The Comparison of Chosen - Bonded with the Use of Classical and Dedicated for 3D Printing Furfuryl Binder - Molding Sands' Properties as a Basis for Development a New Inorganic System

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Abstract

Binder jetting technology (3D printing) in the production of foundry molds and cores is becoming more and more industrially used due to ensuring very good quality of the casting surface. In 3D printing technology as the matrix, quartz sand is mainly used, with a grain size of 0.14-0.25 mm. The binder is an organic binder - most often furfuryl resins. As part of this work, self-hardening molding sands with furfuryl resins dedicated to the classic production of molds and cores, as well as molding sands with resin dedicated to 3D printing, were tested. The aim of the research was to compare the viscosity of binders and the properties of molding sands prepared based on binding systems both dedicated to the classic production of molds and cores and for 3D printing. Tests were carried out on the binding kinetics, bench life, strength properties, permeability, abrasion and hot distortion of molding sands prepared on the basis of a standard medium grain matrix and sieved fine-grain matrix. The carried-out tests have shown that the binding system based on furfuryl resin elaborated for 3D printing of molding sands provides strength properties of the sands similar to the classic system of binding self-hardening molding sands with furfuryl resins. However, it ensures faster binding speed and greater thermal stability measured by the hot distortion parameter. The use of a fine-grained matrix results in a decrease in the strength properties of all the molding sands. On the basis of the results achieved for molding sands with organic binding system, a new inorganic binding system was elaborated.

Keywords: Molding sands, Furfuryl resin for 3D printing, Viscosity, Binder jetting, Sand grains

1. Introduction

Binder jetting technology (3D printing) in the production of foundry molds and cores is increasingly used in the industry in the production of castings from non-ferrous metal alloys. In additive methods, it is classified as the one that does not require additional processing after the printing process [1]. The use of this technique in the production of molds and cores allows obtaining very good quality casting surfaces. This is one of the main factors determining

the quality of the cast element. In 3D printing technology mainly quartz sand is mainly used as a matrix [2, 3], the grain size of which is in the range of 0.14-0.25 mm [4-5], creating subsequent layers with a thickness of 0.28-0.50 mm [6]. The binder is mainly an organic binder (usually furfuryl resins) in an amount of 1-3% [7-8], and even 8% according to D. Snelling et.al. [9].

In the case of a chemical hardening printing process, the sand matrix is mixed with a hardener. A device called a recoater applies a layer, which is then leveled, and the printed head sprays the binder in the designated area. The process is repeated, creating subsequent layers until the printed element is completed [10-12]. The binder, after introduction, penetrates between the grains, where the hardening reaction takes place. The technology enables hardening only that part of the molding sand that is necessary to print the element, which is an advantage of the process. On the other hand, the sand that is not involved in the process is a big problem. Y. Li et.al. [13] attempted to reuse the unhardened mixture of matrix and hardener and research showed that after recycling it is possible to use the material in the production of cores. The possibility of using a smaller amount of binding material was proved but also a negative effect on the permeability of the tested molding sands was shown [13].

A more detailed review of the literature regarding the use of binder jetting technology in the production of foundry molds and cores is presented in the authors' previous work [14].

2. Own research

As part of this work, self-hardening molding sands with organic binders intended for the classic production of foundry molds and cores, as well as sands with binders dedicated to 3D printing, were tested.. Quartz sand from Sibelco Co. was used to prepare molding sands. According to the Polish standard PN-85/H-11001 the tested sand was qualified as medium. In the studied matrix, the value of the main fraction is 84%, which determines the sand as homogeneous. Commercial furfuryl resins were used as binders: "classical" - for preparing self-hardening sands using the classic method and "3D printing" – for 3D printing. Commercial hardeners were used as hardeners: "Classical" - for hardening classic self-hardening sands and "3D printing" - for 3D printing. Tests of selected properties of molding sands, including tests of binding kinetics, bench life, strength properties, permeability, abrasion and thermal deformation (hot distortion) were carried out. Due to the grain size requirements for the matrix intended for 3D printing, the quartz sand was fractionated into sand grains remaining on a sieve with a mesh size of 0.20 mm and 0.16/0.10 mm. Dynamic viscosity tests of the binders used were carried out. The molding sands were prepared in a paddle mixer, where the mixing time of the matrix and hardener was 1 min, and then the binder was added. The mixing time of all ingredients in the mixer was 1 min. Using the WADAP LUZ device for vibrating sand densifying, the following standard fittings were made: dog bone for testing tensile strength, longitudinal for measuring bending strength, and cylindrical for measuring the permeability and abrasion of molding sands [15]. Shapes with dimensions of 114×25.4×6.3 mm were made to measure the hot distortion parameter [15].

