

Synthesis and Application of Modified Starch as a Shell–Core Main Adhesive in a Foundry

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ABSTRACT: To be used as an alternative adhesive for sand cores in a foundry, a solid water-soluble modified starch [carboxymethyl starch (CMS)] was synthesized by a new dry reaction process. With this process, a series of CMS products was obtained with degrees of substitution (DSs) ranging from 0.25 to 0.78 at a high reaction efficiency and characterized with regard to their molecular structure and aqueous solution viscosity. On the basis of the dry synthesis of CMS, the properties of CMS-bonded shell–core sand were investigated, and practical production experiments were carried out. The results show that there was a new sharp peak in the infrared spectrum that represented the carboxymethyl groups and formation of CMS. The viscosity of the CMS aqueous solution increased with increasing DS and amount of CMS. When DS was in the range 0.3–0.5 and the

mass fraction was 5–7%, the CMS aqueous solution had a suitable viscosity, which was helpful for the improvement of the properties, such as flowability, permeability, and strength, of the CMS core sand. In addition, a CMS shell–core with an appropriate wall thickness (10–20 mm) for the purpose of obtaining both sufficient strength and permeability could be made with the CMS-bonded core sand and a hot-core-box process. The final pouring results prove that high-quality iron castings with smooth inner cavities could be produced with the CMS-bonded shell–core and that it (namely the CMS-bonded shell–core) could be used as a replacement for the furan resin-bonded sand core. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2893–2900, 2010

Key words: adhesives; silicas; synthesis

INTRODUCTION

Sand casting will still play a leading role in the foundry industry in the future because of its low cost, high efficiency, and convenient reclamation for molding/core sand.^{1–7} To replace the synthetic resin adhesive widely used in foundries, it is necessary to develop a green and environmentally friendly adhesive, such as starch. At present, starch is often used as an additive for molding/core sand because of its low specific bonding strength.⁸ It is believed that the application of starch as a main adhesive (the main component in the adhesive) in foundries must be based on the improvement of its binding structure.

In this study, a carboxy methylation reaction of starch was conducted, and methanol was found to act as a catalyst during the alkalization of starch. A kind of new method, by which carboxymethyl starch

(CMS) was synthesized, was obtained according to the principle of methanol catalytic action. The method is different from other existing synthesis methods of CMS, such as the water solvent method,⁹ solvent method,¹⁰ dry process,¹¹ and semidry process.¹² It is not only applicable to the synthesis of products with a low degree of substitution (DS) but is also superior to other methods in the synthesis of high-DS products. In addition, this process is characterized by easy reclamation and a high yield of reaction product. Here, the DS of CMS is the average number substituted by carboxymethyl groups for hydroxyl groups in each glucose residue. The introduction of carboxymethyl groups in starch molecules can provide starch macromolecules with the inherent performance of carboxymethyl groups, for example, the solubility of CMS in cold water increases along with the increment in the DS value of CMS, and the properties of CMS solution, such as the water absorption, adhesiveness and film-forming characteristics, are changed simultaneously.

To improve the bonding strength of starch-bonded sand, some researchers have studied the blended

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and chemical modification of starch by using additives when mixing sands. Bian et al.¹³ investigated two kinds of sand-mixing processes for β -starch-bonded sand by using various additives and thought that the optimal sand-mixing process could increase the room-temperature strength of β -starch-bonded sand when the amount of the starch was low (about 4 wt % percentage). Yu et al.¹⁴ developed a water-soluble foundry binder from modified potato starch. The binder-bonded sand had a higher drying strength when the amount of the modified starch was 6 wt %, but the high-temperature strength was not satisfactory, and thus, the rodding of cores was used to strengthen the thin-walled and complicated sand core. Nobuo^{15,16} studied the properties of natural starch-bonded core sand with high water contents by a hot-core-box process. The results show that starch migrated into the surface layer of the sample with the evaporation of water, and the surface was stronger than the inside of the sample. The core sand strength was not even, and its high-temperature strength was also lower. We have promoted studies on molding sand using compound starch as the principal adhesive for cast iron and have confirmed in a series of investigations that the properties of the molding/core sand with the compound starch adhesive are excellent in many aspects.^{17,18}

Although the study on starch as the main binder for foundries has made some progress, its low specific bonding strength and large addition amount in foundry sand remained to be improved. The focus of this study was to synthesize CMS with a suitable DS, to study the properties of the starch-bonded shell-core sand by a hot-core-box process and the influencing factors, and to discuss the possibility of CMS adhesive-bonded shell-core sand used for iron castings. The research of the modified CMS used in the shell-core casting is not reported here.

