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Composite binders for precision casting shell molds

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Abstract

The convert mold process has been investigated, focusing on preparation of shell molds using different composite binder systems. The glassification efficiency of binder systems with different SiO_2 precursor structures were investigated in terms of the Si content and dipping time, and the subsequent effects on fracture strength. Two types of the SiO_2 precursor were used: tetraethyl orthosilicate of the silicate type; and hexamethyl disiloxane (HMDS), octamethyl trisiloxane, and polydimethyl siloxane of the siloxane type. Use of the siloxane type precursor does not produce a hydrolysis reaction, whereas the silicate type precursor is converted into SiO_2 by a hydrolysis and condensation reactions during the drying process. The samples based on the siloxane type (except HMDS) have a much higher fracture strength, nominal value of 8 MPa, than that of samples based on the silicate type. This is a result of the enhancement of glassification. When the siloxane is added to the silicate the fracture strength is as high as about 6 MPa, independent of the Si content and dipping time. Results indicate the importance of the reaction mechanism in achieving fracture strength with related to glassification efficiency.

Keywords: A. Sol–gel processes; B. Composite; C. Mechanical properties; Shell molds; Microstructure; Precision casting

1. Introduction

The convert mold process has been used to prepare shell molds for precision casting, because of the fast processing time, high thermal and dimensional stability, mechanical properties, and collapsibility of the products [1,2]. These features have lead to its use for precision casting in many different applications, for example in automobile and aerospace. Ethyl silicate and colloidal silica aquasols, combined with sodium alkoxide, are used as conventional binders in the convert mold process [3]. The convert mold process is typically divided into four main processes: (1) fabricating the starting mold coated with organic binder, (2) dipping the coated mold into a precursor slurry containing inorganic binders, (3) drying for 1 h at 80 °C, and (4) heat treating for 1 h at 1000 °C [4,5]. A hydrolysis and condensation reactions (generally called a sol–gel reaction) and glassification take place during the above (3) and (4) processes, respectively. Even though the convert mold process affords improved mold collapsibility and thermal stability compared with the conventional mold process, the hydrolysis reaction of inorganic binder precursor needs the control of atmospheric moisture during the process. The hydrolysis reaction of the silica (SiO_2) precursor leads to a reduction in the conversion efficiency of the precursor to the glass phase, which subsequently results in a deterioration of the mechanical and thermal properties of the mold. Therefore, a new convert mold process in which a solid-state binder is used has been proposed [6].

In the present study, a new binder system, which does not produce the hydrolysis reaction, is proposed to increase the glassification efficiency of inorganic binder precursor. It includes a mixed binder system of the silicate and siloxane types. The effects of the SiO_2 precursor structure and dipping time on the glassification and fracture strength were investigated.

2. Experimental

New binder systems were prepared by mixing two precursors of SiO_2 and sodium oxide (Na_2O). The two types of SiO_2 precursor were a silicate type and a siloxane type. For

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Table 1
The chemical composition and various physical properties of substrate.

Chemical composition (%)		Porosity (%)	Bulk specific gravity	Water absorption (%)
Al_2O_3	60.59	2.2	2.72	0.8
SiO_2	36.44			
Fe_2O_3	1.08			
TiO_2	0.72			
CaO	0.20			
MgO	0.08			
K_2O	0.20			
Na_2O	0.35			
P_2O_5	0.27			
Total	99.93			

the silicate, tetraethyl orthosilicate (TEOS, T_b: 166–169 °C, Sigma–Aldrich Korea, Yongin, Korea), which undergoes the hydrolysis reaction, was used. For the siloxane, hexamethyl disiloxane (HMDS, T_b: 101 °C), octamethyl trisiloxane (OMTS, T_b: 153 °C), and polydimethyl siloxane (PDMS, T_b: 182 °C, Sigma–Aldrich Korea, Yongin, Korea) were used (separately); these do not produce the hydrolysis reaction. Sodium methoxide (NaOMe, Sigma–Aldrich Korea, Yongin, Korea) was used as the precursor of Na_2O. The SiO_2 precursor mixtures were prepared by mixing the silicate and siloxane types, as a function of siloxane species. The sample size used for the substrate was 10 mm × 10 mm × 50 mm (according to Metia Co., Ltd., Changwon, Korea); it was prepared using an organic resin binder. The chemical composition and fundamental physical properties of substrate are shown in Table 1. The samples were dipped into the prepared binder systems for 0.5, 1, and 2 h (separately) at room temperature. Dipped samples were first dried at 80 °C for 1 h, and then heat treated at 1000 °C for 1 h. Basic formulations and the experimental ranges of the binders used for preparing samples, which involved converting the organic binders to inorganic binders, are given in Table 2. The cross-sectional microstructure was revealed using a scanning electron microscope (SEM, JEOL Model JSM-5610, Tokyo, Japan). The fracture strength of samples after the final heat treatment was measured with a universal testing machine (UTM, Instron 5560, Seoul, Korea). Tests were carried out at room temperature, at a rate of 0.5 mm/min. At least five measurements were recorded for each condition in order to obtain the standard deviation of the fracture strength.