Table 1.
Composition of tested molding sands

Sym.	Sand matrix	Amount [weight part]	Binder	Amount [weight part]	Hardener	Amount [weight part]
M1	Silica sand	100	Classical 1	1.0	Classical	0.5
M2	Silica sand	100	Classical 2	1.0	Classical	0.5
M3	Silica sand	100	3D printing	1.0	Classical	0.5
M4	Silica sand (grain size 0.20 mm)	100	3D printing	1.0	3D printing	0.5
M5	Silica sand (grain size 0.20/0.16/0.10 mm)	100	3D printing	1.0	3D printing	0.5
M6	Silica sand (grain size 0.16/0.10 mm)	100	3D printing	1.0	3D printing	0.5
M7	Silica sand (grain size 0.20 mm)	100	Classical 1	1.0	Classical	0.5
M8	Silica sand (grain size 0.20/0.16/0.10 mm)	100	Classical 1	1.0	Classical	0.5
M9	Silica sand (grain size 0.16/0.10 mm)	100	Classical 1	1.0	Classical	0.5

2.1. Research methodology

Ultrasonic tests were used to study the kinetics of hardening and the bench life of the molding sands. A sample of the tested molding sand was placed in a special core box. An ultrasonic head was applied to the sampler, which examined the kinetics of sand binding for 24 hours. The system conditions during the hardening of the tested samples correspond to conditions inside the mold close to the cavity at a constant temperature [16]. Self-hardening molding sands are classified as rheologically unstable. During the first phase of hardening, they have the characteristics of a viscoelastic body, as the hardening time progresses, they acquire the characteristics of an elastic-plastic body with decreasing elasticity, so that at the end they acquire the characteristics of a nonlinear-elastic body. This change in the rheological properties of the molding sands has a significant impact on the wave propagation during hardening. The conditions in the binding chamber are comparable to those around the mold cavity [16].

The main physicochemical property of binders used in 3D printing technology of molding sands is their dynamic viscosity. In the research a rheometer modified by Jota was used to determine this parameter. To carry out the test, 25 ml of binder was measured and then subjected to increasing and decreasing speeds of the S1 measuring roll generating shear stresses. Dynamic viscosity is defined as the slope coefficient of a straight line resulting from the dependence of shear stress on shear rate. The parameter value is read from the equation (1) [17].

$$y = a \cdot x + b \tag{1}$$

where:
a – viscosity.

Tests of strength properties, i.e. bending strength and tensile strength, after hardening times of 2, 4 and 24 hours, were carried out on the MultiSerw Morek LRu-2e universal device for determining strength properties. Molding sands' permeability tests were carried out on the WADAP LPiR1 device.

Pouring liquid metal into the molds increases the temperature in the mold cavity. As cores are often suspended in the mold cavity an increased temperature may lead to deformations due to the heating of the bonding bridges in the mold grains. The thermal deformation (hot distortion parameter) was tested on the Multiserw Morek DMA device. According to the research methodology [15, 18], samples with dimensions of 114 × 25.4 × 6.3 mm were heated by two halogen lamps with a power of 500 W to a maximum temperature of 900°C.

