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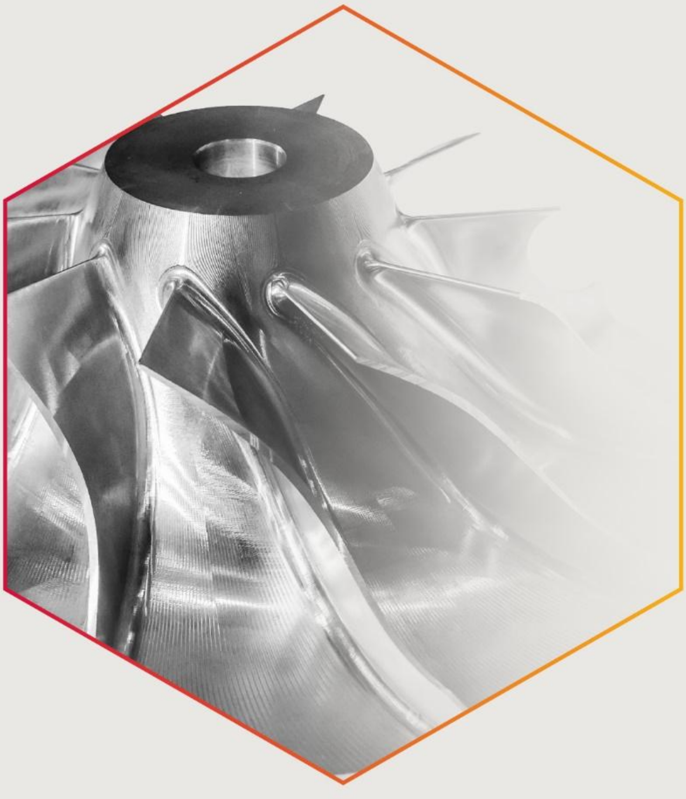

Funded by
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NetCastPL4.0

(Grant Agreement number 101159771)

REPORT no.2 on molding materials

Effect of binder type, including selection of inorganic binder, on properties of molding sands dedicated to 3D printing

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This report shows the results achieved partially within NetCastPL4.0 project. The project is being realized in cooperation between AGH Faculty of Foundry Engineering (Leader), CNR-ICMATE and Aalto University School of Engineering. The results presented in the work were presented during international scientific conferences - XXXI. medzinárodnej vedeckej konferencie slovenských, českých a poľských zlievačov SPOLUPRACA 2025 on 2-4 April 2025 in Rajecke Teplice (Slovak Republik), ECIG 2025 European Cast Iron Group Meeting 2025 on 29 April 2025 in Milan (Italy) and V International Conference of Casting and Materials Engineering ICCME 25 in Krakow (Poland). The work presents the influence of binder type on the properties of molding sands, including sands dedicated to 3D printing. The authors demonstrated the possibility of replacing environmentally harmful organic binders with inorganic binders.

Table of Contents

1. Introduction

1.1 3D printing - binder jetting technology

New solutions like 3D printing coming from the development of additive techniques allow for not only the creation of complex shapes of casting patterns, but also for the production of sand molds and cores [1-2]. Currently, additive techniques (AM) have become part of Industry 4.0 and one of the Rapid Prototyping methods. In accordance with observed trends, in the future, the classical methods of molds and cores production may be partially replaced by printed components. Among many additive technologies, the binder jetting (so-called 3D printing) has become the leading method of sand mold and core production. The process is similar to classic 2D printing, including printers using ink. In the binder jetting technology a drop of binder falls on the prepared layer and locally binds nearby grains and then another layer of material is applied. The layer of material is fine-grained sand. The scheme of 3D printing of molding sands process is shown in Figure 1 [3]. Nowadays the use of 3D printing in molds and cores production is the subject of numerous research. The technology may be a breakthrough for modern foundry engineering. Within this paper literature data concerning types of molding sands dedicated for 3D printing technology, the possible changes in mold construction and finally the impact of the technology on castings properties were analyzed.

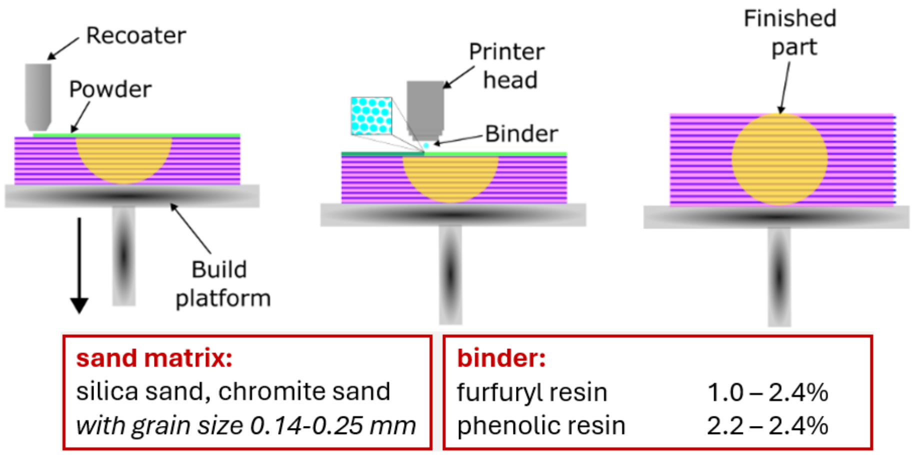


Fig. 1. *Scheme of the sand 3D printing process using the binder jetting method [1-2].*

A drop of binder falls on the prepared layer and locally binds nearby grains, then another layer of material is applied. Layer thickness: 0.28 - 0.50 mm. The process is repeated until the finished element is produced (fig. 2).

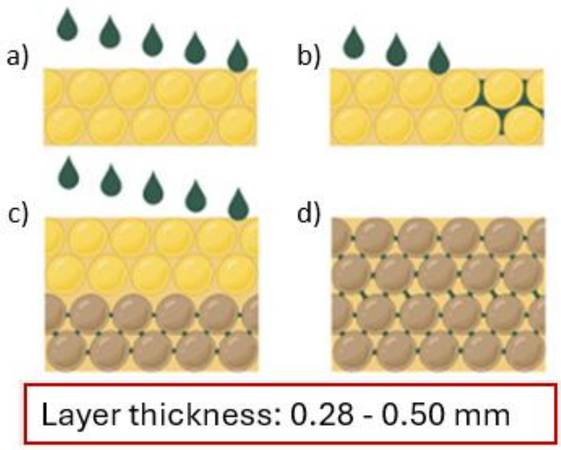


Fig. 2. *Printing process in binder jetting 3D system: a) droplets of liquid binder are applied to layer of matrix; b) binder surrounds sand grains; c) droplets of binder applied to new layer of matrix; d) matrix grains connected by resin bridges [4].*

The technology enables the production of molds and cores with complex shapes that are impossible to achieve using conventional methods, which can be useful in the production of thin-walled cast iron castings. The technology is aligned with **Industry 4.0** concept.

Process **Advantages** are: good dimensional accuracy, low roughness of mold cavity, lower binder content, shorter hardening time, production of shapes not possible to achieve with the use of conventional molding methods (fig. 3-4).

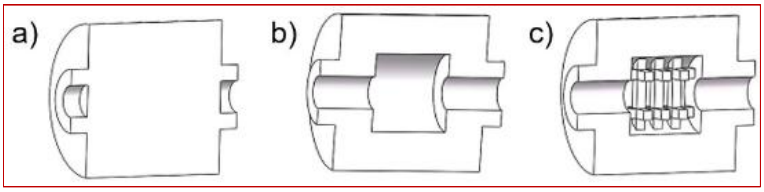


Fig. 3. *Scheme of cores: a) solid b) with a cavity c) with a truss structure [3].*

Among **Disadvantages** can be listed: high machine costs, limitations in large-scale production, possible stepping effect.

