

Effect of binder composition on the shrinkage of chemically bonded sand cores

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Abstract

Modern foundries increasingly use chemically-bonded no-bake sand cores and molds because they provide ease of molding, good surface finish, and collapsibility. One of the most popular binder systems is oil urethane no-bake comprising three parts: alkyd resin, catalyst, and crosslinking agent. Their amounts and ratios can influence mold shrinkage, and thereby dimensional quality of the resulting casting. With rising emphasis on net-shape casting, there is a need to optimize the binder composition to minimize the dimensional errors, while achieving the desired bench life, stripping time and hardness. This work investigates the effect of binder composition on the dimensions of chemically-bonded sand cores (25 mm diameter and 100 mm length) with respect to time. The maximum shrinkage of 0.15% over length was observed when resin content was 2.4% by weight of sand. The rate of shrinkage was higher with increase in the amount of catalyst. Core hardness and reduction in weight were also measured followed by SEM studies to gain a better understanding of the underlying phenomena, including formation of resin bridges between compacted sand particles and evaporation of solvent. This work is expected to aid in selection of the most appropriate binder composition for a given set of molding process constraints and cast product requirements.

Keywords: Alkyd resin, Oil Urethane, Chemically Bonded Core/Mold, Core Shrinkage

1. INTRODUCTION

Sand casting accounts for over 80% of cast parts produced worldwide. It has advantages of lower cost of tooling, wider range of metals, and less constraints in part geometry, especially when compared to permanent mold processes (Saikaew & Wiengwiset, 2012). Several steps are however, involved in producing sand molds, including sand preparation, sand filling in mold, stripping the pattern, and placing the cores. Hence the dimensional accuracy of sand cast parts is considerably poorer compared to metal molds. With increasing demand for near-net parts, there is a need to understand and improve the dimensional accuracy of sand cast parts (Thiel, 2011).

The type of binder system used for sand molding affects dimensional stability. The binders provide the required strength and refractoriness during molten metal filling in mold cavity. At the same time, they should enable the desired bench life (before molding should be completed), stripping time (after which pattern should be removed), hardness (to retain their

shape) and collapsibility (after casting). In recent years, several different binder systems have been introduced in foundry industry, which are reported to have better dimensional accuracy and surface finish compared to green sand casting processes (Iyer et al., 2001). In particular, chemically bonded molds were found to be more suitable (than green sand molding) for producing intricate castings with thin walls and good surface finish (Khandelwal and Ravi, 2014) coupled with ease of use (less ramming required), shorter lead time, and cleanliness.

Selection of the molding process and type of binder depends on the size and number of cores or molds required, production rates and equipment, besides other factors mentioned above. Binder systems can be classified based on the type of chemicals and curing mechanism (Table 1). In no-bake and cold box processes, the molds are cured at room temperature, whereas in shell molding, hot box and oven-bake processes, the molds are cured by heating. The binder and its (binding) mechanism can influence the defects in casting, microstructure after solidification and emission at workplace environment (Giese, Roorda, & Patterson, 2009) (Kim, Kim, & Kim, 2002).

Table 1: Resin binder systems

Category	Process Name	Binder Chemicals	Catalyst/Hardener
Heat-Cured	Shell Process	Phenol-formaldehyde Novolac resin	Hexamethylenetetramine
	Hot Box	Furan or phenolic resin	Chloride and nitrate
	Warm Box	Furan resin	Latent acid
	Oven Bake / Core Oil Binders	Linseed or vegetable oil	Cereal + bentonite + water
Cold box	Phenolic Urethane	Phenolic resin + polymeric isocyanate	Tertiary amine vapor
	SO ₂ Process	Furan binder	SO ₂
	FRC process	Acrylic-epoxy binder	Hydroperoxide + SO ₂
	Phenolic Ester	Alkaline phenolic resin	Vaporized easter catalyst
	Sodium silicate/CO ₂ System	Sodium silicate	CO ₂
No Bake	Furan acid catalyzed	Furan binder	Acid catalyst
	Phenolic acid catalyzed	Phenolic resin	Acid catalyst
	Oil Urethane	Alkyd resin + polymeric MDI	Liquid amine
	Phenolic Urethane	Phenol formaldehyde + polymeric MDI	Liquid amine
	Easter cured alkaline phenolic	Alkaline phenolic	Liquid easter
	Silicate or easter-catalyzed	Sodium silicate	Liquid easter
	Polyol-Isocyanate system	Liquid polyol resin	Liquid polyisocyanate
	Alumina-Phosphate	Liquid Alumina-phosphate	Powered metal oxide

