Hygroscopicity-resistant mechanism of an \( \alpha \)-starch based composite binder for dry sand molds and cores

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Abstract: Hygroscopicity-resistance of an \( \alpha \)-starch based composite binder for dry sand molds (cores) has been studied experimentally and theoretically. Focus is placed on the relationship between the hardening structure and humidity-resistance of the composite binder. The results show that the \( \alpha \)-starch composite binder has good humidity-resistance due to its special complex structure. SEM observations illustrate that the composite binder consists of reticular matrix and a ball- or lump-shaped reinforcement phase, and the specific property of the binding membrane with heterogeneous structure is affected by humidity to a small extent. Based on the analyses on the interplays of different ingredients in the binder at hardening, the structure model and hygroscopicity-resistant mechanisms of the hardening composite binder were further proposed. Moreover, the reasons for good humidity-resistance of the composite binder bonded sand are well explained by the humidity-resistant mechanisms.

Keywords: \( \alpha \)-starch based composite binder; hygroscopicity-resistant mechanisms; heat hardening

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1. Introduction

Synthetic resin is regarded as a development trend in the foundry industry because of its high dry strength, excellent collapsibility and surface finishes for castings. Furan resin is one of the most common synthetic resins. However, it is limited applications in sand foundries \(^1\)-\(^6\). This is because that the furan resin bonded sand has some disadvantages such as high cost, low ductility, possible subcutaneous blowholes and serious environmental pollution and so on. Starch binders do not have the above-mentioned shortcomings, but their low specific bonding strength and poor hygroscopicity-resistance due to the molecular structure makes it difficult to be used as a main binder (when starch is the main component in binder) for molding or core-making \(^7\). In other words, a starch must be modified by physical or chemical methods to improve its structure and binding property in applications to foundry as a main binder.

\( \alpha \)-starch based composite binders \(^8\)-\(^10\) developed by the authors in earlier stage can be regarded as a main starch binder for foundry. The composite binder is mainly composed of \( \alpha \)-starch, bond clay, dextrin, sodium silicate, phosphate and appropriate moisture. And the composite binder bonded sand has an excellent combination of properties such as higher strength, better humidity-resistance, etc. In addition, it also has unique characteristics of no-pollution and self-curing \(^11\) at green state as well as many side usages. All these are related to the structure formed by the composite binder according to different binding and hardening mechanisms at different temperatures.

The interactions of various ingredients in the composite binder at green and dry states were analyzed by several combined test methods; the binding and self-curing characteristics of the composite binder at green state have been published earlier \(^11\)-\(^13\). However, the hygroscopicity-resistance of the composite binder has not been reported.

In this work, the humidity-resistance, the structure of the heat-hardened binder at 160~200 °C for one hour, and the relationship between the two were investigated. Further investigations were carried out to develop a binding structure model for this composite binder at dry state. The hardening and humidity-resistant mechanisms of the binder were also proposed.

2. Experimental method

The research work in this project was divided into two sections. The effects of different factors on the hygroscopicity strengths of the composite binder bonded sand were experimentally studied and analyzed in the first section. The second section addressed the special structure and
The hygroscopicity-resistance of the heat hardening binder without sand or with a sand base and the relationship between the two.

2.1 The hygroscopicity-resistance of α-starch based composite binder

The hygroscopicity-resistance of the α-starch based composite binder can be expressed in a hygroscopic coefficient of the composite binder bonded sand. The hygroscopic coefficient means the ratio of the lost strength after a given retention time under the condition of higher relative humidity (RH) and the strength before moisture absorption. The smaller the hygroscopic coefficient is, the better the hygroscopicity-resistance is.

2.2 Preparation and characterization of samples used in the experiment

Standard dog bone sand samples were prepared by the ingredients and procedures given in another paper [9] and were heated to 160~200°C for one hour. The preparation and treatment of the composite binder samples without sand were described in an earlier publication [13].