3. Results and discussion

The fracture morphologies and surfaces of samples prepared with the different SiO_2 precursors are shown in Fig. 1. All heat-treated samples had white areas, irrespective of the dipping

Table 2
Formulations and experimental ranges of binder systems.

Run number	TEOS (wt%)	HMDS (wt%)	OMTS (wt%)	PDMS (wt%)	NaOMe (wt%)	Isobutyl alcohol (wt%)	Degree of glassification (%)	Dipping time (h)
1–1	38	N/A	N/A	N/A	56	6	6.20	0.5
1–2								1
1–3								2
2–1	N/A	38	N/A	N/A	56	6	3.69	0.5
2–2								1
2–3								2
3–1	N/A	N/A	38	N/A	56	6	15.02	0.5
3–2								1
3–3								2
4–1	N/A	N/A	N/A	38	56	6	20.35	0.5
4–2								1
4–3								2
2–1–1	30.4	7.6	N/A	N/A	56	6	–	0.5
2–2–1								1
2–3–1								2
3–1–2	30.4	N/A	7.6	N/A	56	6	–	0.5
3–2–2								1
3–3–2								2
4–1–2	30.4	N/A	N/A	7.6	56	6	–	0.5
4–2–2								1
4–3–2								2

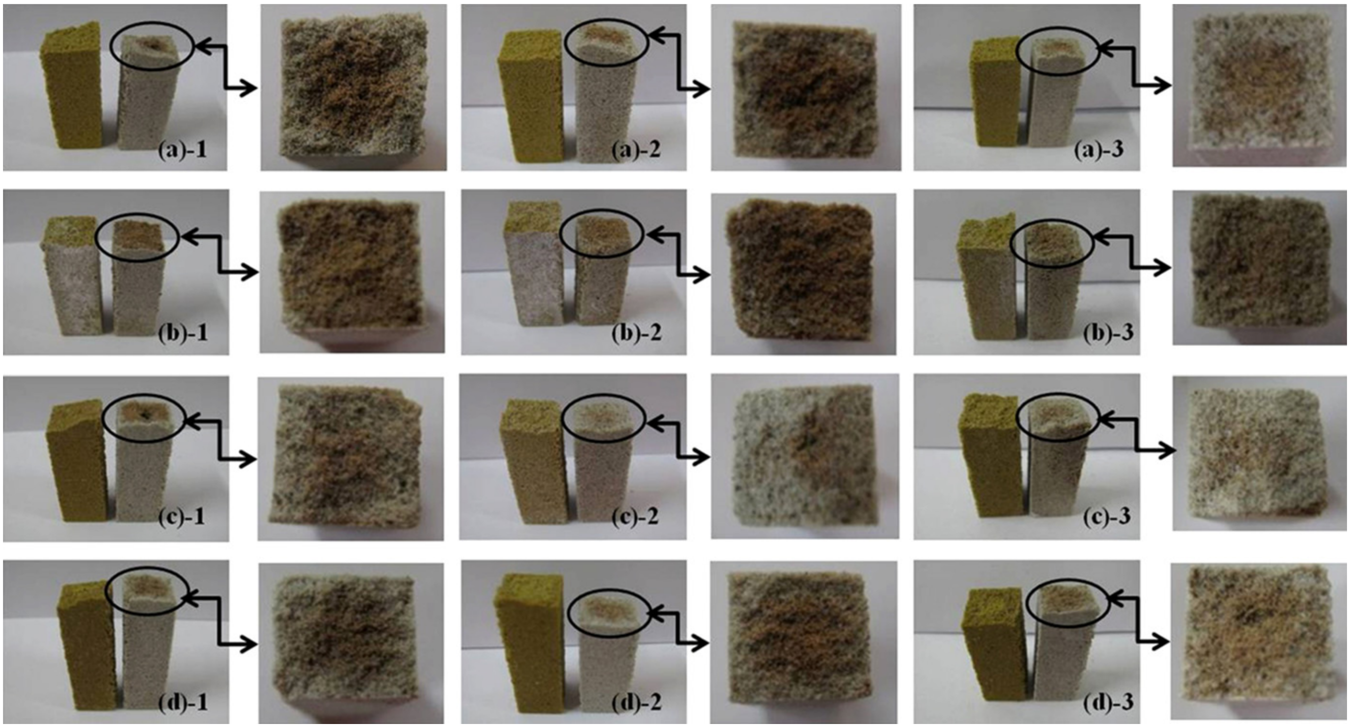

Fig. 1. Fracture surfaces of samples prepared with different SiO_2 precursors: (a) TEOS, (b) HMDS, (c) OMTS, and (d) PDMS. The numbers 1, 2, and 3 indicate dipping times of 30 min, 60 min, and 120 min, respectively. Samples on the left and the right show the sample status before and after heat treatment at 1000 °C, respectively. Arrows indicate magnified images of facture surfaces. The white regions indicate the reaction areas.