Dimensional accuracy has become very important with rising emphasis on near-net and light-weight parts. Castings with thin walls have lower allowable margin of error, especially when cores are involved. In complex-shaped thin-wall castings like cylindrical block and head, it is important to investigate and control every possible cause of dimensional variation. Such castings are produced as an assembly of cores, making it difficult to produce dimensionally accurate castings (Ayoola, Adeosun, Sanni, & Oyetunji, 2012). Core shrinkage has been identified as a major cause and usually compensated by adjusting the overall shrinkage factor in the design of tooling. There is however, a lack of experimental data related to various factors affecting shrinkage in resin-bonded cores and molds.

A few researchers have investigated and reported the effect of chemically bonded molds, including dimensional changes (Lowe & Showman, 2011). Influence of varying binder content of phenolic urethane binder on heat the transfer rate for thin wall casting has been investigated (Giese et al., 2009) (Giese, Ravi, Boss, & Biersner, 2012). Studies of dimensional changes in phenolic urethane cold box process showed only a small amount of shrinkage over a period of 24-48 hour (Showman et al., 2009). Their work, as well as a few others (Werling 2004) relied on dial indicators to observe core shrinkage. Lowe & Showman (2011) investigated dimensional changes in core by varying sand grain size in humid environment. They studied PUCB (phenolic urethane cold box), PUNB (Phenolic urethane no bake) with SO₂ catalyst, AECB (acrylic epoxy cold box) with CO₂ catalyst, Furan No-bake with an acid catalyst, and heat cured binder system.

In recent years, alkyd oil urethane no-bake resin binder system has become increasingly popular in both ferrous and non-ferrous foundries. It is also known as polyester urethane or three-part no-bake system. Part A is alkyd oil urethane resin. Part B is liquid amine or metallic catalyst, also called as alkyd activator. Part C is a polymeric MDI (methyl diisocyanate), which is a crosslinking agent. Major advantages are high strength, moderate rate of gas evolution, good humidity resistance, and fair erosion resistance (Walton & Opar, 1981). The alkyd resin provides a long work time and still achieves maximum hardness when completely cured. It is found to be equally suitable for producing small, medium or large molds (Foundryman, 1999). There is however, very little reported work on the effect of binder composition on the dimensions and properties of the cores and mold produced by three part binder system. This has been taken up in the present work.

2. Experimental Procedure

This research work focuses on oil urethane no-bake binder with the goal of studying and understanding the effect of binder composition, including the content and ratio of the three parts (alkyd resin, catalyst, and crosslinking agent) on shrinkage along the length of cylindrical cores produced using the binder. The detailed methodology is described here.

Core Making

As mentioned earlier, the oil urethane no-bake binder is a three part system comprising: (a) alkyd oil urethane resin, (b) liquid amine or metallic catalyst, and (c) polymeric MDI crosslinking agent. The resin and catalyst control the degree and time of binding, respectively. These two are mixed first, and added to silica sand of suitable grain size. This is referred to as premix. Then the crosslinking agent is mixed in the premixed sand. The final mixture of sand and chemicals is poured in a core box. The polymeric MDI begins to crosslink with the resin at a rate controlled by the catalyst.