EXPERIMENTAL

Materials

The basic sand, bentonite, and graphite used in this study were obtained from Dalian Heavy Cast Iron Plant, Dalian Heavy Machinery Enterprise Groups, Ltd. (Dalian, China). Native corn starch was purchased from Langfang Starch Co. (Hebei, China). All other chemicals and solvents used in the study were analytical grade.

Synthesis and performance measurements of CMS

First, starch and fragmentlike, solid sodium hydroxide (NaOH) were added to a blender; Then, a small amount of methanol was added to the blender, and mixing agitation was conducted for 1.5 h. Next, a

certain amount of powderlike chloroacetic acid was added to it again, and the reactor was cooled with cold water if necessary. Finally, the aforementioned reacting substances were allowed to react with one another for different times at 50°C according to the DS value of the final product, and the reaction was carried out for 1–5 h. After the reaction was finished, the resulting CMS was purified by filtration and washing with 85% methanol until the filtrate gave a negative response to a silver nitrate solution. The obtained starch was then dried in an oven at 40°C.

The DS of CMS was determined by the incineration method.¹⁹ The apparent viscosities of CMS paste solutions with different concentrations were determined at 25°C with a NDJ-79 rotational viscometer (Shanghai Balance Instrument Factory, Shanghai, China) equipped with a coaxial cylinder cell. Depending on the range of viscosity determined, a number 4 rotor was used, and the speed of the rotor was 6 rpm. Infrared spectrum measurements of native corn starch and CMS were performed on a Nicolet 20DX Fourier transform infrared spectrophotometer (American Nicolet Corp., Madison, WI). Samples of native corn starch and CMS were ground with dried KBr powder. The KBr disk was dried again and subjected to Fourier transform infrared spectrophotometry. Transmittances were recorded at wave numbers between 3900 and 600 cm^{-1} .

Processing property measurements of the CMS-bonded shell-core sand

Preparation of the shell-core sand samples

First, foundry silica sands with 50/100 and 270 meshes were blended into a mixture at a ratio of 8 : 2, and these were used as foundry basic sand. Powdery substances, such as the modified CMS, a small amount of bentonite, graphite, phosphate, and surfactant were well mixed with water, and then, a starch/silica sand slurry was made by the addition of the basic sand. The components, including the basic sand, CMS, bentonite, graphite powder, phosphate, and surfactant, and water in the mushy shell-core sand were in the ratio of 100 : 4.0 : 0.5 : 0.3 : 0.01 : 0.03 : (14–20) correspondingly. The permeability of the hollow core should have been higher than 200 when it was made with the mushy mixture of the starch/silica sand. Therefore, the mushy mixture had to be stirred until a foam was formed to enhance its permeability. A schematic drawing of the stirring device is shown in Figure 1, and the stirring speed and stirring time were 2500 rpm and 90 s, respectively. The ϕ 50 \times 50 mm cylindrical sample was used in the room-temperature experiment, and the ϕ 10 \times 100 mm cylindrical sample was used in the high-temperature test. When the sand core

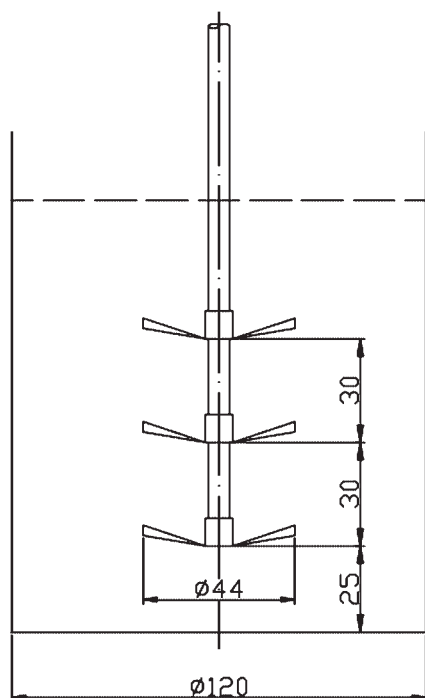


Figure 1 Schematic diagram of the stirring device for the starch and silica sand slurry.

samples for room-temperature testing were made, the hot-core box of 130°C was first filled with the shell-core sand and held for 3–5 min before the core box was opened, and then, the samples were taken out and hardened for about 2 h in the microwave oven of 130°C. The samples for high-temperature testing were retained for about 2 min in the oven after the aforementioned process.