1.2 Molding sands in 3D printing

The most popular in sand 3D printing is no-bake technology, in which molding sand consist of matrix, binder and hardener. Curing is conducted in ambient temperature and is initiated after adding the last component to the mixture.

In foundry plants molds and cores are printed with the use of organic binders [5-6].

Within own research molding sands with furfuryl resins for both classical technology and dedicated to 3D printing were tested and compared [7]. The composition of tested molding sands is presented in Table 1 and the results of research are presented in figs. 4-9.

Table 1. *Composition of tested molding sands with organic binders [7].*

no.	sand matrix	amount [weight part]	binder	amount [weight part]	hardener	amount [weight part]
M1	silica sand	100	classical resin	1.0	classical	0.5
M2	silica sand	100	classical resin_2	1.0	classical	0.5
M3	silica sand	100	3D printing resin	1.0	3D printing	0.5
M4	silica sand (grain size 0.20mm)	100	classical resin	1.0	classical	0.5
M5	silica sand (grain size 0.20mm)	100	3D printing resin	1.0	3D printing	0.5
M6	silica sand (grain size 0.20/0.16/0.10mm)	100	classical resin	1.0	classical	0.5
M7	silica sand (grain size 0.20/0.16/0.10mm)	100	3D printing resin	1.0	3D printing	0.5
M8	silica sand (grain size 0.16/0.10mm)	100	classical resin	1.0	classical	0.5
M9	silica sand (grain size 0.16/0.10mm)	100	3D printing resin	1.0	3D printing	0.5

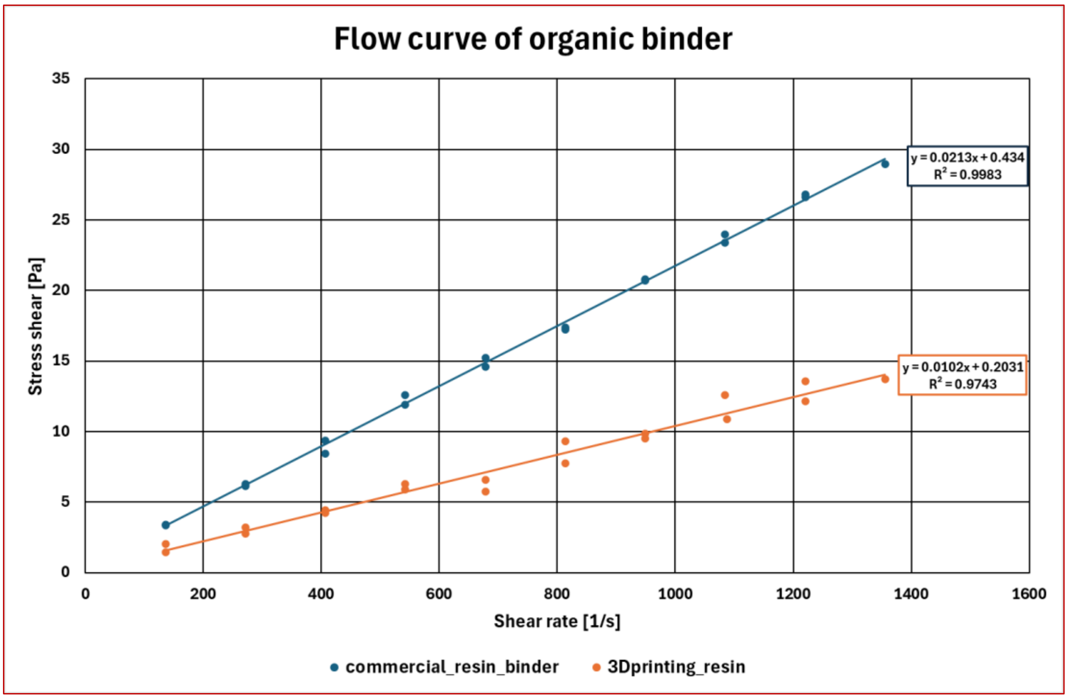
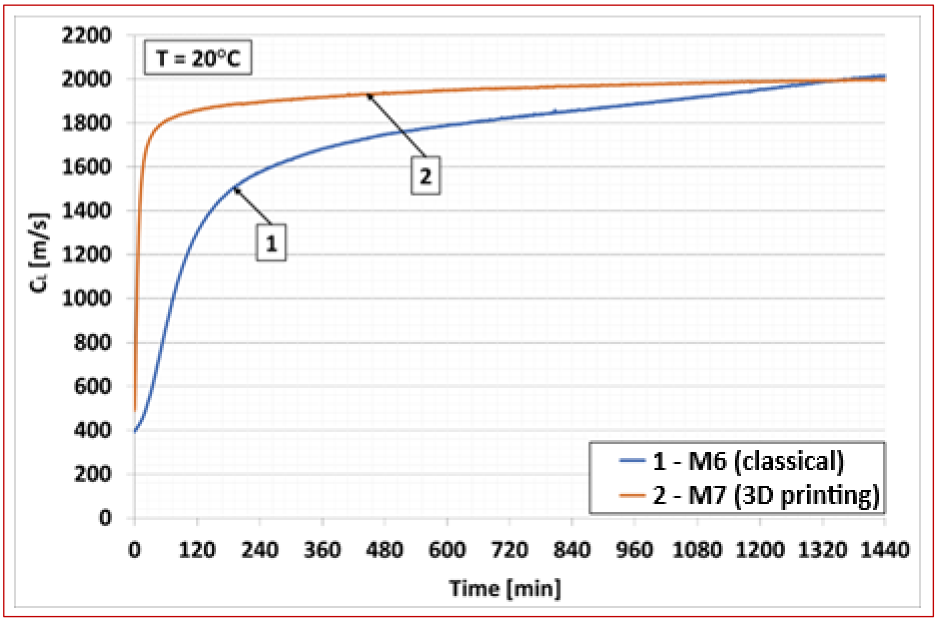
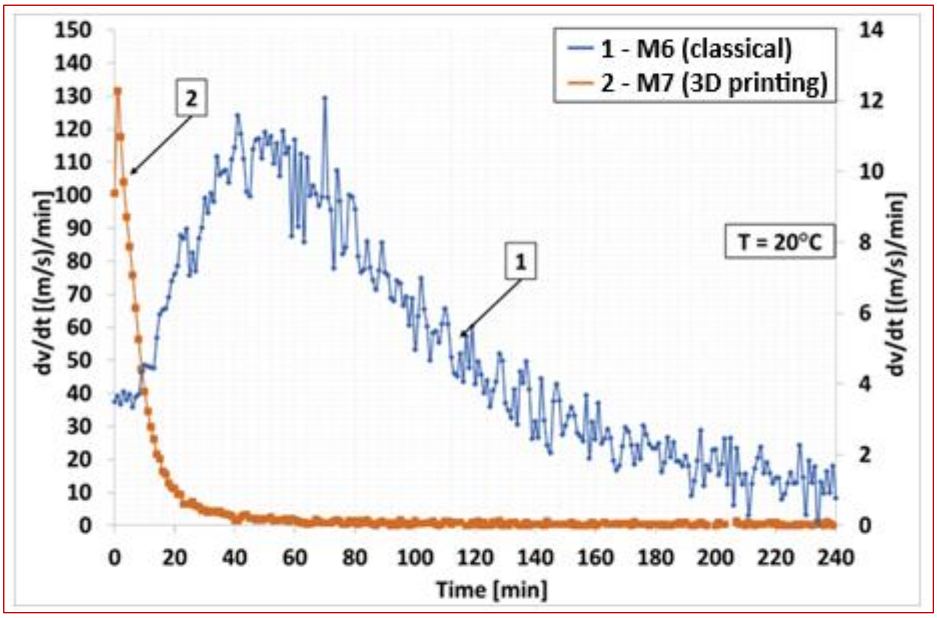