In a series of experiments carried out in this investigation, the composition of the binder was varied as shown in Table 2. While the amounts as well as ratios of alkyd resin and catalyst were varied, the amount of crosslinking agent was kept at 20% of alkyd resin for all experiments. All cores had the same dimensions: diameter of 25 mm, and length of 100 mm.

Table 2: Binder composition for different experiments

Experiment	Sand Weight (g)	Alkyd resin		Catalyst		Crosslinking Agent	
		Weight (g)	% Weight of sand	Weight (g)	% Weight of sand	Weight (g)	% Weight of sand
1	100	2.4	2.4	0.36	15	0.48	20
2	100	2.4	2.4	0.24	10	0.48	20
3	100	2.4	2.4	1.12	5	0.48	20
4	100	2.0	2.0	0.30	15	0.40	20
5	100	2.0	2.0	0.20	10	0.40	20
6	100	2.0	2.0	0.10	5	0.40	20
7	100	1.6	1.6	0.24	15	0.32	20
8	100	1.6	1.6	0.16	10	0.32	20
9	100	1.6	1.6	0.08	5	0.32	20

Shrinkage Measurement

A fixture as shown in figure 1 was set up for measuring core shrinkage. A spring-loaded dial gauge with a least count of 0.001 mm was placed in the fixture. The cores produced as mentioned above were immediately placed in the fixture, in an inclined position, to reduce the possibility of core deflection. The dial gauge readings were taken initially at an interval of 15 minutes, and afterwards every hour, for total period of 24 hours.



Fig. 1: Core shrinkage measurement fixture



Fig. 2: Mold hardness measurement

SEM Imaging

Scanning electron microscopy (SEM) studies were carried out to gain a better understanding of the shrinkage mechanism. For this purpose, separate cylindrical specimens of 15 mm diameter and 10 mm length were prepared with the chemical binder composition for the second experiment given in Table 1. The SEM imaging was performed on the specimens using ZEISS Ultra-55 SEM available in IIT Bombay. The resolution of this instrument, which was about 1.2 nm, allowed the detection of fine particles in the specimens.

Weight Reduction

To gain addition insight, continuous weight reduction of bare chemical mixture was also investigated. For this purpose, samples were prepared using the composition shown in Table 2, but without any sand. An analytical balance (Sartorius model CPA 324S), with a resolution of 0.1 mg, was used to measure the weight of samples.

Core Hardness

Measurement of hardness of oil urethane resin-bonded cores was also carried out to obtain further insight. Nine rectangular blocks of size 15cm x 15cm x 5cm were produced with the same sand mixture used for making the earlier cores for shrinkage measurement. Their hardness was tested three hours after mixing, using a hardness tester shown in figure 2. Its knife-edge radius tipped carbide plough is pressed against the core surface and pulled slowly over a distance of about 25 mm to obtain the hardness reading.

3. Results and Discussion

The shrinkage measurements were carried out on two samples of each core for 9 different compositions (binder content and ratio) over a 24 hour period using a dial gauge mounted in a special fixture as described earlier. The results, including the average value of two measurements for each experiment, are given in Table 3.

Figure 3 shows the graph of average core shrinkage plotted against time for all (9) compositions. All showed a clear trend of increasing shrinkage over the time period of 24 hours, initially at a rapid rate, and gradually slowing down. Figure 4 shows the shrinkage for experiments 2, 5 and 8, in which alkyd resin content was varied as 2.4%, 2% and 1.6% of sand weight, respectively; the catalyst was held at 10% of resin, and crosslinking agent was held at 20% of resin in all these three experiments. It is observed that core shrinkage increases with binder content, reaching 0.14 mm per 100 mm at the end of 24 hours, for experiment 2. The lowest shrinkage was 0.082 mm per 100 mm, for experiment 8. Nearly half of the shrinkage takes place within the first three hours after mixing, and can be ascribed to the initial rapid curing of binder system. Figure 5 shows core shrinkage when resin content is kept at 2% of silica sand, and the catalyst content is varied from 15% in experiment 4, to 10% in experiment 5, and further to 5% in experiment 6. The overall shrinkage value remains the same in all these experiments, though a higher amount of catalyst gives a slightly higher rate of initial curing (and therefore high shrinkage).