Performance measurements of the CMS-bonded shell-core sand

The property experiments of the CMS-bonded shell-core sand at room temperature and high temperature were carried out with conventional methods based on the standard sample and with the specified process, except the foaming rate.²⁰ The foaming rate was expressed by the increased volume percentage of the shell-core sand after it was stirred for a certain time. The strength properties of the CMS shell-core sand at room temperature and at high temperature were tested on a SWY hydraulic universal strength testing machine (Wuling Shiqiang Casting Instrument Factory, Changde, Hunan, China) and a TKW high-temperature bending-strength tester (Jiangmen Santech Instrument Co., Ltd., Guangdong, China), respectively, whereas its permeability was tested on a STZ direct-reading permeability meter. To obtain quantitative permeability test results, quantifiable room-temperature gas first went through a standard $\phi 50 \times 50$ mm column sand

sample under the condition of constant pressure; the time recorder and pressure gauge were then used to determine the time for the gas to pass through the sample completely and the gas pressure at the front end of the sample separately. The permeability of the molding/core sand thus could be described with eq. (1)

$$K = \frac{Q \times H}{P \times F \times t} \quad (1)$$

where K is the permeability ($\text{cm}^4 \text{g}^{-1} \text{min}^{-1}$), which is generally regarded as a nondimensional value; Q is the gas volume through the sample (cm^3); H is the height of the standard sample (50 mm); P is the gas pressure at the front end of the sample (Pa); F is the cross-sectional area of the sample (mm^2); and t is the time for the gas to go through the sample (min).

RESULTS AND DISCUSSION

Effect of the reaction parameters on DS of CMS

In the substitution reaction of CMS synthesis, the main factors affecting the reaction results included the reaction time, the reaction temperature, and the compounding ratios of chloroacetic acid to starch and alkali to starch separately.²¹ The ratio of chloroacetic acid to starch were first determined according to different demands for DS of CMS. In this experiment, the carboxy methylation reaction of starch was conducted for 4 h at 50°C, and the molar ratio of chloroacetic acid to starch was 1 : 1. The relationship between the amount of NaOH and DS of CMS is shown in Figure 2.

As shown in Figure 2, the final DS increased continuously when the NaOH/CMS ratio changed from 1.0 to 2.0, and then, it began to decrease after the

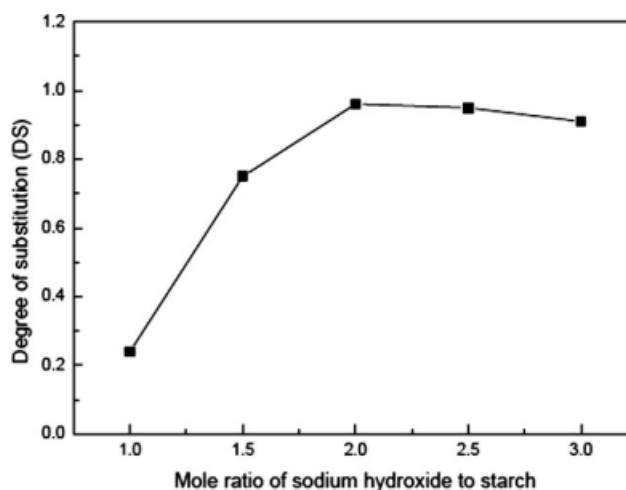


Figure 2 Effect of the NaOH/CMS ratio on the DS of CMS.

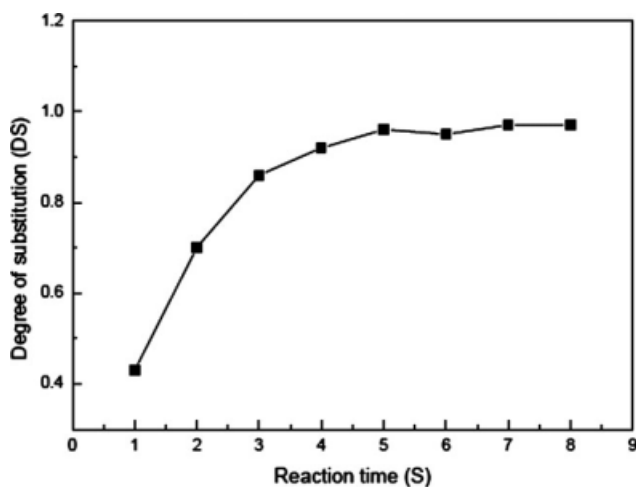


Figure 3 Change in the DS of CMS with the reaction time.