Fig. 4. *Flow curve and dynamic viscosity of tested organic binders [7]*



a)



b)

Fig. 5. *The influence of binder type on: a) ultrasonic wave velocity (CL) with time and b) kinetics of hardening of tested molding sands with organic binder [7].*

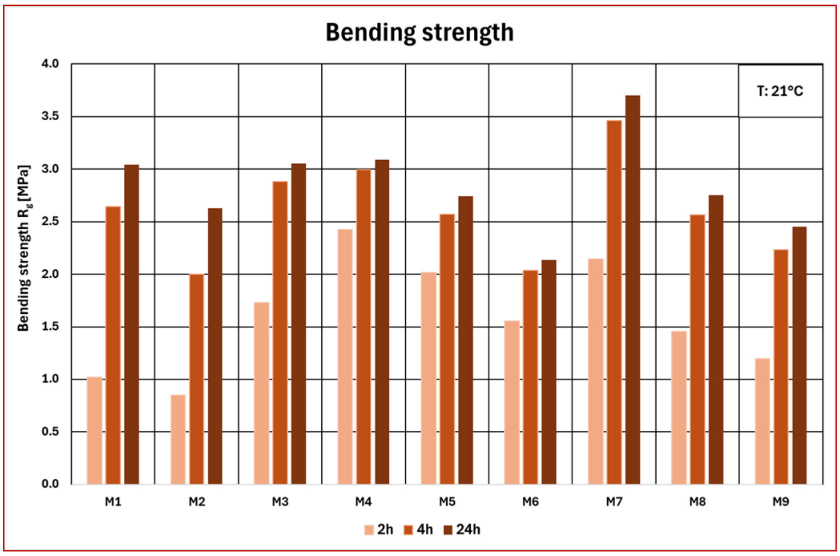


Fig. 6. *Bending strength of tested molding sands with organic binders [7].*

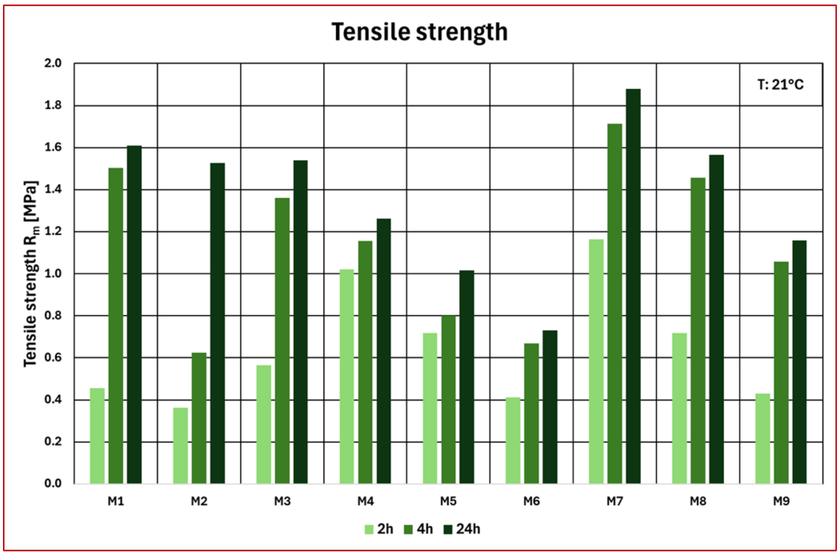


Fig. 7. *Tensile strength of tested molding sands with organic binders [7].*

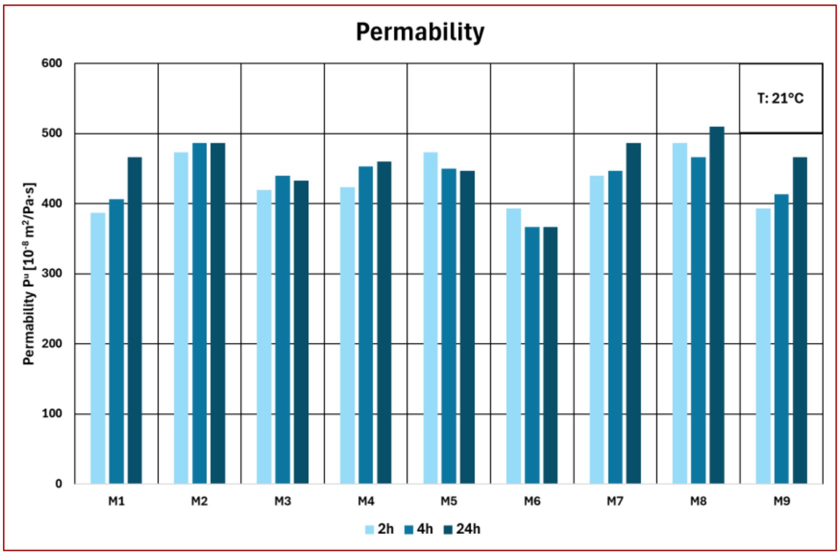


Fig. 8. *Permeability of tested molding sands with organic binders [7].*

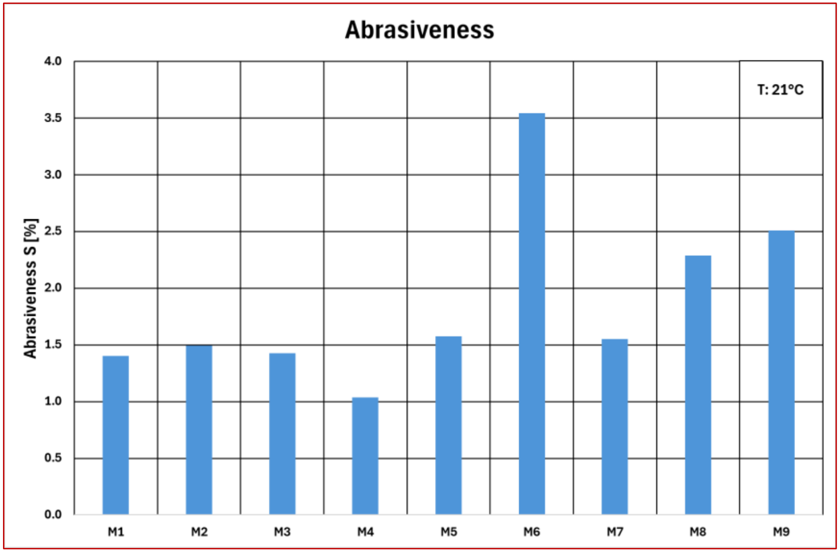


Fig. 9. *Abrasion of tested molding sands with organic binders [7].*

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) [7].

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.

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 [7].

How about & why inorganic binders?

1.3 Foundry molding sands vs. Green Deal policy

Modern industry requires implementation of new innovative technologies. Innovative molding sands technologies must ensure the appropriate technological properties of produced molds and cores and high process efficiency [8].

