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Study on Binder System of CO_2 Cured Phenol-Formaldehyde Resin Used in Foundry

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ABSTRACT

An aqueous alkaline resol phenol-formaldehyde resin was prepared from phenol and formaldehyde using NaOH as catalyst; we have got the optimum synthetic process finally. After passing carbon dioxide gas through the resin sand, the high as-gassed strength and strength after 4 h and 24 h can be achieved by adding some cross-linking agents. The behavior of bonding bridge fracture has been analyzed by SEM.

Keywords: cold-box, phenol-formaldehyde resin, chemical synthesis.

1. INTRODUCTION

The cold-box process is a technology which can make cores rapidly by blowing a gaseous catalysts into box to cure the sand under the room temperature, such as tertiary amine set process, SO_2 - set process, β - set process etc. The cold- box process has many advantages, such as it is efficient in core-making, the core boxes need not to be heated to high temperature and can be used for a longer time, it is very beneficial to save energy in the production, etc. As a fine process with a bright future, it specially suits to make cores in large quantity.

But the poisonous and harmful gaseous catalysts used in the conventional cold-box process as catalyst or hardeners makes the application of the processes suffered restrict strictly. Therefore, it is necessary to develop a new cold box process with harmless gas to human body and environment [1].

The CO_2 cured phenol-formaldehyde resin system is developed to be match the requirement of casting quality and environmental protection with very desirable prospect, for example, ECOLOTEC 2000- a water-soluble phenol-formaldehyde resin from the Foseco company of England in 1989, is a best binder material from viewpoint of the ecology (ECOLOGY) and technique (TECHNOLOGY) in 21 century. It is so good in technical performance that has got extensively attention from many domestic and international scholars these years; the research in this respect has increased progressively [2–4].

The binder which can be cured by carbon dioxide gas consists of an alkaline aqueous solution of a resol phenol-formaldehyde resin and an oxyanion capable of forming a stable complex with the resin under low alkaline conditions. While passing carbon dioxide gas through the sands, a stable complex with the resin can be form and thereby resin is hardened.

The strength of above-mentioned binder is lower than the traditional cold box processes; it leads to higher addition level of the binder and high core-making cost, hence restricting widely application of the process in foundry.

Researching a new phenol formaldehyde resin binder systems which can react with carbon dioxide gas and gel rapidly to set up the higher initial strength and final strength is the key of this process for the extensive use. The main component of the binder is the phenol formaldehyde resin which synthetic process has been studied at first in this paper, the synthetic process parameters of the resin was optimized using orthogonal experiment. On the basis of appropriate amount of cross-linking agent borax and of dispersant alkali, through adding a certain amount organic active agents, higher strength can be obtained after passing carbon dioxide gas through the sand mix.

2. THE MATERIALS AND THE METHOD USED IN THE TEST

2.1 Main materials in the test

The main materials include phenol, formaldehyde, borax, sodium- hydroxide, potassium-hydroxide, lithium-hydroxide, silane, etc.

The test apparatus includes an ordinary device for synthesizing, a viscosimeter (∅4 mm), a machine for the sample's making, a rotermeter, a SWY strength testing machine of sand, SEM, etc.

2.2 The synthetic process of resin

Process A, the process of charging formaldehyde directly:

Charge the phenol, formaldehyde and alkaline catalyst which have been weighed and heated to 65° slowly, then the resin was cooled to counteract exothermic reaction and maintain at 65° for 1.5 h, then heated to 85° in about 10 min, finally maintain at 85° for certain time.

Process B, the process of charging formaldehyde by dropping:

Charge the phenol and alkaline catalyst which have been weighed and heated to 65° slowly, then added formaldehyde by dropping for 0.5 h, maintain at 65° for 1 h, then heated to 85° in about 10 min, finally maintain at 85° for certain time.