ratio was up to 2.0. This was related to the reaction activation centers formed by the bonding reaction between the NaOH and hydroxyl groups of the starch molecular chain. The activation centers of starch by the alkali treatment increased when the amount of NaOH increased in a certain range; this resulted in a higher chloroacetic acid reaction (the main reaction) rate and a higher DS of CMS. However, when the NaOH/starch ratio was more than a certain limit, an increase in the amount of NaOH also enhanced the hydrolysis (the side reaction) of sodium chloroacetate, which resulted in a lower final DS. The fact that the final DS decreased with an increase in the NaOH/starch ratio was caused by the competition between the main reaction and the side reaction.

The relationship between DS of CMS and the reaction time is shown in Figure 3, when starch, chloroacetic acid, and NaOH were in a molar ratio of 1 : 1 : 2.

As shown in Figure 3, DS increased with the prolongation of reaction time, but it did not increase again after the reaction continued for 5 h. When chloroacetic acid and NaOH were kept in a molar ratio of 1 : 2, DS of CMS increased, but the reaction efficiency decreased with increasing chloroacetic acid amount, and this is shown in Table I. The previous phenomena could be explained from two aspects: (1) on the one hand, when the amount of sodium chloroacetate increased, more sodium chloroacetate molecules around starch molecules were involved in the synthesis reaction of CMS, so the degree of carboxymethylation, DS, and viscosity of CMS all increased, and (2) on the other hand, because the amount of starch was definite, a relatively small number of hydroxyl groups in the starch molecules resulted in decreases in the CMS reactive collision probability and reaction rate with increas-

ing amount of sodium chloroacetate, whereas the increasing side-reaction rate also enhanced the formation of sodium glycolate, which resulted in a lower reaction efficiency. The reaction efficiency (RE) was calculated as follows:

$$RE[\%] = \frac{\text{Amount of bonded } \text{CH}_2\text{COONa}}{\text{Initial amount of } \text{CH}_2\text{COONa}} \times 100 \quad (2)$$

As shown in Table I, the reaction efficiency was usually up to more than 90% when CMS with a DS value lower than 1.0 was synthesized by the new dry method, whereas the reaction efficiency was not up to 80% by the solvent method.²²

The reaction temperature also had an effect on the DS of CMS to some degree, especially when CMS with a high DS was synthesized. The gelatinization temperature for CMS was often lower than for native starch and was a strong function of DS; thus, the reaction was difficult to conduct at high temperatures. To avoid gelatinization and irreversible swelling, a temperature of 50°C was selected as the optimal reaction temperature in this study.

Infrared spectrum and paste viscosity analysis of the native starch and CMS

To confirm the effectiveness of the synthesis, infrared spectrum analyses were conducted for native (unmodified) starch and two types of CMS specimens with different DSs (0.52 and 0.78, respectively) by contrast. The correlation analytical results are shown in Figure 4. Strong absorption peaks for CO_2^- asymmetric and symmetric vibrations occurred near the frequencies 1620 and 1415 cm^{-1} separately in all of the CMS infrared spectrograms. Thus, it was proved that the carboxymethyl group existed in the modified starch.

CMS can be used as a core sand adhesive, and this was related to its paste viscosity. The viscosity usually increases with increasing DS when it was lower than 1.0.²³ The change in the viscosity was not a constant with increasing paste concentration in an ordinary way. The viscosity curves of the CMS samples as a function of paste concentration are shown

TABLE I
Effect of the Amount of Chloroacetic Acid on the DS and Reaction Efficiency

$\text{ClCH}_2\text{CO}_2\text{H}/\text{AGU}$ (mol/mol)	DS	Reaction efficiency (%)
0.4	0.39	97
0.8	0.75	94
1.2	1.06	88
1.4	1.15	85
1.6	1.20	80