Table 3: Core shrinkage (mm) with time for different binder content

Time (h) Expt.	0	0.25	0.5	0.75	1	3	5	14	18	24
1-1	0	0.016	0.032	0.044	0.06	0.074	0.090	0.117	0.130	0.143
1-2	0	0.016	0.036	0.048	0.058	0.086	0.102	0.119	0.130	0.145
1-Avg	0	0.016	0.034	0.046	0.059	0.080	0.096	0.118	0.130	0.144
2-1	0	0.014	0.028	0.044	0.058	0.072	0.090	0.112	0.127	0.143
2-2	0	0.010	0.028	0.040	0.050	0.066	0.086	0.116	0.129	0.141
2-Avg	0	0.012	0.028	0.042	0.054	0.069	0.088	0.114	0.128	0.142
3-1	0	0.012	0.028	0.039	0.052	0.074	0.086	0.112	0.126	0.144
3-2	0	0.010	0.026	0.043	0.050	0.068	0.084	0.112	0.116	0.140
3-Avg	0	0.011	0.027	0.041	0.051	0.071	0.085	0.112	0.121	0.142
4-1	0	0.010	0.026	0.032	0.040	0.064	0.076	0.098	0.103	0.118
4-2	0	0.014	0.028	0.036	0.040	0.058	0.066	0.092	0.101	0.115
4-Avg	0	0.012	0.027	0.034	0.040	0.061	0.071	0.095	0.102	0.1165
5-1	0	0.012	0.026	0.036	0.040	0.057	0.070	0.091	0.102	0.114
5-2	0	0.012	0.025	0.034	0.038	0.063	0.072	0.097	0.104	0.116
5-Avg	0	0.012	0.0255	0.035	0.039	0.06	0.071	0.094	0.103	0.115
6-1	0	0.016	0.026	0.033	0.040	0.060	0.069	0.096	0.102	0.116
6-2	0	0.013	0.024	0.033	0.034	0.058	0.069	0.090	0.099	0.116
6-Avg	0	0.0145	0.025	0.033	0.037	0.059	0.069	0.093	0.1005	0.116
7-1	0	0.010	0.020	0.025	0.026	0.042	0.046	0.062	0.074	0.084
7-2	0	0.006	0.012	0.019	0.024	0.036	0.046	0.066	0.074	0.080
7-Avg	0	0.008	0.016	0.022	0.025	0.039	0.046	0.064	0.074	0.082
8-1	0	0.008	0.018	0.020	0.024	0.039	0.052	0.065	0.072	0.079
8-2	0	0.008	0.014	0.020	0.022	0.033	0.044	0.064	0.074	0.085
8-Avg	0	0.008	0.016	0.020	0.023	0.036	0.048	0.0645	0.073	0.082
9-1	0	0.006	0.014	0.016	0.020	0.030	0.038	0.062	0.071	0.082
9-2	0	0.008	0.013	0.020	0.022	0.036	0.046	0.064	0.071	0.078
9-Avg	0	0.007	0.0135	0.018	0.021	0.033	0.042	0.063	0.071	0.080