2.3 The preparation of sand sample

At first 1 000 g of standard sand was mixed with 30 g binder for 2 min, then about 165 g of the sand mixture was used to prepare ∅50 mm × 50 mm sand samples in the sample barrels, the samples were hardened by the passage of carbon dioxide gas with a certain velocity and volume for a certain time, finally the samples of sand are taken out from the barrels to get ready for test.

2.4 The measurement of the compressive strength of sand samples

The compressive strength of sand samples is tested as main parameter, the initial strength (σ_0) of compression strength is measured immediately after gassing, and the strength of 4 h later (σ_4) and final strength (σ_{24}) is measured after 4 h and 24 h respectively.

3. THE TEST RESULT AND DISCUSSION

Different synthetical process of the resin (synthetical time, concentration, catalyst, temperature, etc.) and the molar ratio of raw materials all have great influence on the performance of the resin. So the synthesis process and the molar ratio of raw materials were researched at first.

For the synthetic process of the resin, reacting at low temperature is helpful to form large quantities of hydroxymethyl groups, reacting at high temperature is mainly polycondensation, in order to get better molecular weight distribution, the terminal of reaction should be controlled accurately.

3.1 The selection and analysis on the parameters of chemical synthesis

3.1.1 The influence of different catalyst on the resin properties

The $Ca(OH)_2$, $LiOH{\cdot}H_2O$, KOH, NaOH are used as catalyst to make contrast test in the synthesis of alkaline phenol formaldehyde resin, the results obtained are tabulated in Table 1.

The results from Table 1 show that, under the same synthetic process, the strength of the synthetic resin using NaOH as the catalyst is better, though KOH usually acts as catalyst in all kinds of resin; however NaOH is preferred as the catalyst in this test. The synthetic process is relatively steady and the activity of reaction is moderate.

3.1.2 The influence of molar ratio of phenol to formaldehyde on the resin properties

The molar ratio of phenol to formaldehydes in the resin is 1:2.3, 1:2.5, and 1:3.0 and the result obtained is shown in Table 2.

As shown in Table 2, in the synthetic process of the alkaline phenol formaldehyde resin, when the molar ratio of phenol

Table 1

Influence of different catalyst on the strength of the resin properties

Catalyst	Viscosity(s)	σ_0(MPa)	σ_4(MPa)	σ_{24}(MPa)
$Ca(OH)_2$	25	0.98	1.25	1.67
$LiOH{\cdot}H_2O$	25	1.19	1.55	1.81
KOH	25	1.32	1.70	2.01
NaOH	25	1.45	1.85	2.25

Table 2

Influence of mol-ratio of phenol to formaldehyde on the resin properties

Test number	Molar ratio	Viscosity (s)	Catalyst	σ_0(MPa)	σ_4(MPa)	σ_{24}(Mpa)
1	1:2.3	100	NaOH	1.02	1.42	1.87
2	1:2.3	50	NaOH	1.10	1.70	1.78
3	1:2.3	30	NaOH	1.48	2.25	2.39
4	1:2.5	50	NaOH	1.65	2.12	2.21
5	1:2.5	30	NaOH	1.59	2.16	2.20
6	1:2.5	25	NaOH	1.62	2.32	2.48
7	1:3.0	50	NaOH	0.93	1.20	1.07
8	1:3.0	30	NaOH	1.27	1.30	1.58
9	1:3.0	23	NaOH	1.52	1.62	1.82

Table 3

Influence of adding manner of the formaldehyde on the resin properties

Test number	Process	Viscosity(s)	σ_0(MPa)	σ_4(MPa)	σ_{24}(MPa)
1	A	50	1.65	2.12	2.21
2	A	30	1.59	2.20	2.20
3	A	25	1.62	2.32	2.48
4	b	50	1.68	2.18	2.31
5	b	30	1.70	2.26	2.57
6	b	25	1.75	2.38	2.60

to formaldehyde is in the range of 1:2.5, the strength of the resin is higher; hence the molar ratio (1:2.5) of phenol to formaldehyde is preferable.