But currently, the dominant factor in the development of molding sands technologies is the need to meet high environmental standards. It's even being done at the expense of reducing the technological properties of the materials.

Due to mentioned before requirements the molding material technologies that have been used successfully in foundry production processes for decades have been replaced by more environmentally friendly solutions. These include: coal dust – a necessary additive ensuring high quality of castings surface, alcohol protective coatings – replacing with water coatings, molding sands with ethyl silicate – the binder was replaced with colloid silica, furan molding sands – considered within this work and the problem in that case is the content of free furfuryl alcohol (now limited to 40%), cold-box technology – the technology which dominated the serial production of sand cores; now there are five generations of the process and in the newest two inorganic solvents in binding materials are used.
Of course there is no reason to complain Thanks to strict environmental regulations and the trend in European industry to move away from harmful technologies over the past few decades, the negative impact of European industry on the environment has been reduced. However, **it is necessary to implement new innovative technologies** to make the industry more ecologically friendly [8-9].

1.4 Development trends – own research

In Molding Materials Laboratory of AGH University FFE for many years researchers have been dealing with issues related to the environmentally friendly molding sands. The following technologies, among others, were elaborated: ecologically friendly molding sands with organic binders, green molding sands (sands with clays) with reduced harmfulness, molding sands for ablation casting, molding sands with **sodium silicates** with increased knock-out properties, molding sands with **sodium silicates** with better quality of reclaim obtained after their mechanical reclamation [9].

Sodium silicate can be an alternative for harmful organic binders. Molding sands with this binder are hardened chemically (CO_2, ester technology), by dehydration – thermally, including microwaves, and with the use of new - combined method.

In Table 2 the influence of hardening technology on molding sands' strength is presented. The composition of molding sand is stable. As can be seen, molding sands hardened by dehydration are characterized by approx. 10 times higher strength than chemically hardened compounds.

Table 2. *Comparison of compressive strength obtained for hydrated sodium silicate sands prepared using different technologies [9].*

molding sands' components [weight part]	hardening technology	compressive strength [MPa]
silica sand 100 sodium silicate (M=2.2) 4.0	dehydration	10.0 – 11.0
	CO_2	1.0 - 1.2
	ester/4h	0.8 - 1.3

However, within this work authors will focus on molding sands with sodium silicate hardened in ester technology because that technology is similar to no-bake system used currently in 3D printing.

2. Conducted Research

2.1 Materials

Two types of molding sands were tested; both self-hardened: molding sands with organic binder in no-bake technology and molding sand with inorganic binder in ester technology with two different ester hardeners. The used matrix was silica sand.

Self-hardening molding sands compositions chosen for tests are presented in Table 3 [11]. Two molding sands with organic binders were tested: for classical technology and dedicated to 3D printing. Eight self-hardening molding sands with inorganic binders were tested: with commercial binders A & B for classical technologies and with new binders elaborated on the basis of binders A & B – marked: A_{3D} & B_{3D}. In case of molding sands with inorganic binders two different hardeners were used: classical Flodur 5 (based on ester of acetate acid) and Ixional elaborated in our laboratory for better reclaim quality - based on ester of carbon acid. Microwave hardened molding sands compositions chosen for tests are presented in Table 4 [12]. In that case also binder based on aluminosilicates (C and C_{3D}) was tested.

Table 3. *Composition of tested self-hardening molding sands with inorganic binders [11].*

no.	sand matrix	amount [weight part]	binder	amount [weight part]	hardener	amount per binder content [%]
M1	silica sand	100	organic	1.0	hardener	50
M2	silica sand	100	$organic_{3D}$	1.0	$hardener_{3D}$	50
M3	silica sand	100	inorganic A	2.5	Flodur 5	10
M4	silica sand	100	inorganic A_{3D}	2.5	Flodur 5	7.35
M5	silica sand	100	inorganic A	2.5	Ixional	10
M6	silica sand	100	inorganic A_{3D}	2.5	Ixional	7.35
M7	silica sand	100	inorganic B	2.5	Flodur 5	10
M8	silica sand	100	inorganic B_{3D}	2.5	Flodur 5	7.35
M9	silica sand	100	inorganic B	2.5	Ixional	10
M10	silica sand	100	inorganic B_{3D}	2.5	Ixional	7.35

Table 4. *Composition of tested microwave hardened molding sands with inorganic binders [12.]*

no.	sand matrix	amount [weight part]	binder	amount [weight part]	hardening time [min]	power [W]
MA1	silica sand	100	inorganic A	2.0	6	800
MA2	silica sand	100	inorganic A_{3D}	2.0	6	800
MB1	silica sand	100	inorganic B	2.0	6	800
MB2	silica sand	100	inorganic B_{3D}	2.0	6	800
MC1	silica sand	100	inorganic C	2.0	6	800
MC2	silica sand	100	inorganic C_{3D}	2.0	6	800

Used sand matrix:
silica sand with the grain size:
0.20/0.16/0.10, where 85% were 0.20 grains.

2.2 Research Methodology

The conducted tests are divided to tests of binders and tests of molding sands.

For binders viscosity, contact angle (on silica substrate) and the penetration depth were tested (with the station designed on the basis of the height of the print head of the Kocel AJS 300A printer and mathematical models of liquid penetration into porous material, which is presented in figure 10). According to the developed methodology, a drop of binder from a burette is dripped onto a loose sand bed with a grain size of less than 0.20 mm. After 1 minute, the depth of binder penetration into the substrate is measured.

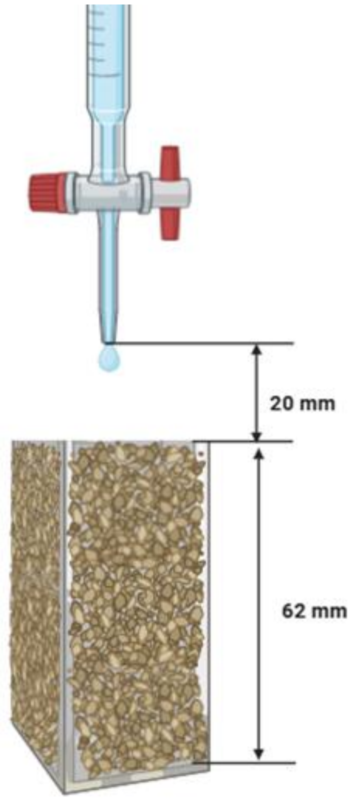


Fig. 10. *Scheme of the measuring station of the depth of penetration of the binder into the sand bed [7].*

The molding sands were prepared in a paddle mixer with mixing time of sand and hardener: 60 s and mixing time after adding the binder: 60 s. Than the kinetic of curing, chosen technological properties and Hot-distortion parameter, according to the presented scheme (fig. 11), of molding sands were tested. Fittings prepared for measurements were compacted by vibration.