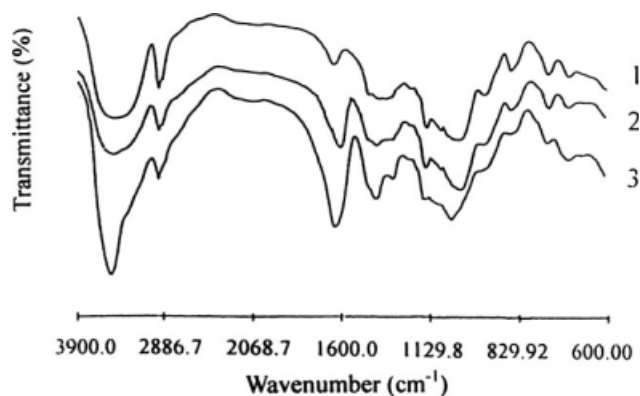


Figure 4 Infrared spectra of the native starch and CMS: (1) native starch, (2) CMS with DS = 0.52, and (3) CMS with DS = 0.78.

in Figure 5. For comparison, the viscosity curve of the native starch versus the concentration is also shown in the figure.

As shown in Figure 5, the viscosity curves of the CMS samples were notably different from that of native starch. Compared with the native starch, the viscosity of the CMS decreased, and the higher the DS was, the lower the decrease in the viscosity was. In addition, the viscosity curve of the CMS was less steep than that of the native starch, which indicated that the viscosity of the CMS did not significantly vary in certain concentration ranges and, thus, the CMS had good dilution resistance. On the basis of these results, we concluded that the key to the application of CMS to foundries lies in the determination of a suitable DS and concentration. When the CMS paste with a suitable DS and concentration is used in foundry core sand, it can ensure both the appropriate thickness of the binding film among sand grains and the easy shaping of the core sand because of good flowability. Meanwhile, this will also be beneficial to the reduction of the performance sensitivity of common starch molding/core sand to moisture content and will increase the bonding strength.¹⁸

Properties of the CMS-bonded shell-core sand

Sand casting is a complex process, and thus, casting sand should have excellent formability, high strength, enough permeability, suitable deformability and collapsibility, good reusability, and so on. Obviously, it is almost impossible for any kind of molding/core sand to have various excellent performances at the same time. There exist some difficulties in the manufacturing of foundry sand cores with complex shapes.²⁰ However, core sand must have a good permeability and fluidity and enough high-strength properties at room and high temperatures. CMS-bonded shell-core sand with relatively more water was mixed according to the given process in

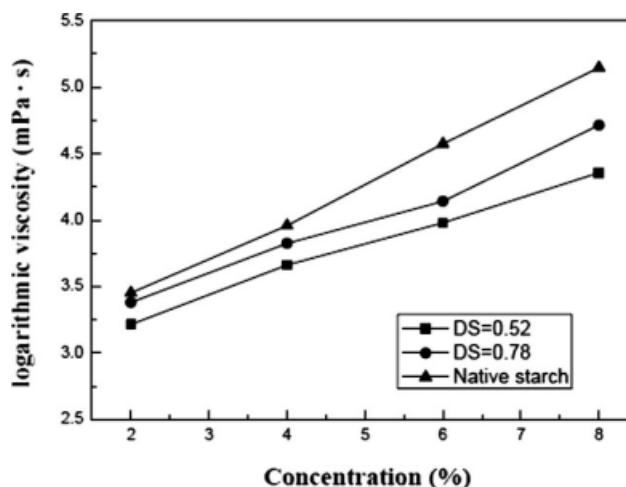


Figure 5 Change in the logarithmic viscosity with the concentration for CMS with different DS values.

this article. Here, CMS products with different DS values were used as shell-core sand adhesives. The CMS-bonded shell-core sand samples were prepared by the hot-core-box method, and the performances of the core sand were measured.

Permeability of the CMS-bonded shell-core sand

Figure 6 shows the relationship between the stirring time, foaming rate, and permeability of the CMS shell-core sand when the added amount of water was 16 wt % and the other components remained unchanged in the core sand. We found that the foaming rate and permeability increased with the prolongation of the stirring time, whereas the trend for the change in the sand core strength was just the opposite.²⁰ When the stirring time was 90 s for the CMS (DS = 0.52)-bonded core sand, the foaming rate and permeability come to nearly 120% and over 200, respectively. Under the aforementioned