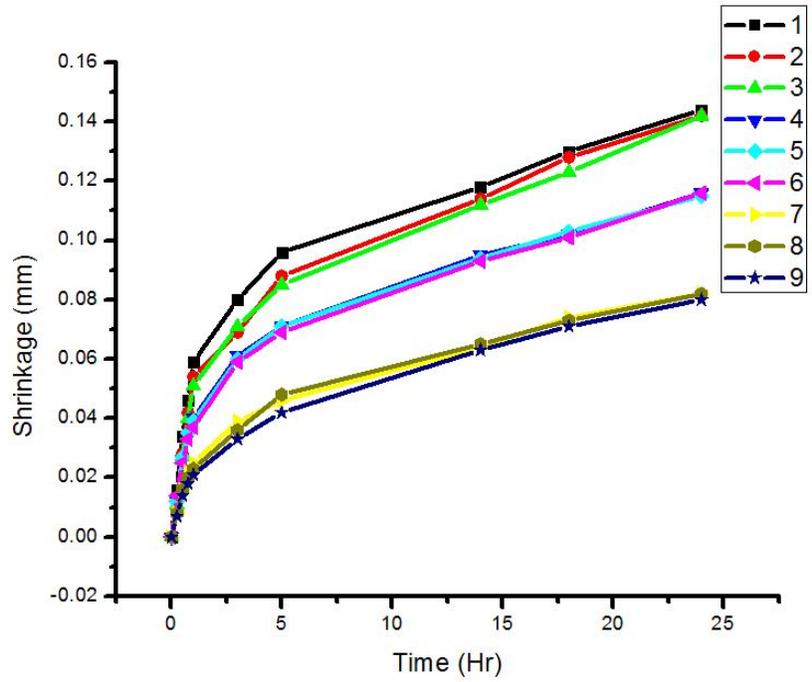


Fig. 3: Shrinkage of nine sand cores with different binder composition

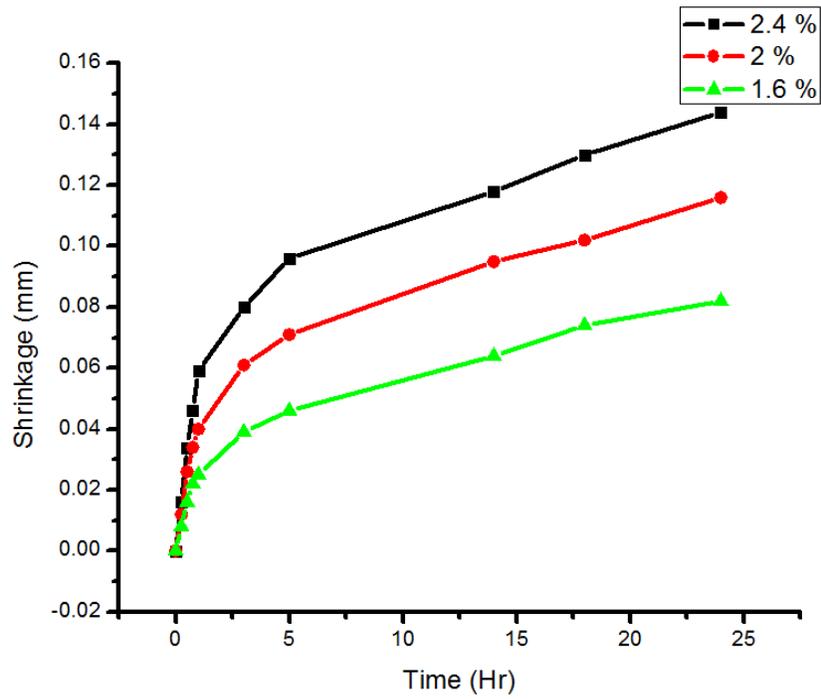


Fig. 4: Shrinkage of sand cores with varying resin content

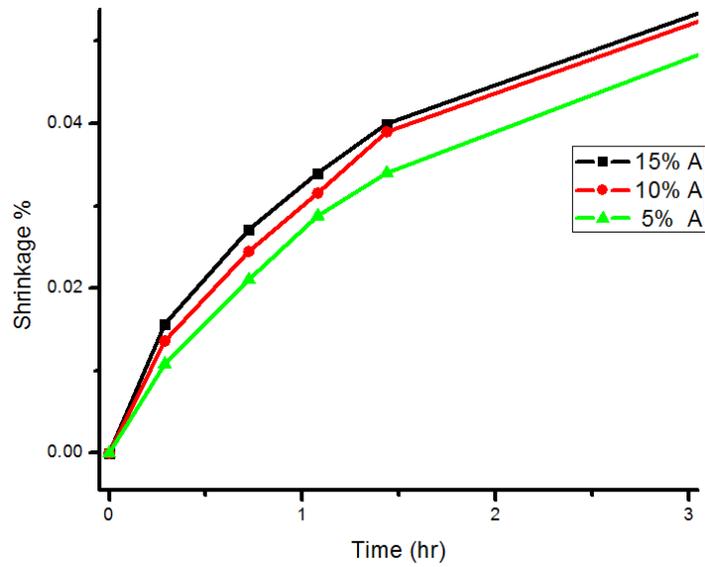