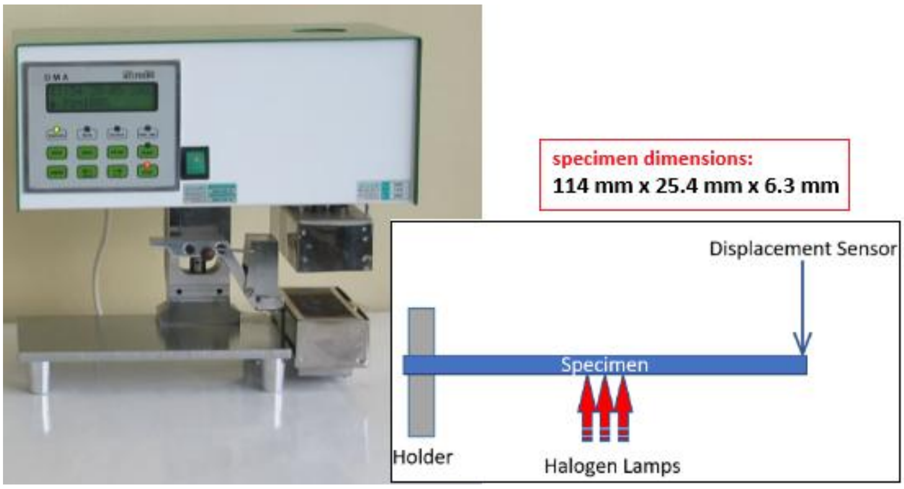


Fig. 11. *Prototype device for measuring molding sands deformation at elevated temperatures, type DMA with schematic diagram of the Hot Distortion Test, adapted from [9-10].*

2.3 Research results

2.3.1 Viscosity of tested binders

The basis for the development of new inorganic binders for 3D printing was research on the viscosity of a commercial organic binder for 3D printing (results are presented in figure 4) and the technical parameters of the Kocel AJS 300A 3D printer. The new binders were developed by changing the viscosity - adding an appropriate amount of solvent to the basic inorganic binders.

2.3.2 Contact angle & penetration depth of tested binders

Wettability tests showed that inorganic binders wet silica substrates slightly worse than organic binders. However, it should be emphasized that all tested binders wet silica substrates well – the contact angle is < 90°. Modification of binder viscosity had a positive effect on the wettability of binder A.

The penetration depth of basic inorganic binders is worse than organic binders. Modification of binder viscosity changed the number of penetrated layers from 11 to 22 for binder A and from 15 to 22 for binder B. It is five layers more in comparison to organic 3D binder. That's why it will be considered to use modifiers to improve that property. The results are presented in figs.12-13 [11, 13-14].

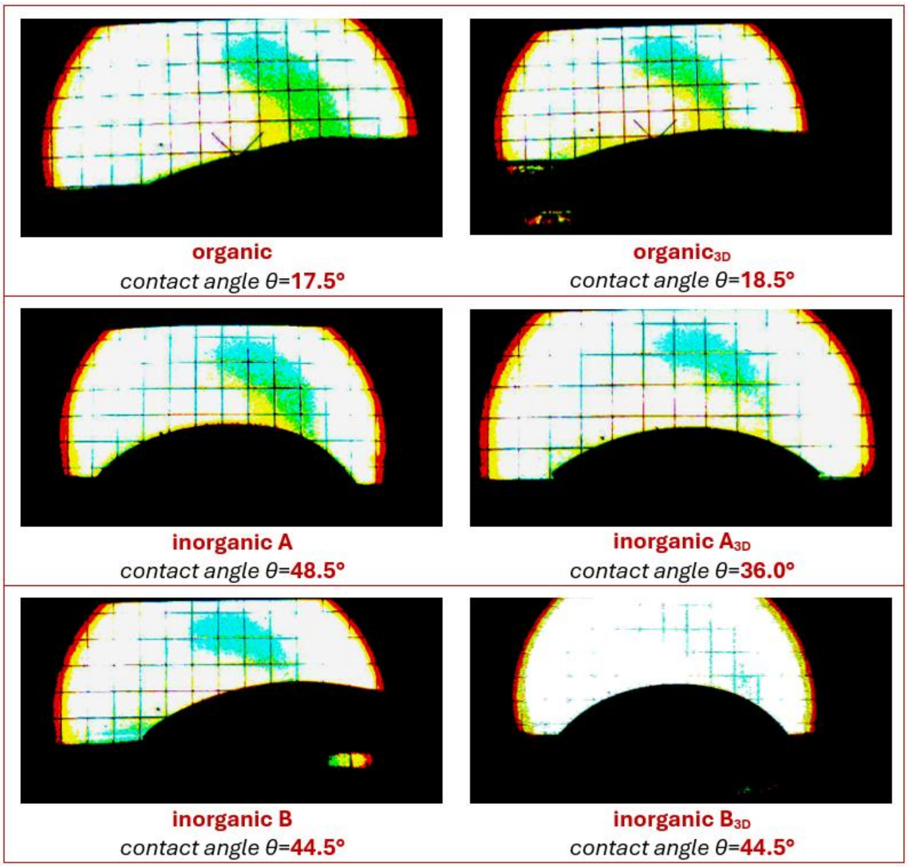


Fig. 12. *Results of contact angle tests [7, 11, 13].*

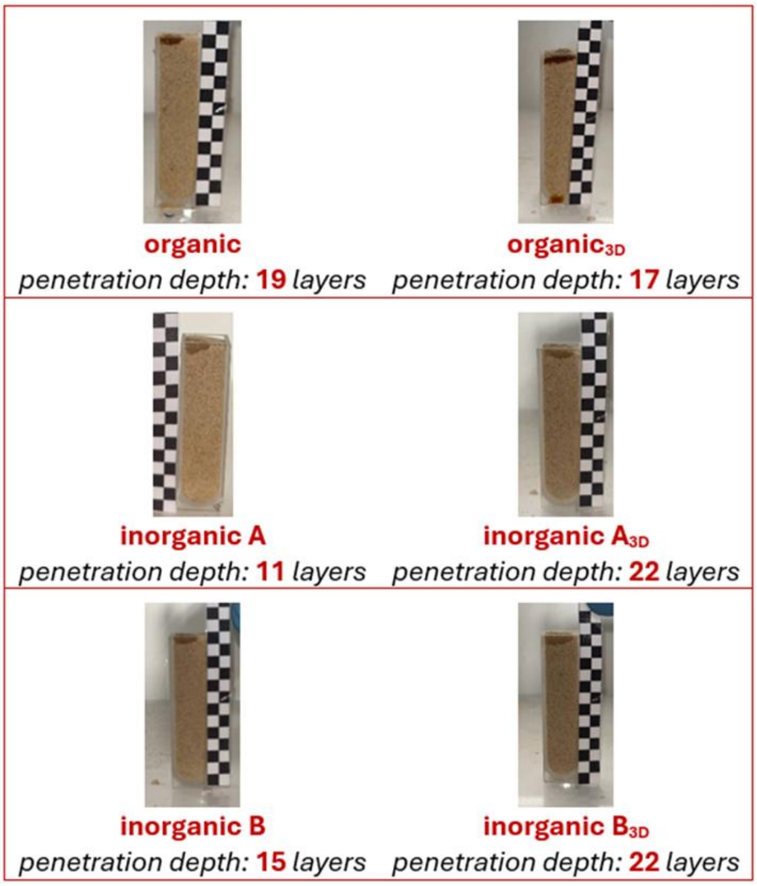


Fig. 13. *Results of penetration depth tests [7, 11, 13].*

2.3.3 The kinetic of curing of molding sands

Curing kinetic tests were carried out for selected compounds presented in the table as M1, M2, M4, M6, M8 and M10 (table 2). The results were presented on figs. 14-16 [5, 11, 13-14]. The tests showed that organic system used in compounds intended for 3D printing is more reactive than system for compounds intended for traditional mold and core production methods. In the case of inorganic systems, both binders A and B cured with Ixional hardener exhibit bonding kinetics similar to those of organic binders for 3D printing.