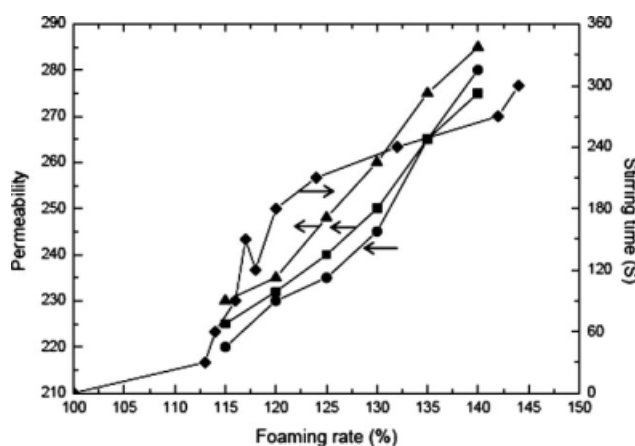


Figure 6 Relationship of the stirring time, foaming rate, and permeability of the CMS core sand: (●) DS = 0.25, (■, ◆) DS = 0.52, and (▲) DS = 0.78.

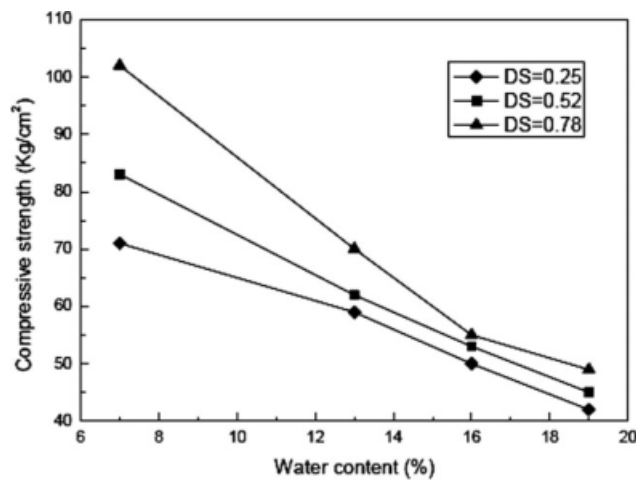


Figure 7 Relationship of the dry strength and water content of the CMS-bonded sand samples.

conditions, the permeability of the shell-core sand could meet the requirements of foundries. In addition, the permeability of the core sand depended on the stirring time of the shell-core sand and was influenced little by DS of CMS under a defined stirring time (90 s).

Room-temperature properties of the CMS-bonded shell-core sand

The change in the compressive strength of the CMS-bonded $\phi 50 \times 50$ mm sand samples after drying with the added amount of water is shown in Figure 7. As shown in the figure, the higher the water addition was, the lower the dry strength was; the dry strength of the sand core decreased with decreasing CMS DS under the same water content conditions. However, the lowest strength of the CMS sand core still met the requirements of the ultimate strength (40 kg/cm²) within the range of the afore-

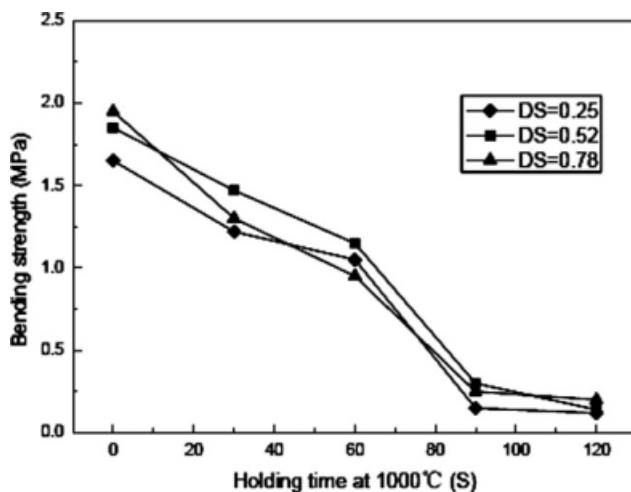


Figure 8 Relationship of the bending strength and holding time of the CMS-bonded sand samples at 1000°C.

mentioned experiment. To make this study convenient and representative, the amount of water added in the CMS shell-core sand was identified as 16 wt %, whereas the other components remained unchanged in the following experiments.