Fig. 5: Shrinkage of sand core with varying catalyst content

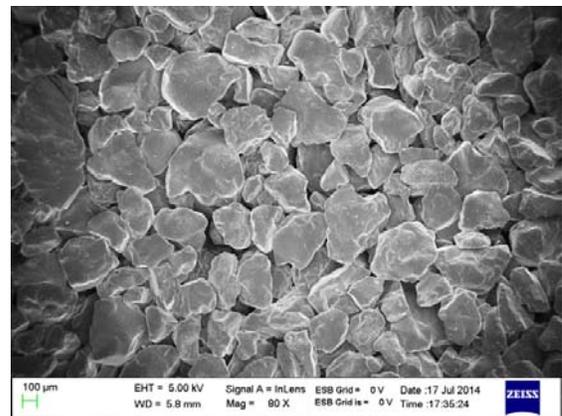
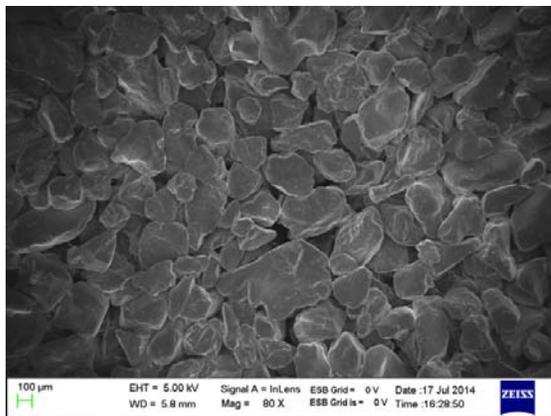


Fig. 6: SEM micrograph shows irregular sand grains bonded with Alkyd resin

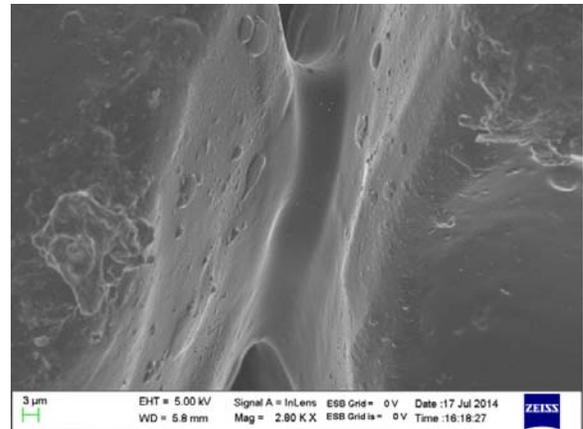
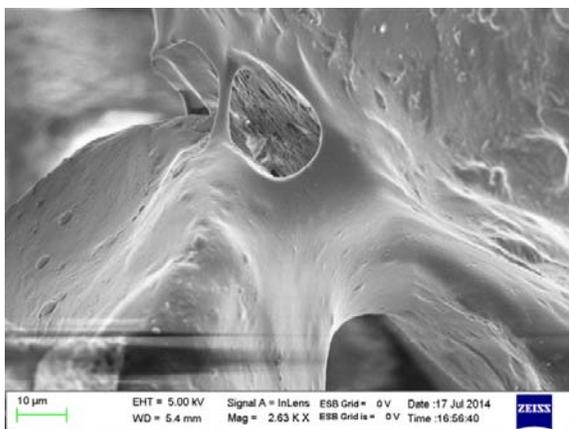