time and precursor structure used. Generally, precursors of the transmittance liquid are converted into a white solid during the drying and heat-treatment processes. Namely, white area (reaction area) is the glass phase occurred by reaction of precursors. Therefore, the content of the precursor in the sample is decreased by generation of glass phase during the drying and heat-treatment processes. In particular, the concentration of the precursor decreases rapidly at the surface, showing a high reactivity. Consequently, the surface of sample is more glassified than the inner region, as investigated with EDS analysis in our early work [7]. The samples based on the siloxane (OMTS and PDMS) except in the case of HMDS show a broader reaction area than the sample based on the silicate (TEOS), which means that OMTS and PDMS have a high degree of glassification. However, in the case of HMDS, the reaction area is not definitely distinguished in spite of the siloxane type. This is probably because of the decrease in the glassification efficiency by evaporation of HMDS with relatively low boiling point of 101 °C during the drying process. Glassification efficiencies of various binder systems are represented in Table 2, showing that OMTS and PDMS without hydrolysis reaction have higher glassification efficiency than TEOS with hydrolysis reaction. As above mentioned, HMDS shows the lowest degree of glassification among the others, suggesting the decrease in the fracture strength of sample.

The dependence of the fracture strength values on the dipping time, precursor structure, and precursor composition is shown in Fig. 2. The strength values do not depend on the dipping time, for both conditions (OMTS and PDMS), as indicated in Fig. 1. Samples prepared using OMTS and PDMS have a fracture strength that is about two times higher than that of samples prepared using TEOS, as a result of an increase in glassification. In the case of TEOS, glass phase is formed by reaction between the SiO_2 and sodium hydroxide (NaOH) generated by the hydrolysis reaction of both precursors (TEOS and NaOMe) [8], which will reduce the glassification efficiency and result in the relatively low fracture strength. However, in the case of the siloxane type (OMTS and PDMS), no hydrolysis reaction takes place, indicating better glassification efficiency of precursors. The difference of precursor mixtures with silicate or siloxane types after hydrolysis was measured and proved with IR and XRD analysis in our early work [7,9].

The new binder system that includes OMTS and PDMS (runs 3 and 4 in Table 1) has the highest fracture strength, nominal value of 8 MPa. This implies that the reaction mechanism is an important factor in determining both the fracture strength and the reactivity of the precursor. However, the binder system that includes HMDS has the lowest fracture strength, nominal value of 1 MPa. This is caused by insufficient glassification, because of the high vaporization of HMDS. In an effort to increase the strength of the binder system that exhibits hydrolysis, the SiO_2 precursor mixture was prepared by incorporating the siloxane type into the silicate type. Addition of the siloxane to the silicate resulted in an increase in the strength, to about 6 MPa, independent of the Si content and dipping time, even though the additional amount is only 7.6 wt%. Therefore, the relationship between the reaction mechanism, glassification of the precursor, and fracture strength should be considered when determining the optimum conditions for preparing the binder system in fabricating mold for precision casting.

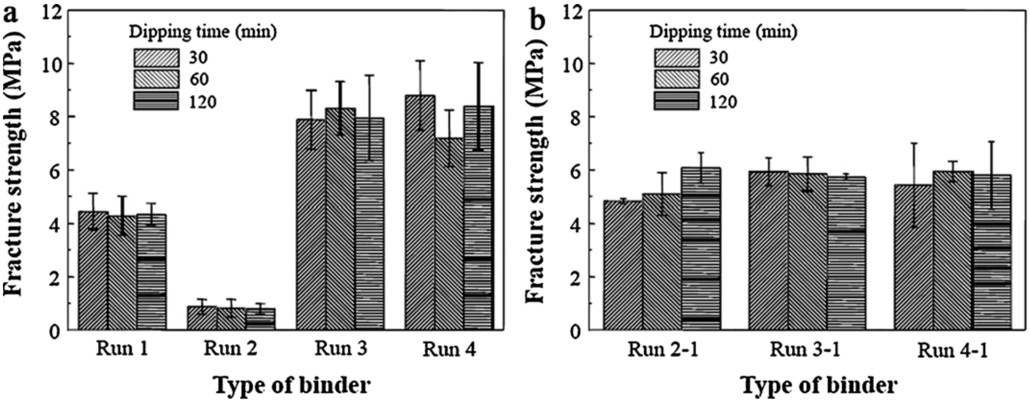

Fig. 2. Fracture strength values of heat-treated samples prepared with different SiO_2 precursors: (a) mono-precursor system and (b) bi-precursor system, using different dipping times.