3. Results and discussion

3.1. Dynamic viscosity of tested binders

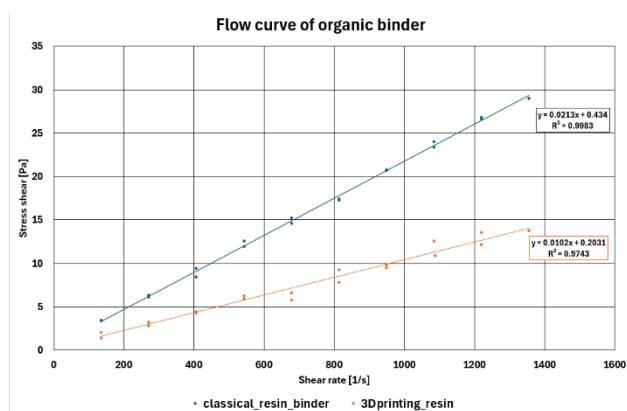Fig. 1 shows the course of the flow curves and the dynamic viscosity values of the tested binders.

Fig. 1. Flow curves and dynamic viscosity values of the tested binders

The obtained flow curves have a linear character, where the shear stress τ (shear) is proportional to the shear rate γ described by the Newton equation (2).

$$\tau = \eta \cdot \gamma \ [Pa \cdot s] \tag{2}$$

The viscosity of the fluid under simple shear conditions is described by η [19].

On the basis of the obtained relations of shear stress τ as a function of the shear rate γ the values of the viscosity parameter η were determined (fig. 2).

Research has shown that the dynamic viscosity value of the binder used in 3D printing technology (0.0102 Pa/s) is 47% lower compared to the resin used in the classic production of molds and cores (0.0213 Pa/s).

3.2. Hardening kinetics of molding sands

The hardening kinetics were tested for molding sands with composition M1 and M3 (Table 1). Fig. 2 shows the course of changes in the ultrasonic wave speed in sands with resin for the classic production of molds and cores and resin dedicated to 3D printing. Fig. 3 shows the course of binding kinetics of the tested molding sands.
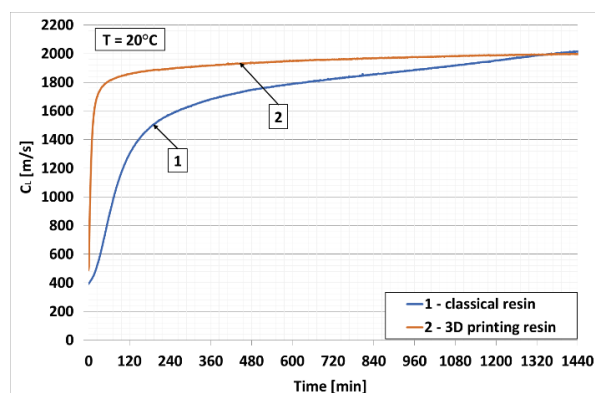

Fig. 2. Comparison of the course of changes in the velocity (C_L) of wave passage in the tested molding sands
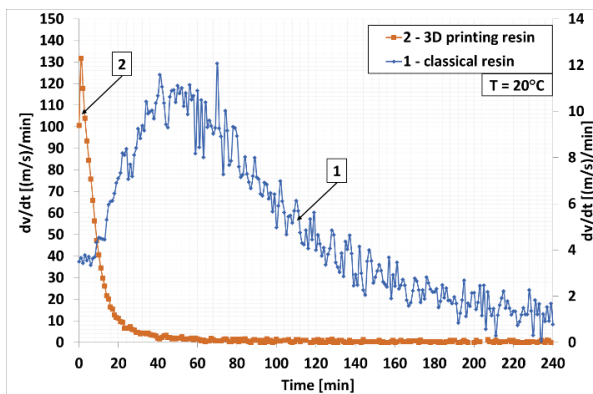
Fig. 3. Kinetics of the tested molding sands versus time

Based on the analysis of the curves presented in Fig. 3, it can be concluded that the hardening reaction of the molding sand with the resin dedicated to 3D printing occurs rapidly and at high speed. After about 2 hours, the reaction rate curve stabilizes. In the case of a molding sand with "classical" resin, the reaction speed curve is gentler. After 24 hours of the hardening process, the changes in the wave speed are similar for both sands, which means similar strength values of the tested sands after 24 hours of hardening. The analysis of the curves in Fig. 4 shows that the molding sand for 3D printing reaches the maximum rate of change in the hardening speed at approximately 130 (m/s)/min. The time after which dv/dt has its maximum value is less than 2 minutes. This time determines the bench life of the molding sand. In the case of classic self-hardening molding sand, the maximum dv/dt value is much lower and amounts to 11 (m/s)/min. Its bench life is approximately 50 minutes.