Dry tensile strengths of the sand samples were determined with an universal sand strength testing machine. SEM observations on the fracture surfaces of the sand samples under different humidities and the structure of the heat hardening composite binder without sand were carried out on a JEOL JSM-35CF scanning electron microscope.

3. Results and discussion

3.1 The effects of different factors on the humidity-resistance of α-starch based composite binder bonded sand

Dry tensile strength to retention time relationships at different RH for the α-starch based composite binder bonded sand are shown in Table 1. Under the condition of different α-starch contents, the retention strengths of the composite binder bonded molding sand decrease with the lengthening of the retention time under different humidities; besides, the greater the humidity is, the greater the ratio of the strength decrement is (i.e. the hygroscopic coefficient); but the strength decrements after 72 h retention under different humidities tend to be stable and the hygroscopic coefficient of the composite binder is similar to that of furan resin [9] even under 90% of high relative humidity conditions.

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>α-starch (%)</th>
<th>$\sigma_0$ [MPa]</th>
<th>$\delta_{24}$ [MPa]</th>
<th>$\sigma_{24}$ [MPa]</th>
<th>$\delta_{48}$ [MPa]</th>
<th>$\sigma_{48}$ [MPa]</th>
<th>$\delta_{72}$ [MPa]</th>
<th>$\sigma_{72}$ [MPa]</th>
<th>$\sigma_{96}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH=75%</td>
<td>2.5</td>
<td>1.36</td>
<td>1.06</td>
<td>0.78</td>
<td>0.71</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.20</td>
<td>0.81</td>
<td>0.56</td>
<td>0.51</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RH=90%</td>
<td>2.5</td>
<td>1.36</td>
<td>0.65</td>
<td>0.50</td>
<td>0.42</td>
<td>0.40</td>
<td>1.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.20</td>
<td>0.46</td>
<td>0.34</td>
<td>0.26</td>
<td>0.16</td>
<td>(86.7)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: (1) The contents of other ingredients in the composite binder keep unchanged except α-starch;
(2) $\sigma_0$ immediate dry tensile strength of sand samples heated to 160~200 °C for 1 h; $\sigma_{24}$, $\sigma_{48}$, $\sigma_{72}$ and $\sigma_{96}$ tensile strengths of dry sand samples after 24 h, 48 h, 72 h and 96 h retention separately under the condition of different humidities and a-starch contents; $\sigma_{96}$ immediate dry tensile strength of sand samples re-dried after 72 h retention under RH 90% conditions;
(3) $\delta_{24}$, $\delta_{48}$, $\delta_{72}$ and $\delta_{96}$ hygroscopic coefficients of dry sand samples after 24 h, 48 h, 72 h and 96 h retention respectively under different conditions.

As noted above, the α-starch based composite binder demonstrated better hygroscopicity-resistance, and the hygroscopicity of the composite binder is characterized by reversibility. On the other hand, the humidity-resistance of the a-starch based composite binder is mainly influenced by humidity. Although increased amount of a-starch can lead to poor humidity-resistance, it is believed that the real reason for poor humidity-resistance is the improper ratio of different ingredients in the composite binder.

3.2 The relationship between the structure and humidity-resistance of the heat hardening a-starch based composite binder

Fig.1 shows the special structure of the composite binder hardened at 180 °C. The microstructure of the a-starch composite binder is a heterogeneous system. The matrix has a reticular structure formed by the reactions.
of sodium silicate and phosphate with mixed starch respectively. This opaque structure, similar to that of the starch macromolecule, can be only seen in a super-thin structure. And the reinforcement phase in the form of a "ball" or "lump" is composed of kaolin particles or their aggregates adsorbed in the matrix. It is reasonable to conclude that the special structure of the composite binder has the effects of raising strength and improving humidity-resistance. Fig.2 shows the SEM micrographs of the sand samples after 72 h retention under different humidities.