3.1.3 The influence of adding manner of the formaldehyde on the resin properties

As noted previously, in process A, formaldehyde is added directly; in process B, formaldehyde is added by dropping. The contrast test result of both adding manner of formaldehyde in resin synthesis is shown in Table 3.

It can be found out from Table 3: with different manner of adding, the strength of the resin has some differences, the formaldehyde added by dropping is better. It can raise the content of hydroxymethyl and increase the reactivity of methyl phenol formaldehyde resin to improve the strength of the resin.

3.1.4 The influence of reacting time at high temperature in the synthesis

Polycondensation reaction mainly occurs at high temperature, in order to obtain the better resin properties; the reaction temperature of 85 is used in the test and keeps the reaction at this temperature for a certain period of time. According to the data analysis of experiment, the resin viscosity should be controlled to about 25 s, the resin viscosity depends on the reaction time, and generally the time is preferably about 120 min.

As shown in Table 4, the strength of resin is reduced to some extent with an increase of reacting time. In the actual test, the reacting time can be controlled flexibly according to the viscosity of the resin. With the increase of reacting time, the molecular weight of resin increases meanwhile and the polycondensation reaction speed will be faster and faster, so the terminal of reaction should be controlled accurately in order to prevent polymerizing violently of the resin.

3.2 The influence of organic active agents on the binder properties

In the tests, the proper cross-linking agent borax and dispersant agent of K0H have been introduced into the resin to get certain strength of binder. In order to further improve the strength of binder to meet the request of foundry production, many kinds of organic additive agents are tried to add in the binder directly to find effective ones. Finally, the silane and two kinds of organic active agents are more efficient when introduced in the binder.

3.2.1 The influence of silane on the resin properties

The silane of KH-550 is used, which can improve the combination between phenol formaldehyde resin and the grains of silica sand to increase the bonding strength. The influence of silane's addition on the bonding strength is shown in Table 5 and the optimum addition is 1% by weight of the binder.

3.2.2 The influence of organic active agents on the strength of binder

It is known that, after some organic active agents have been added into the resin, the strength and surface stability of binder is increased and the flowability of sand is also improved.

Table 4

Influence of reacting time at high temperature on strength and viscosity of the resin

Test number	Reacting time (min)	Viscosity (s)	σ_0 (MPa)	σ_4 (MPa)	σ_{24} (MPa)
1	90	23	1.40	1.58	1.95
2	100	25	1.63	1.86	2.32
3	120	30	1.52	1.78	2.24
4	130	45	1.65	1.69	2.12

Two kinds organic additives designated as coded A and B agent are introduced into the binder to improve the strength of binder and the marked effect is obtained. A-agent is an organic solvent and B-agent is an organic compound of ether.

Finally, the addition level of A-agent is about 5% by the weight of binder.

According to the results, the adding amount of B-agent corresponding good final strength (σ_{24}) and initial strength is above 30% and 15% respectively, but 15% B-agent by the weight of binder is introduced from the standpoint of production cost.

3.3 The analysis on the function of organic active agent to the binder

The organic active agents can improve the strength of the resin obviously; the behavior of bonding bridge fracture is analyzed using SEM.

Fig.1: The micro-fracture pattern of the bonding bridge with no addition of the organic active agent. σ_0=0.45 MPa, σ_{24}=1.30 MPa, the strength of binder is relatively low. The fracture of bonding bridge is relatively smooth with many