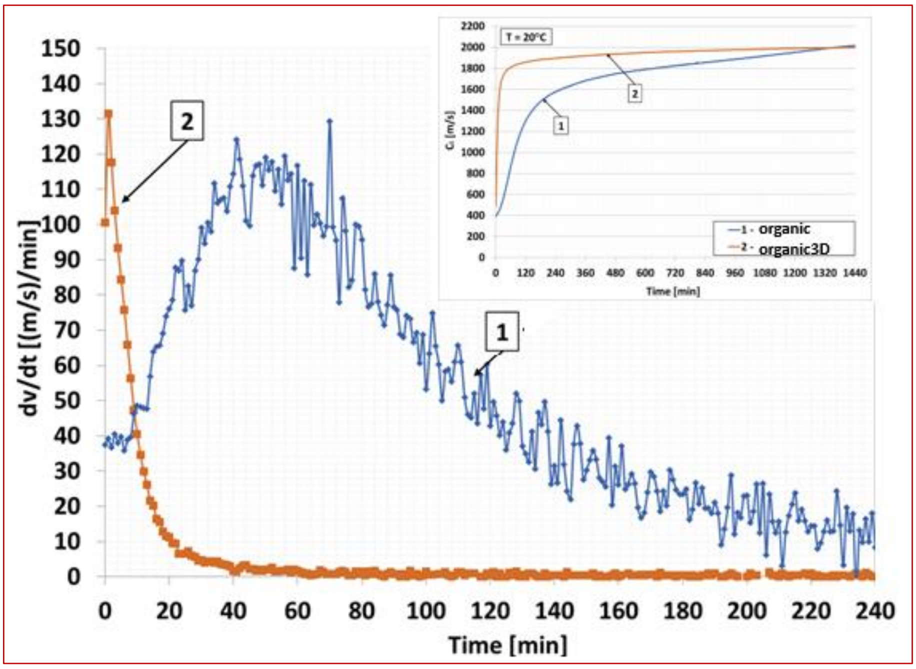


Fig. 14. *Kinetics of the curing process for organic binders [5].*

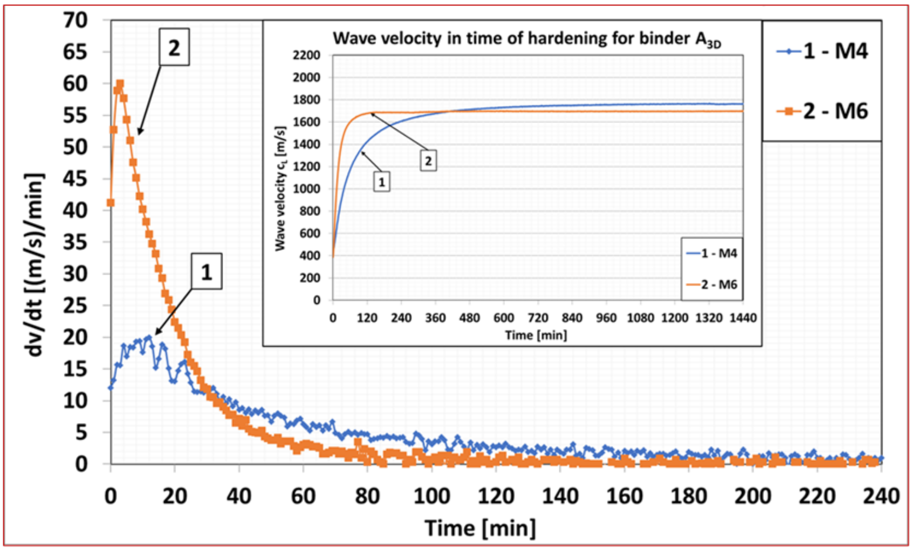


Fig. 15. *Kinetics of the curing process for inorganic binder A [11, 13-14].*

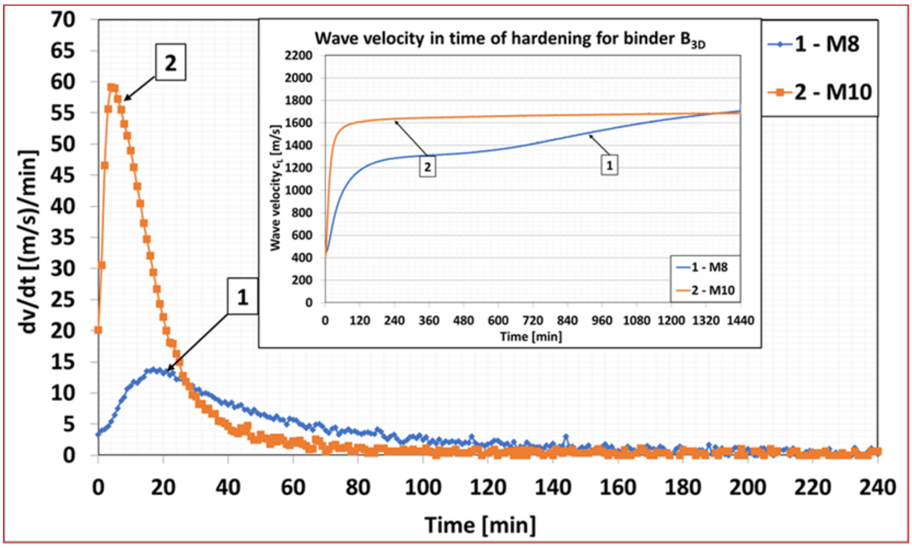


Fig. 16. *Kinetics of the curing process for inorganic binder B [11, 13-14].*

2.3.4 Strength, permeability & friability of tested molding sands

Tests on technological properties such as strength, permeability, and friability of self-hardening molding sands were carried out (figs. 17-19) [11, 13-14]. The results showed that mixtures with organic binders have higher strength than mixtures with inorganic binders, which is well known. However, it is worth noting that the modification of the basic binders did not affect the strength of the mixtures containing them.

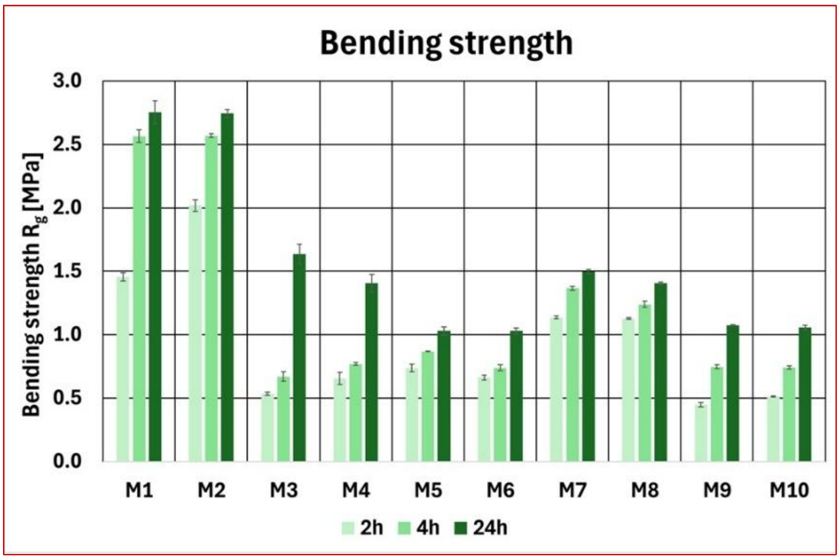


Fig. 17. *The influence of binder type on molding sands' bending strength [11, 13-14].*