High-temperature properties of the CMS-bonded shell-core sand

It was difficult to measure the true compressive strength of the $\phi 50 \times 50$ mm sand sample because of uneven distribution of starch in the CMS sand core. This uneven distribution phenomenon of starch was attributed to the migration of starch toward the surface of the sand core during sand hardening in the hot-core box.²⁴ However, the migration of starch had little influence on the bending strength of the $\phi 10 \times 100$ mm sand sample. The relationship between the bending strength and holding time of the sand sample at 1000°C when DS of CMS changed from 0.25 to 0.78 is shown in Figure 8. The experimental results indicate that the bending strength of the sand sample at high temperature decreased with increasing holding time, but it changed little with DS of CMS. This was because the strength of the hot-box sand core was influenced by the migrated starch amount, and the latter was related to the heating temperature of the core box.¹⁵ In addition, it was found from the figure that all samples had strengths greater than 0.1 MPa when the holding time was 2 min because of heat-resistant material AlPO₄ formed by reaction of trace additives.²⁵ Because the CMS shell-core sand had a higher high-temperature strength and better permeability when high-temperature molten iron was poured into the casting mold, qualified castings without casting defects (e.g., sand inclusion and gas hole) could be poured out.

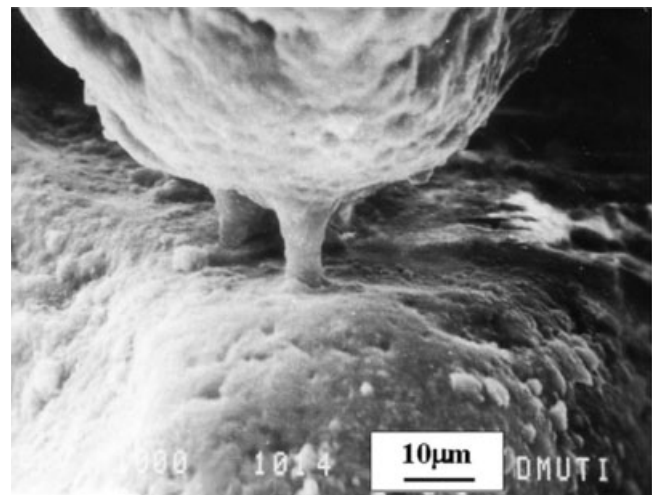


Figure 9 SEM micrograph of the bonding bridge on the surface of the CMS-bonded sand grains.

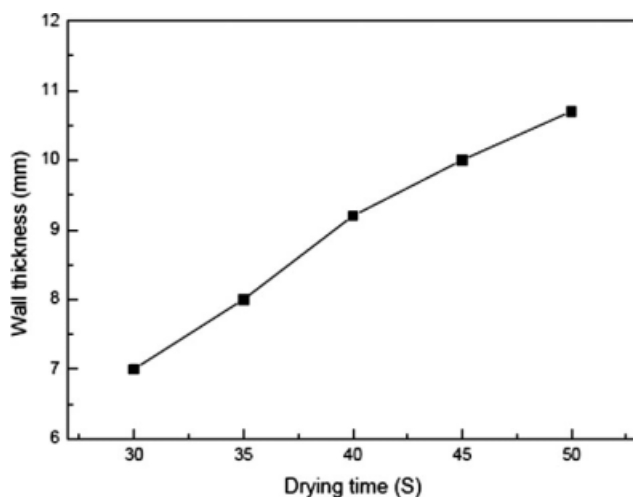


Figure 10 Relationship of the drying time and wall thickness of the CMS-bonded shell-core.

On the whole, CMS-bonded shell-core sand had better combination properties, such as higher gas permeability and strength characteristics. The aforementioned performance characteristics of CMS-bonded sand were related to the following two aspects. On the one hand, a uniform and dense binding membrane structure (see Fig. 9) was formed by the interaction between modified starch and water in shell-core sand at green state. The binding bridge with a larger area among sand grains showed that the binder itself had a high cohesive strength, and the binding film could be coated on the surface of the sand grains evenly. On the other hand, the strength and permeability of CMS shell-core sand were further improved by dehydration hardening when heated. Considering the cost of the CMS product, we think that the properties of the CMS-bonded sand can meet the needs of shell-core making when DS of CMS is in the range 0.3–0.5.

Preparation of the CMS shell-core and its application

As stated previously, the CMS starch and silica sand slurry can fully meet the performance requirements of shell-core sand. The strength in the center of the sand core decreased because of the migration of starch and heat-resistant material from the center to the surface of the shell-core. Moreover, when the core box temperature was in the range 100–200°C and the added amount of water in the core sand was a little higher (14–20%), the higher the temperature is and the more water there is, the greater the migration amount is. So a shell-core with an excellent performance was formed by timely turnover and the vibration of the core box to pour out the unhardened core sand according to the optimized process.