3.3. Molding sands' strength properties

As part of this work, tests of the bending and tensile strength of the molding sands were carried out. The results are presented in Figs. 4-5.
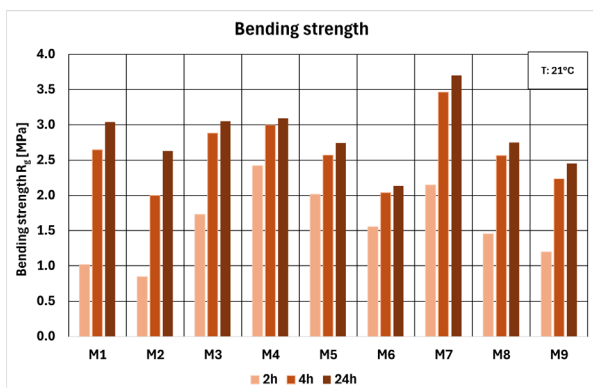

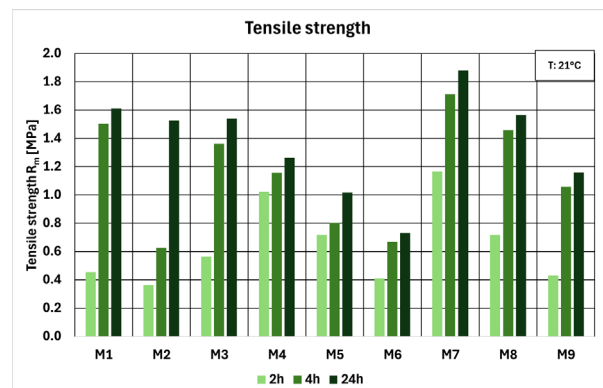Fig. 4. Influence of hardening time on the bending strength of the tested molding sands

Fig. 5. Influence of hardening time on the tensile strength of the tested molding sands

The strength properties of molding sands marked M1, M2 and M3 are similar (approximately 3.04 MPa), which was also shown in tests of the speed of passage of the ultrasonic wave through the porous medium (Fig. 3). The strength value of the M3 sand after 2 hours of hardening is 1.730 MPa, and the M1 sand is 1.019 MPa, as shown by the tests on the hardening kinetics (Fig. 3). The influence of grain size on the strength properties of the molding sands was determined with the use of fractionated matrix (M4-M9). The conducted research has shown that in the case of a fractionated matrix, the "Classical 1" resin allows to achieve slightly better properties compared to the resin used in 3D printing. The lowest values of bending strength were obtained in both cases for the matrix with a grain size of 0.16/0.10, which is obvious from the point of view of the increased specific surface area of the matrix grains. In order to improve the strength properties of sands made on the basis of a fine-grained matrix, it is necessary to increase the amount of binding material. The course of changes in tensile strength is analogous to changes in bending strength. However, when a fine-grained matrix is used, the tensile strength values of M4-M6 sands are much lower than those of M7-M9 sands. The lowest values of tensile strength, as in the case of bending strength, were obtained for molding sands prepared on the basis of a matrix with a grain size of 0.16/0.10 – bending strength was 2.137 MPa and tensile strength was 0.731 MPa.