Fig. 7: SEM micrograph shows resin bridges between sand grains

The curing mechanism of oil urethane no-bake binder system, which affects core shrinkage, is difficult to understand because of two separate curing stages. After mixing the binder in sand, polymeric MDI starts crosslinking with alkyd resin at a rate controlled by the catalyst. This action produces a thin and uniform layer of liquid urethane coating on sand grains. The sand is introduced into the mold box after this stage. This brings the sand particles closer; the liquid coated surfaces of adjacent sand grains come in contact with each other, experience surface tension, and form resin bridges. Then the second stage of curing takes over, when oxygen in air combines with the alkyd resin and polymerizes it fully to form a tough urethane bond.

Figure 6 shows the SEM image of two similar samples of sand core at the end of 24 hours of curing. Before imaging, the samples were gold sputtered in order to increase their electrical conductivity, leading to a reduced noise level and enhanced image contrast. The crosslinking resin bridges between sand grains can be clearly observed (Figure 7). Curing allows resin bridges to harden and form a network, providing strength to core.

The curing mechanism however, also results in shrinkage, which has been explained in different ways by previous researchers. The main theory is that thermoset resins cure by crosslinking of the polymer chain (polymerization reaction), which results in resin bridges to shorten and pull the sand grain closer together (Lowe & Showman, 2011). This leads to higher strength as well as shrinkage of the cores. The curing process continues for 24 hours, though at a slower rate later, accompanied by increasing strength and shrinkage. An alternate explanation for the shrinkage is in terms of the solvent, which is used in resin binders to reduce their viscosity. The solvents (up to 30% by weight) are relatively volatile and tend to evaporate over time, resulting in volumetric reduction of resin bridges and shrinkage of core. A more volatile solvent will show faster shrinkage.

Another series of experiments, using the chemicals alone, were conducted to further understand the underlying phenomena. The chemicals were mixed in the same ratio as indicated in table 2, except that no sand was added. Table 4 shows the amount of chemicals used for these experiments: 100 grams of alkyd resin along with catalyst and crosslinking agent. The chemicals were mixed and continuously weighed for 3 hours. Figure 8 shows the reduction in weight in the three experiments. The rate of weight reduction decreases with reduced content of catalyst, from experiment 1 to 2 to 3. The higher rate of weight reduction with higher amount of catalyst can be ascribed to the higher rate of solvent evaporation. This also explains the higher rate of shrinkage, caused by a faster rate of reaction due to the larger amount of catalyst, as shown earlier in figure 5.

The results of core hardness testing are shown in figure 9. It is observed that core hardness decreases with decreasing resin percentage (from 2.4 to 2 to 1.6%). For the same percentage of resin, core hardness was observed to reduce with decreasing percentage of catalyst. Clearly, the rate of reaction slows down with decreasing amount of catalyst, leading to reduced core hardness. The same explanation also holds good for core shrinkage.

Table 4: Binder composition for weight reduction experiments

Experiment	Alkyd Resin (g)	Catalyst (g)	Crosslinking Agent (g)
1	100	15	20
2	100	10	20
3	100	5	20