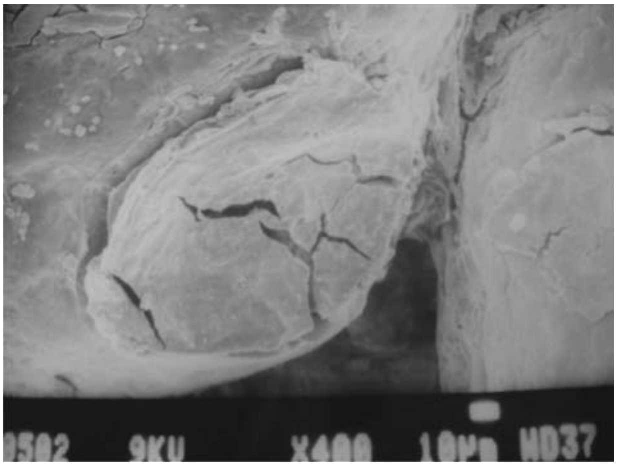

Fig. 1 : The electron microscopic photo ×400 multiple

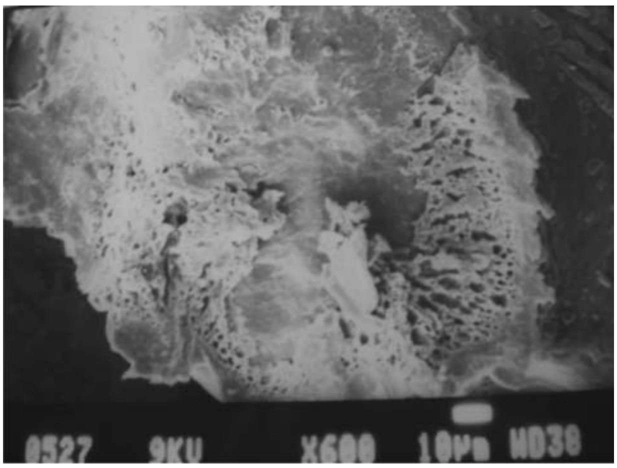

Fig. 2 : The electron microscopic photo ×600 multiple

Table 5

Influence of silane on the bonding strength of resin

addition %	σ_0(MPa)	σ_4(MPa)	σ_{24}(MPa)
0	0.76	1.18	1.62
0.50	0.85	1.10	1.88
0.75	1.08	1.42	2.25
1.0	1.25	1.66	2.65
2.0	1.15	1.65	2.10

Table 6

Influence of A-agent on the strength of binder

Content %	σ_0(MPa)	σ_4(MPa)	σ_{24}(MPa)
0	0.75	1.00	1.35
3%	0.82	1.16	1.68
5%	1.10	1.35	1.98
7%	0.78	1.09	1.50
9%	0.86	1.25	1.78
12%	1.15	1.60	2.23

Table 7

Influence of B-agent on the strength of binder

Content %	σ_0(MPa)	σ_4(MPa)	σ_{24}(MPa)
0	0.98	1.21	1.68
5%	1.35	1.58	2.38
10%	1.66	1.95	2.80
15%	1.79	2.18	3.07
20%	1.50	2.37	3.32
30%	1.65	2.50	3.50
35%	1.48	2.63	4.05

cracks across which occur during the dehydration of the binder. The shrinkage of the gel influences the bonding strength naturally in the course of cross-linking.

Fig.2: The micro-fracture pattern of bonding bridge with an addition of 5% A-agent, 15% B-agent added in the binder. σ_0=2.16 MPa, σ_{24}=3.7 MPa, the strength of binder is increased greatly. The fracture mode of the bonding bridge is the typical cohesive fracture with no crack and the bonding bridge turns into an intricate form, just like a peony.

It is obvious that the fracture pattern of the bonding bridge had changed obviously after the organic active agents are added. The organic active agents are believed to play an important role in cross-linking of resin and have great promotion to the strength increment of binder.

4. CONCLUSIONS

1. NaOH is used as catalyst and the mol ratio of phenol to formaldehyde is 1:2.5 in synthesis of resin with formaldehyde added by means of dropping.
2. The viscosity should be controlled to about 25 s; the reaction time at 85! is about 120 min.
3. The binder with 1% Silane, 5% A-agent and 15% B-agent can achieve a satisfied strength.
4. The organic active agents are analyzed to play a role of cross-linking mainly in the binder.

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