The abrasion resistance of molding sands is a parameter related to their strength. Fig. 6 shows the results of sand abrasion tests.
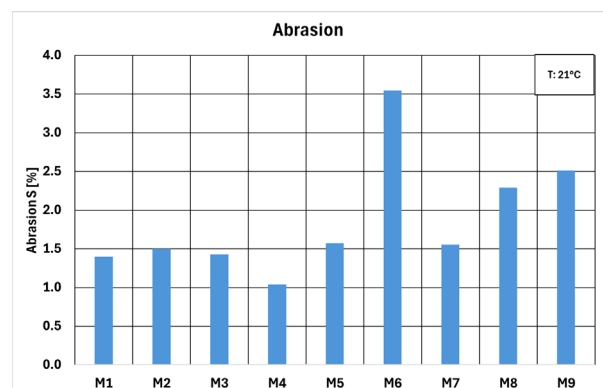

Fig. 6. Influence of molding sand composition on their abrasion

The tested sands with resins: "Classical 1", "Classical 2" and "3D printing" achieved similar abrasion values (approx. 1.5%). When using a matrix with a grain size of 0.20, the molding sand prepared with 3D printing resin (M4) is characterized by the lowest abrasion (1.037%), while the sand prepared with "Classical 1" resin (M7) reaches a value similar to that of M2 (1.497% and 1.552%). The highest abrasion value was obtained for the molding sand made with the use of matrix of grain size (0.16/0.10) with 3D printing resin (M6) - 3.546%, which is 248% more comparing to the molding sand with standard matrix (M3) - 1.428%. This molding sand is also characterized by the lowest strength properties.

3.4. Molding sands' permeability

The influence of hardening time on the permeability of the tested molding sands was shown on Fig. 7.
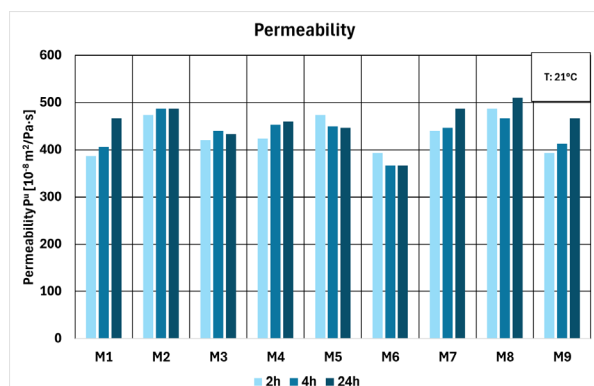

Fig. 7. Influence of hardening time on the permeability of the tested molding sands

Permeability tests showed that the parameter increases with hardening time and remains at a similar level after 24 hours of hardening for most tested sands M1-M5 and M7-M9 (from 433.33 to 510.00·10^{-8} m²/(Pa·s)). The lowest permeability value was obtained for the sand made using resin intended for 3D printing and a matrix with a grain size of 0.16/0.10 (M6) – 366.67·10^{-8} m²/(Pa·s).

3.5. Molding sands' thermal deformation

The results of molding sands' thermal deformation tests measured by hot distortion parameter are presented on Fig. 8-9. All tested sands show the typical course of thermal deformation for self-hardening sands with furfuryl resin. The M2 molding sand was omitted because it was made with the use of a classical binder.
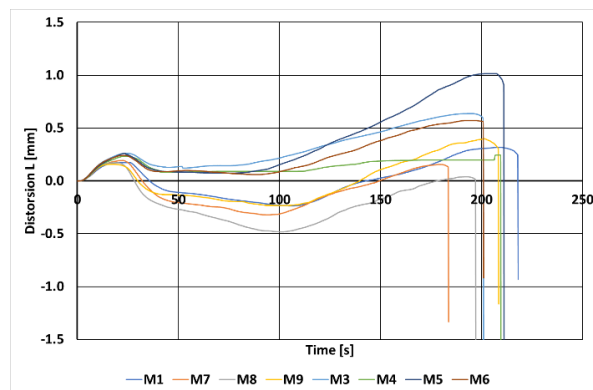

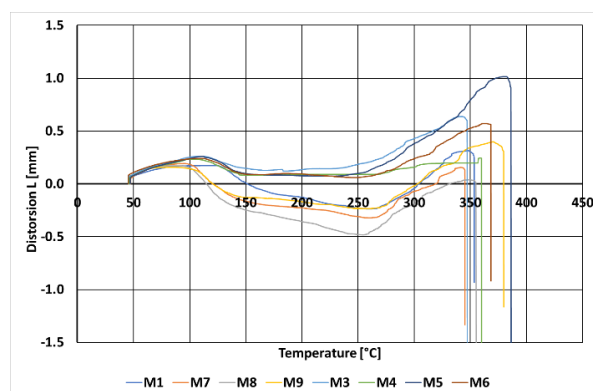Fig. 8. Thermal deformation in the function of heating time

