak of 3600cm\(^{-1}\)~2850cm\(^{-1}\) N-H or O-H in the animal glue’s infrared spectrum which is modified by glycerol, its intervals narrowed the peak shifted to the right, this is because the esterification reaction led to change reduction of O-H and disappearance of -NH\(^3+\). The prominent peak at about 2931cm\(^{-1}\) proved that the methylester C-H stretching vibrating absorbed. While corresponding range between 1451cm\(^{-1}\)~1335cm\(^{-1}\) intervals indicated that glycerol and animal glue have esterification cross-linking reaction. In addition, double bond which can show more characteristics in -C=O ester 1650cm\(^{-1}\) appeared strong absorption effect, and ester C-O-C appeared in 1242cm\(^{-1}\) and 1035cm\(^{-1}\) about the antisymmetric and symmetric vibration absorption peak, it further turned out that the carboxylic acid ester existing, suggesting that the animal glue polymerization with the glycerol form space network structure under the guidance of esterification reaction.

The glycerol was added to a solution of animal glue, glycerol is wire bond structure, glycerol hydroxyl - OH and animal glue side chains’ carboxyl has esterification cross-linking reaction, on one hand, it extended the alkaline hydrolysis of gelatin molecular chains’ length, on the other hand its reaction formed a three-dimensional network structure. Consequently, animal glue bonding has been improved, modified animal glue binder; the compressive strength of the sand control were also improved. Such as esterification cross-linking reaction of type 1 (R is the giant molecular).

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{COOH} \\
\text{CH}_\text{OH} + \text{NH}_2 & \quad \text{C} - \text{H} \\
\text{CH}_2\text{OH} & \quad \text{R} \\
\text{R} & \quad \text{H}_2\text{O}
\end{align*}
\]

Ethanol modified effect on animal glue

The structure of the modified adhesive by ethanol was characterized by Fourier infrared spectrometer. The product was characterized by the structure of the binder
and the ethanol modified. Figure 4 is the infrared spectrum of the product was characterized by IR spectrum.

It is clearly that from figure 4: O-H molecules’ shock absorption peak in the vicinity of 3385cm⁻¹ changed, it has transformed from the original strongly blunted peak to strongly pointed peak after modifying, absorption wave number region became smaller, which the esterification crosslinking reaction between animal glue macromolecules and ethanol. However, the wide and strong NH₃+ stretched vibration bands before modifying. After esterification, it has been replaced by the sharp and strong NH₂ stretching vibration, its sharp degree also increased with rising carbon chains; Also the group C-H in the 2937cm⁻¹ near region whose apparently absorption rate of the absorption peak appeared strong vibration, irregular vibration related to the -CH₂-CH₃ also changed in the vicinity of 1454cm⁻¹~1336cm⁻¹ area; with strong absorption peak appearing in the -C=O 2161cm⁻¹ area, primary alcohol ester molecular structure are enhanced alcohol absorption peak of O-H (1081cm⁻¹-1031cm⁻¹),these functional groups provided a powerful evidence to the change of infrared absorption peak of the body by the esterification reaction with carboxylic ester. What’ more, Symmetrical characteristic functional groups C-O-C (1035cm⁻¹) and asymmetric (near 1242cm⁻¹) absorption peak appeared.1655 cm⁻¹ absorption peak verified that carboxylic acid esters existence. In the vicinity of the 1543cm⁻¹ is the stronger secondary amide –CONHR’s absorption peak. Under alkaline conditions, -NH₂ of animal glue protein molecules’ H+ reacted with and -OH who are from the donor -OH. The molecule of RN- (R-) was grafted onto the animal glue protein molecules. Accordingly, it should be noted that animal glue has an esterification reaction with ethanol, animal glue’s molecular chains has been extended. According to the above factors, we can get a conclusion that ethanol has an esterification reaction with animal glue, which increased the length of molecular chain.

Ethanol also through esterification and crosslinking reaction with animal glue to have modified process. The esterification crosslinking reaction between Ethanol and animal glue prolonged the molecular linear length after alkaline hydrolysis. Specific reaction equation is shown in type 2 (R is giant molecular):

\[
\text{C}_2\text{H}_5\text{OH} + \text{NH}_2\text{C}_2\text{H}_5 \rightarrow \text{NH}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

\[
\text{COOH} \quad \text{COO}−\text{C}_2\text{H}_5
\]

(2)

**The analysis of fracture morphology adhesive film between binder and sand.**

Animal glue adhesive sand sample fracture morphology analysis can be made full use of after modification, to research adhesive mechanism of modified animal binder. Adhesive' strength, as well as mechanism, can be analyzed in the light of fracture morphology. The fracture morphology of before and after animal glue adhesive sand modified is shown in Figure 5 (a) and (b).
As shown in Figure 5, this is a kind of damage occurred in the inner layer, the fracture were in the bond bridge between sand, happening in the adhesive layer, there were still a layer of adhesive film on the sand surface, which further illustrated the internal fracture occurred in the bonding layer, the fracture morphology was the cohesive failure, due to the reason that active groups in the animal glue binder were more before modification, the combining power among the binder and sand surface were dropping. Some cohesive fracture occurred, the binder cannot give full play to the role of the binder; From Figure 6 we can see that the fracture morphology, a part of the sand surface exposed, at the same time certain adhesive film existed, which illustrated it not only has cohesive failure but also attached mixture damage. It showed that the adhesive power of binder and sand surface are awesome while adhesive of sand is strong enough. According to the destroyed form, we can determine the means and directions of improving interface strength; interface strength can be improved by increasing the cohesive strength of the binder when the failure owed to cohesive failure.

SUMMARY

(1) Alcohol modified animal glue binder, through the sand compressive strength test, glycerol and ethanol are the optimum modifiers.

(2) Through the infrared spectrum of the product characterization, the modified animal glue binder not only exists acylamino groups but also has obvious carboxylate stretching vibration absorption peak, which shows that modified animal glue undergo carboxyl esterification reaction.

(3) By analysis of scanning electron microscopy (SEM) on sand bonded bridge fractography, the sticky conjunctival fracture between modified binder and sand surface is a mixed fracture.

REFERENCES