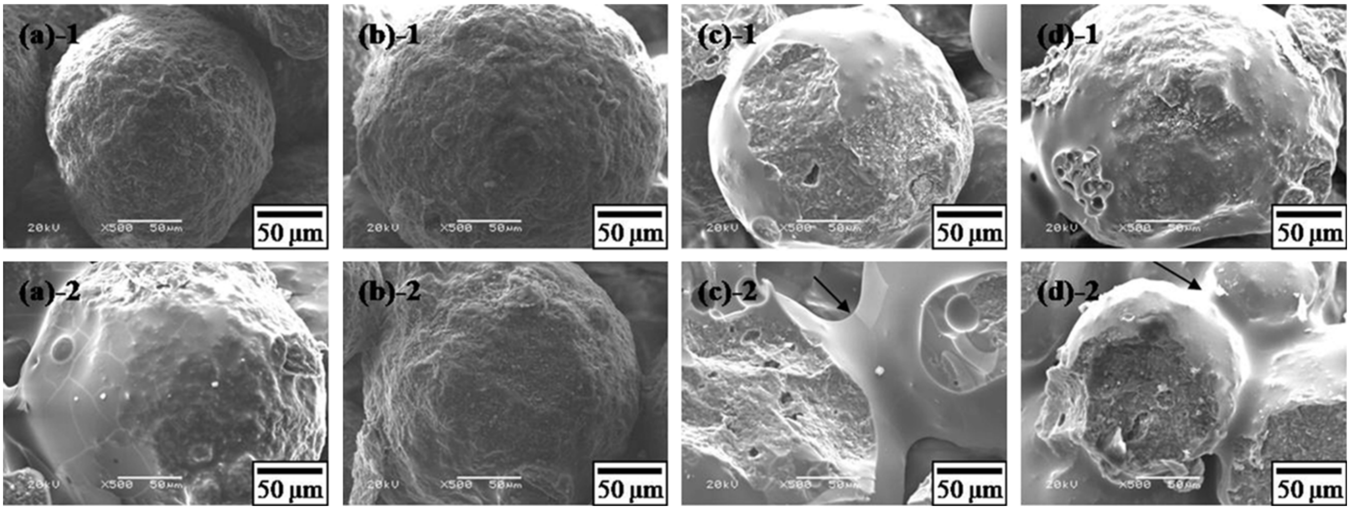

Fig. 3. SEM morphologies of heat-treated samples prepared using different SiO_2 precursors: (a) TEOS, (b) HDMS, (c) OMTS, and (d) PDMS. The numbers 1 and 2 indicate the inner part and the surface of the samples, respectively. Arrows indicate the glass phase formed between particles.

Typical SEM morphologies of samples prepared using the different binder systems, with different precursor structures, at the fracture surface after exposure to bending strength tests are shown in Fig. 3. Generally, prior to heat treatment, many cracks appear at the interface between the particles and the surfaces of the particles, but these cracks disappear after heat treatment because of the formation of the glass phase. In this study, good glassification was achieved at the interface and surface of samples prepared using OMTS and PDMS (indicated with arrows in Fig. 3). However, in the case of HMDS (Fig. 3b), the glass phase is not evident at the interface between the particles, which leads to the low fracture strength. Furthermore, the surface of samples is more glassified than the inner parts because of the high reactivity at the surface and the diffusion of the precursor, as evident in Fig. 1.

4. Conclusions

New binder systems for shell molds have been successfully developed using nonhydrolyzable siloxane type binders, such as OMTS and PDMS, and a binder mixture comprising the silicate and siloxane types. All precursors, except HMDS, showed good reactivity and were readily transformed into glass phase. The fracture strength values of samples prepared using the new binder systems based on OMTS and PDMS were higher than that of the sample prepared using TEOS; they exhibited values of up to 8 MPa. This improvement is ascribed to the enhancement of glassification because of the increase in reactivity of the SiO_2 precursor, in the absence of a hydrolysis reaction. By adding a siloxane type binder to a silicate type, the strength values increased to about 6 MPa, independent of the precursor structure, dipping time, and precursor composition. The fracture strength was only slightly affected by the precursor composition and the dipping time after reaching maximum values in both SiO_2 precursor systems of mono-precursor and bi-precursor. The glass phase at the surface and the interface of the samples based on the siloxane type, except HMDS, was better formed than in the case of samples based on the silicate type, and the surface of the samples showed better glassification compared with the inner part. The glassification efficiency of the precursor is therefore an essential feature in achieving an increase in the facture strength, and this is controlled by the reaction mechanism, which in turn depends on the structure of the precursor.

Acknowledgments

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