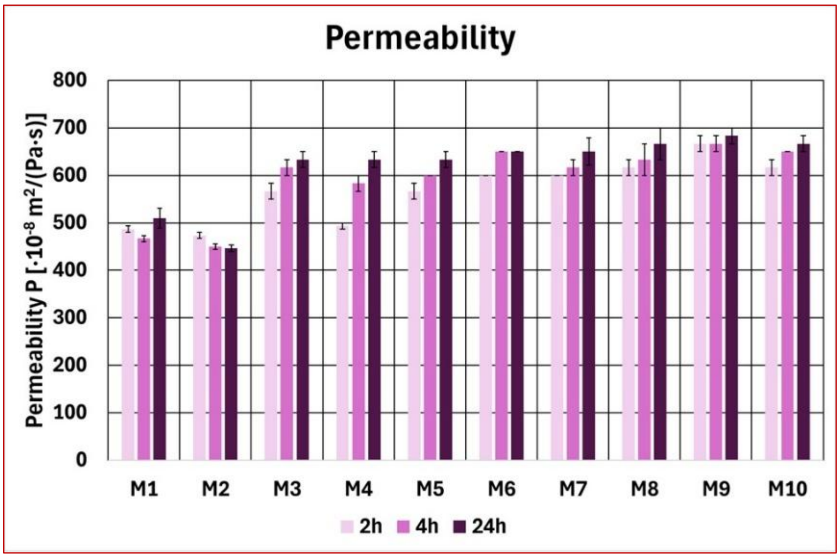


Fig. 18. *The influence of binder type on molding sands' permeability [11, 13-14].*

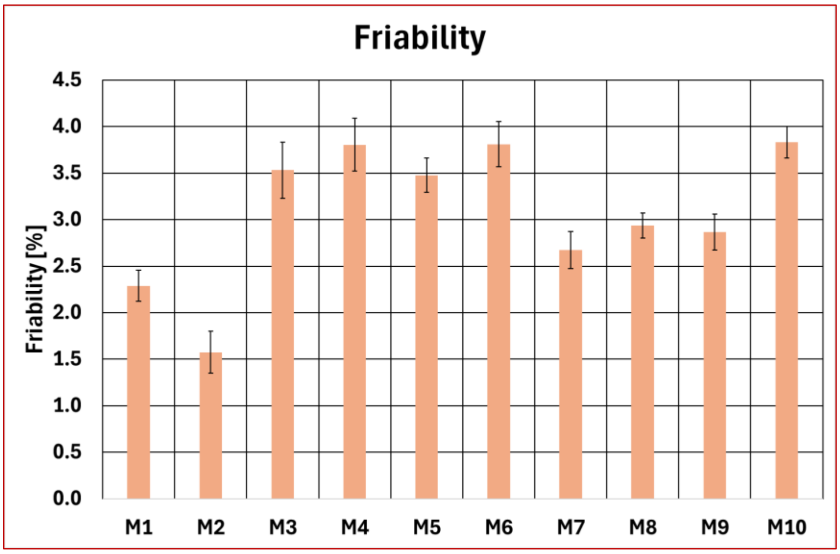


Fig. 19. *The influence of binder type on molding sands' friability [11, 13-14].*

The permeability of all molding sands with inorganic binders is at a similar level.

Friability tests follow the results of strength tests. All molding sands with inorganic binders are characterized by higher friability than sands with organic binders.

Tests on technological properties such as strength, permeability, and friability of microwave hardened molding sands were carried out (figs. 20-22) [12]. The strength of molding sands made with modified binders is on average 80% of the initial bending strength, while in the case of tensile strength it is 86% of the initial value [12].

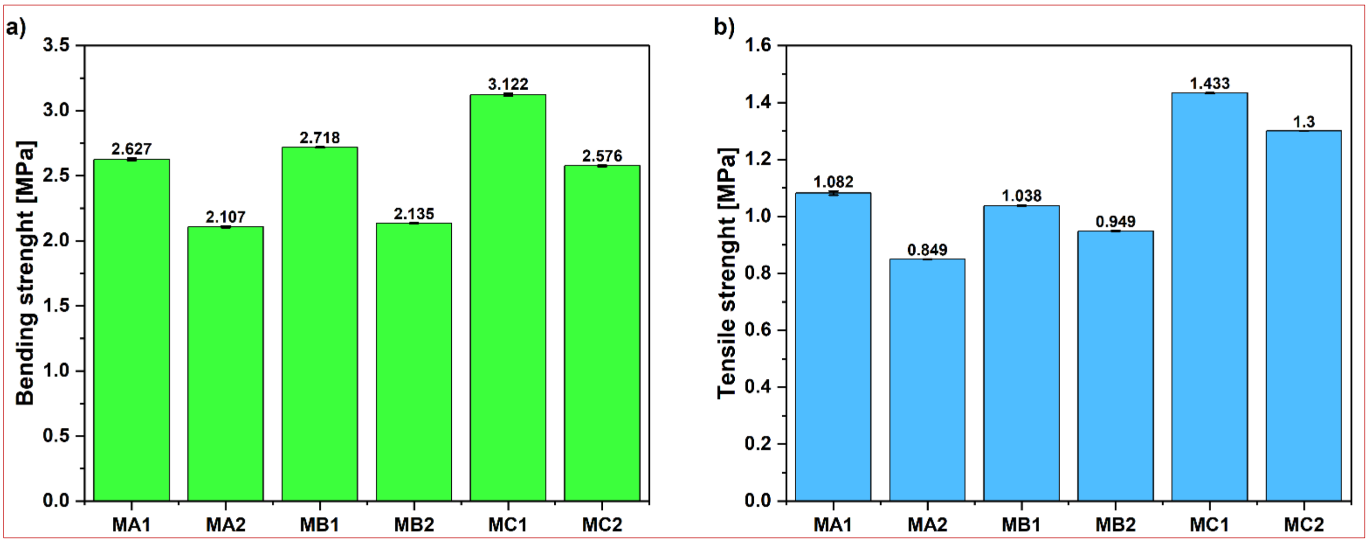


Fig. 20. *a) Bending strength b) tensile strength of microwave hardened molding sands [12].*