Fig. 9. Thermal deformation in the function of temperature

The initial deformation course of the tested molding sands is similar. There is an initial increase in deformation, and then sands made using "Classical 1" resin (M1, M7-M9) deform towards negative values, after which their deformation increases upwards, and the fitting is destroyed. In the case of molding sands made using "3D printing" resin (M3-M6), greater thermal stability of the molding sands was observed in the temperature range of approx. 150-250°C. When this temperature is exceeded, the deformation of the sands increases, and the fitting is destroyed at a temperature of approximately 340-390°C. The shortest heating time (183.8 s) after which the fitting was destroyed was observed in the case of sands bonded with "Classical 1" resin based on a matrix with a grain size of 0.20 (M7). The longest heating time (218.3 s) was observed for a fitting also made using "Classical 1" resin but based on a standard grain matrix (M1). In the case of the resin used for 3D printing, all shapes were destroyed after approximately 200 s.

4. Molding sands with inorganic binding system – initial solution

According to the results obtained for molding sands with organic binders, an attempt was made to develop an inorganic binding system using a commercial inorganic binder. Molding sands with water glass cured with liquid hardeners were tested: a hardener based on acetic acid esters (ESTER) (MC1, MC2),

carbonic acid esters (CARBO) (MC3, MC4) and both esters mixture (MC5, MC6). The composition of the tested molding sands was as follows: quartz sand from Sibelco Co. qualified as medium according to the Polish standard PN-85/H-11001 (the same as mentioned in chapter 2) – 100 weight part; water glass 145 (MC1, MC3, MC5), water glass 145 with reduced viscosity (MC2, MC4, MC6) - 2.5 weight part; hardener 10% in relation to the binder. The results obtained for the strength of the molding sands are shown in Figure 10.
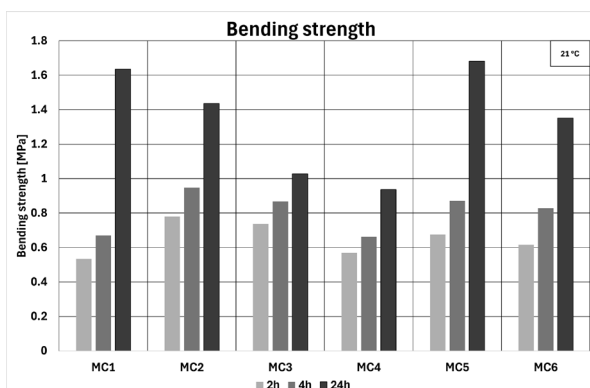

Fig. 10. The influence of curing time on bending strength of molding sands with commercial water glass and water glass with reduced viscosity cured with selected ester hardeners [20]

The research shows that changing the viscosity of the inorganic binder slightly affects the strength values of the tested molding compounds with inorganic binders. The lowest strength values were obtained for the CARBO (MC3, MC4) binder, while the most similar values were obtained for the ESTER binder (MC1, MC3). [20]

4. Conclusions

Based on the conducted research, the following conclusions can be drawn:

- An organic binding system based on furfuryl resin intended for 3D printing provides strength properties of the molding sands similar to the classic system of binding self-hardening sands with furfuryl resins.
- The organic binding system designed for 3D printing of molding sands is characterized by a higher binding speed compared to the classic system.
- Molding sands made on the basis of a system designed for 3D printing are characterized by better thermal stability.
- The use of a fine-grained matrix (0.16/0.10 mm) decreases the strength properties of the molding sands, which is caused by the insufficient amount of binding material to cover the larger specific surface of the grains.
- Lowering the viscosity of the inorganic binder results in a slight decrease in the strength of molding sands with inorganic binding systems dedicated to 3D printing.

The research will be continued, and future works will be focused on the development of an inorganic binder system dedicated to 3D printing technology of molding sands.

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