Figure 10 shows the relationship between the holding time of the slurry in the hot-core box of about 130°C and the wall thickness of the shell-core. Under the aforementioned conditions (i.e., 4.0% CMS with DS 0.5, 16% water, other invariant component contents, and a 90 s mixing time), the slurry had to be held for 45 s in the metal core box to get a 10 mm wall thickness of the shell-core. In addition, different wall thicknesses of the shell-cores could be made by the adjustment of the holding time.

The photographs of the finished hollow core and corresponding box casting poured by the shell-core are shown in Figure 11. The box casting was made of QT450-10 and had a weight of 33 kg. The pouring temperature was 1400°C. Pouring experiments showed that high-quality castings with a smooth internal surface, high dimension precision, and no defects could be made with the CMS-bonded shell-core formed in this study.

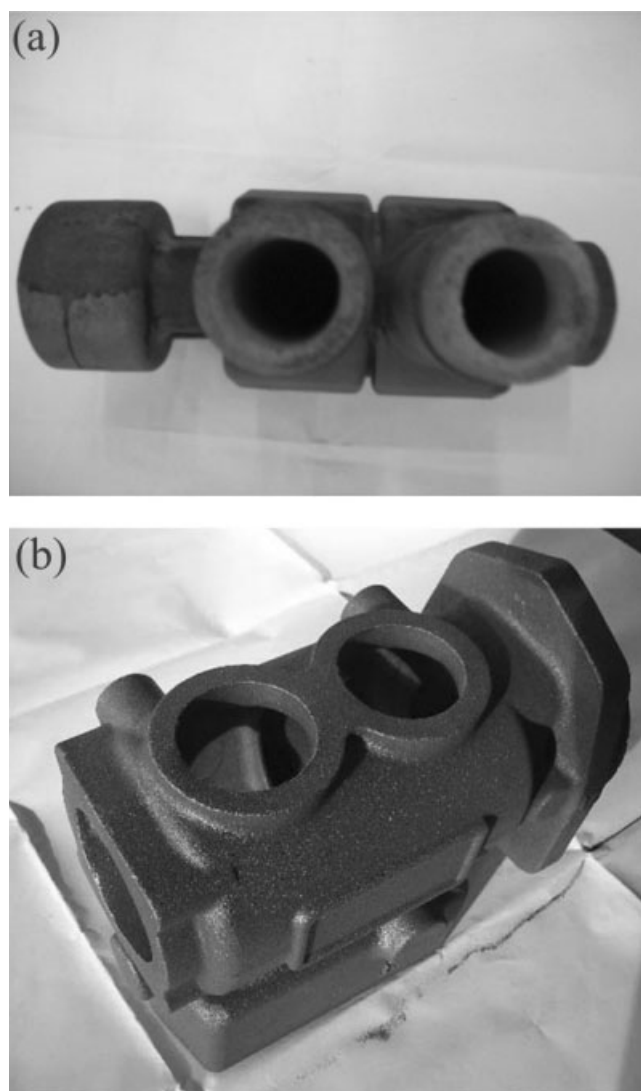


Figure 11 Photographs of (a) the CMS-bonded shell-core and (b) the poured box casting.

CONCLUSIONS

Carboxymethyl corn starches synthesized by a new dry process proved suitable for foundries. This dry method was characterized by having a high reaction efficiency, and the CMS product had a high DS and a wide DS distribution compared with existing synthesis methods of CMS. The high DS and wide DS distribution had a good influence on the characteristics of CMS, such as viscosity, flowability, and specific adhesive strength, whereas these properties are very important to the CMS as a main foundry adhesive. With the CMS and silica sand slurry and the hot-metal core-box method, sand shell-cores with different wall thicknesses were obtained. Under the added amounts of CMS and water and when the thicknesses of the CMS shell-core were definite, the properties of the CMS-bonded shell-cores were highly dependent on DS of CMS. To prepare the CMS-bonded shell-cores with excellent combination properties and lower cost, CMS with a moderate DS value (0.3–0.5) and a CMS-bonded shell-core with a smaller thickness (10 mm) are preferred. Practical pouring experiments of the CMS-bonded shell-core showed that application of the CMS adhesive to a casting shell-core can improve the casting quality, reduce foundry industry pollution, reduce costs, and increase production efficiency. Therefore, the CMS adhesive is feasible and valuable for foundry application.

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