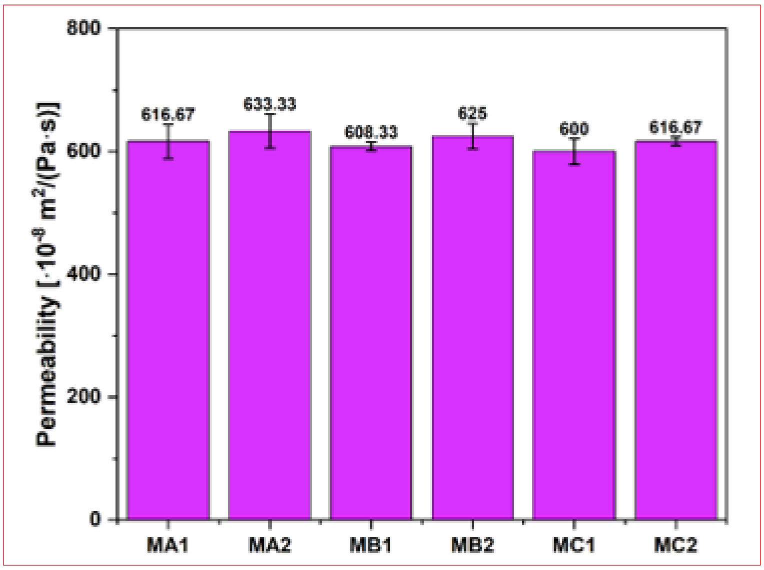


Fig. 21. *Permeability of microwave hardened molding sands [12].*

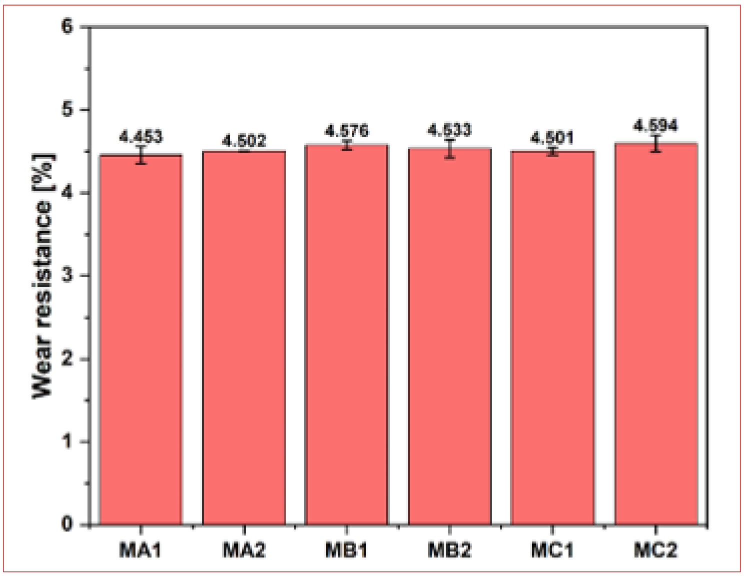


Fig. 22. *Friability of microwave hardened molding sands [12].*

2.3.5 Thermal deformation of tested molding sands

Thermal deformation tests were conducted based on the measurement of the hot-distortion parameter. The results were presented on figs. 23-24 [11-14]. Compounds with organic binders exhibit typical curve patterns with an initial increase in deformation and rapid destruction of the fittings. The thermal deformation of compounds with inorganic binders is more stable, but occurs in a shorter time and at a lower temperature. The exception is the molding sand with modified binder A - A_{3D} and hardener Ixional, and the molding sand with modified binder B - B_{3D} hardened with Flodur. These sands are characterized by good thermal stability. Microwave hardened molding sands made with modified binders (A_{3D}, B_{3D}, C_{3D}) are characterized by a longer thermal resistance time (hot-distortion parameter) [12].

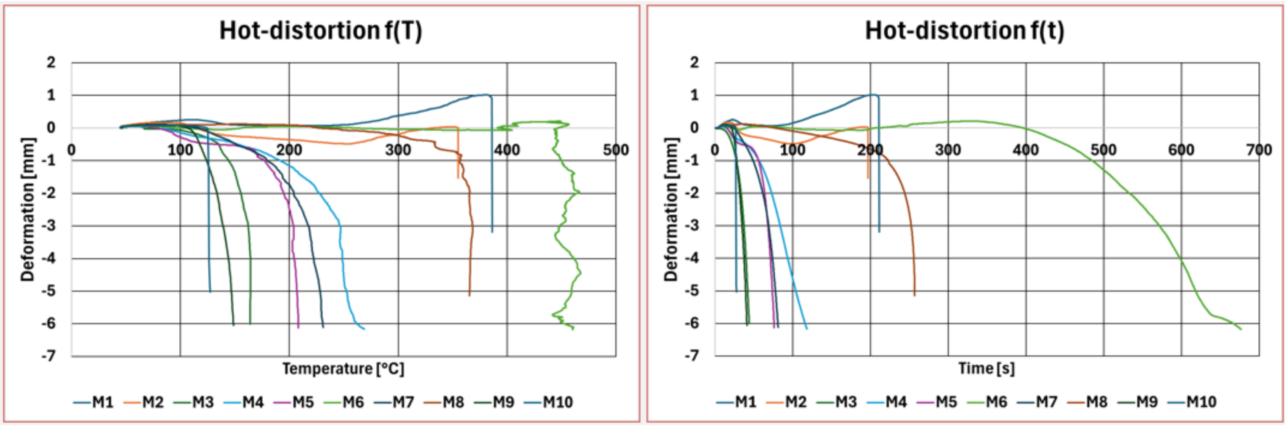
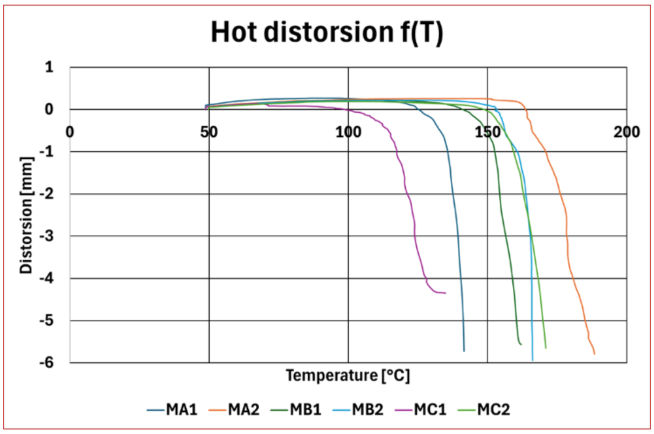


Fig. 23. *The influence of binder type on self-hardened molding sands' thermal deformation in the temperature function (left) and in the time function (right) [11, 13-14].*



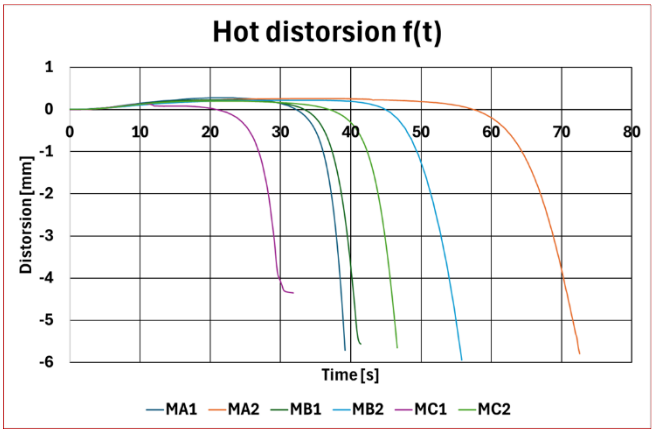


Fig. 24. *The influence of binder type on microwave hardened molding sands' thermal deformation in the temperature function (left) and in the time function (right) [12].*

3. Conclusions

The following conclusions were drawn based on data analysis and own research:

1. 3D printing enables the production of molds and cores with complex shapes that are impossible to achieve using conventional methods, which can be useful in the production of thin-walled cast iron castings.
2. Strict regulations in the Green Deal policy force the search for new technologies in the field of foundry molding sands.
3. Inorganic binder systems are environmentally friendly technologies and can be an alternative to organic binder systems in modern technologies.
4. The physicochemical properties of commercial inorganic binders can be adapted to the properties of binders dedicated to 3D printing.
5. High reactivity of Ixional binder may be useful in inorganic molding sand systems intended for 3D printing.
6. Microwave hardening of molding sands with inorganic binder ensures high mold and core properties with reduced binder consumption.

Future research will be focused on optimizing the hardening process of molding sands with inorganic binders and finally, their impact on thin-walled castings' properties.

Funding/Acknowledgments:

The research is co-financed within NetCastPL4.0 project. The project is funded by the European Union under the Horizon Europe programme, Grant Agreement No. 101159771.

The research was co-financed by AGH University Research Project No 16.16.170.654 and by the National Science Centre (NCN) - Grant No. 2021/41/B/ST5/02632.

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