It can be seen that the cohesive split appeared on the fracture surface of the sample at 75% of relative humidity. This is because that a stronger valence electron pairing bond \(^\text{[14]}\) is formed between the binder and silica sand; and its bonding energy is greater than the cohesion of the composite binder itself. Unlike the previous condition, the fracture of the sand sample at 90% of relative humidity is a compound split. It is also found that retention strengths of sand samples at 90% of relative humidity decreased slightly (0.65 MPa to 0.42 MPa) as compared to that of sand samples at 75% of relative humidity \(^\text{[9]}\). This shows that the reticular structure of the composite binder and the polar linkage formed between the composite binder and silica sand make water molecules hardly spread to the binding interface and interior of the composite binder, thus, resulting in an increase of the dry strength and hygroscopicity-resistance of the composite binder.

3.3 The hardening and hygroscopicity-resistant mechanisms of the composite binder at dry state

From the above mentioned, it is thought that good humidity-resistance of the composite binder can be attributed to its dense structure. The humidity-resistant mechanisms of the composite binder were proposed by using the structure \(^\text{[15,16]}\) of starch macromolecule for reference. Starch particles are composed of amylose and amyllopectin which arrange in the form of radiation from the centre according to certain regulations. A few amylose molecules disperse in amyllopectin ones, while the great majority of amyllopectin molecules take the shape of bushy structure (colloid bundle) formed by parallel arrangement of many dendritic branches. The size of the colloid bundles and the distance between them are definite. They make up the crystalline region of starch macromolecule. Although the configuration of amyllopectin molecule in water is affected by branch structure and complex molecular interplays, the configuration of its crystalline region is the same as amylose one, namely, in the form of double helix as shown in Fig.3. The crystalline parts take the shape of bundles and the colloid bundles are linked by noncrystalline parts of glucose chains. The layer structure of starch particles is formed by the crystalline and noncrystalline parts together.

On the basis of the structure of starch macromolecules and the interplays \(^\text{[11,10]}\) of different ingredients in the a-starch based composite binder at dry state, the structure of the composite binder was analyzed. The glucose chain in starch particles with layer structure and starch-silicic acid ester as well as starch-phosphoric acid ester, the latter...
two were produced by the reactions of sodium silicate polymer and phosphate with starch, respectively, and cross-linked by branch points one another and formed the matrix with network structure. And bond clay grains or their aggregates as a strengthening phase were well distributed in the matrix. Moreover, there was stronger polar adsorption existing between the reinforcement phase and the matrix. The special structure of the heat hardening composite binder is shown in Fig.4.

![Fig.3 Double helix configuration of starch](image)

Fig.3 Double helix configuration of starch

![Fig.4 Structure diagram of the heat hardening α-starch composite binder](image)

Fig.4 Structure diagram of the heat hardening α-starch composite binder

It is clear that the special structure of the composite binder has higher dry strength and is hard to be deformed etc. In addition, it also has better hygroscopicity-resistance because the surfaces of bond clay particles are surrounded by the reticular structure, forming big stereoscopic obstacles and thus making it difficult for water molecules to get into starch molecular chains and bond clay grains.

4. Conclusions

(1) The dry molding sand bonded by an α-starch based composite binder has good humidity-resistance, which is similar to that of furan resin bonded sand, after long time retention under high relative humidity conditions. Moreover, the composite binder is characterized by other advantages such as low cost, no pollution, high dry strengths and recoverable hygroscopic properties.

(2) Good hygroscopicity-resistance of the composite binder bonded sand is due to its heterogeneous special structure and the valence electron pairing bonds formed between the binder and silica sand.

(3) Based on the analyses on the interactions of different ingredients in the composite binder at dry state (160~200 °C) and the structure observations of the heat hardening binder, the structure model and hygroscopicity-resistant mechanisms of the heat hardening binder were proposed. The mechanisms on the relationship between the humidity-resistance and the special structure of the composite binder can not only explain why the binder has good humidity-resistance, but also provide theoretical guidance for preparation of new humidity-resistant binders.

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References


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