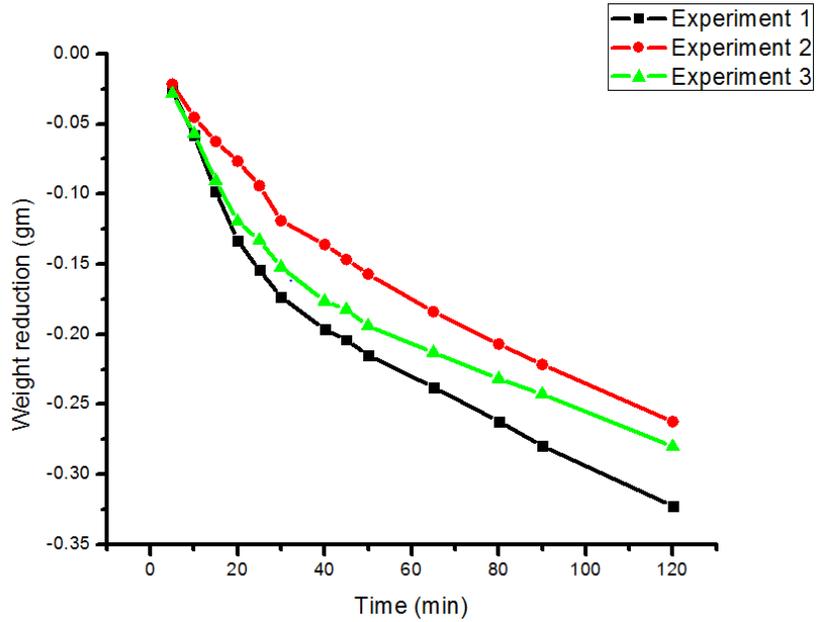


Fig. 8: Continuous weight reduction with varying catalyst content

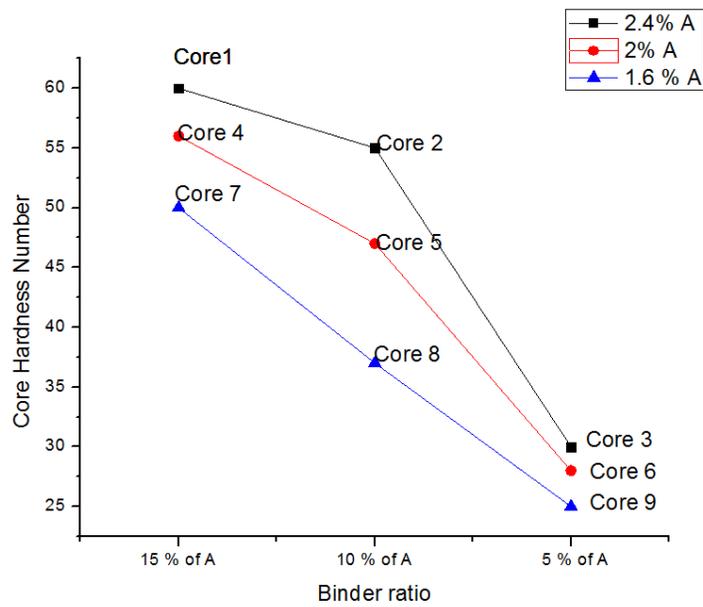


Fig. 9: Hardness of cores (with varying resin content) after 3 hours

4. Conclusion

In this work on oil urethane no-bake binder system, the effect of binder composition, in terms of the amount and ratio of the three parts (resin, catalyst and crosslinking agent) on the shrinkage of cores has been investigated. The dial indicator used in the fixture developed for measurement of dimensional changes was easy to use and gave reproducible data. The main observation is that a higher amount of resin leads to increased shrinkage of cores; up to 0.15% in length when resin content was 2.4% by weight of the sand. An increased amount of catalyst (keeping resin content constant), showed almost the same extent of total shrinkage, though it increases the initial rate of shrinkage (during the first three hours after curing). Further investigations using SEM, weight measurement and hardness testing shed some light on the shrinkage mechanism. During polymerization reaction of the resin, bridges are formed between sand particles compacted in mold. The solvent present in the resin bridges gradually evaporates, resulting in shortening of the bridges and leading to core shrinkage. This was proved by weight reduction measurement experiments involving chemical mixture alone (without sand). Another useful observation is that a higher percentage of catalyst leads to faster curing, and thereby a higher initial rate of core shrinkage. This is supported by both weight reduction experiments and hardness measurement experiments. We hope that this work will help in optimizing the binder composition and bench time to obtain the desired core hardness along with high dimensional accuracy.

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