2014

The environmental performance of biobased resin within phenolic-urethane nobake binders: A feasibility study

Ian David Morgan Williams
University of Northern Iowa

Recommended Citation

Williams, Ian David Morgan, "The environmental performance of biobased resin within phenolic-urethane nobake binders: A feasibility study" (2014). *Dissertations and Theses @ UNI*. 54.
https://scholarworks.uni.edu/etd/54

THE ENVIRONMENTAL PERFORMANCE OF BIOBASED RESIN WITHIN PHENOLIC-URETHANE NOBAKE BINDERS:

A FEASIBILITY STUDY

An Abstract of a Thesis

Submitted

in Partial Fulfillment

of the Requirements for the Degree

Master of Arts

Ian David Morgan Williams

University of Northern Iowa

May 2014

ABSTRACT

The objectives of this research were to investigate the discovery and development of a biobased nobake binder resin for use within the foundry industry toward improved energy efficiency and environmental performance. The performance of polysaccharides within biobased resins was evaluated using industry-accepted methods and standards such as cure rate, tensile-strength development, and casting performance based upon step cone core results. Biobased nobake resins comprised of polysaccharide raw materials cure at a rate that is comparable to conventional nobake sand binders. Upon reaching stripping time, the development of biobased resin reveals a rapid increase in tensile strength, reaching 80% of its 24-hour strength within the first 10 minutes. Step cones produced with polysaccharide resins possess greater resistance to the formation of veining and penetration defects within ferrous castings. Based upon the physical characteristics of the binder and the defect analysis of the step cones, polysaccharides can serve as a complete substitute for oil based components of a nobake binder system.

THE ENVIRONMENTAL PERFORMANCE OF BIOBASED RESIN WITHIN PHENOLIC-URETHANE NOBAKE BINDERS:

A FEASIBILITY STUDY

A Thesis

Submitted

in Partial Fulfillment

of the Requirements for the Degree

Master of Arts

Ian David Morgan Williams

University of Northern Iowa

May 2014

This Study by: Ian David Morgan Williams

Entitled: THE ENVIRONMENTAL PERFORMANCE OF BIOBASED RESIN WITHIN PHENOLIC-URETHANE NOBAKE BINDERS: A FEASIBILITY STUDY

has been approved as meeting the thesis requirement for the

Degree of Master of Arts

Date Dr. Scott Giese, Chair, Thesis Committee Chair

Date Dr. Shoshanna Coon, Thesis Committee Member

Date Dr. Julie Zhang, Thesis Committee Member

Date Dr. Michael J. Licari, Graduate Dean

TABLE OF CONTENTS

PAGE

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Statement of the Problem and Purpose of the Study

Consumer demand for oil, oil-based products, and products produced with oil continues to grow. Consequently, manufacturing companies, such as those within the foundry industry, not only compete for limited resources, but pay an increasingly higher premium for these resources. Additional cost originates in the adherence to environmental regulations, which limits the release of hazardous compounds commonly used in metalcasting processes. Reducing the demand for oil within foundries is therefore of vital importance if this industry is to remain competitive within the global marketplace.

The U.S. Department of Energy has encouraged research into the possible application of alternative biobased adhesive materials, which can replace chemicals produced from oil. The ultimate goal is to find an innovative solution to reducing the "carbon footprint" of foundry technology and limit the dependence on oil within the industry. Chemical binders are synthetic-resin material used to hold grains of sand together in molds and cores (Thomas-Sabowski, 2005). Binders are mixed with sand grains and packed in a *pattern*, which is a positive impression used to form a cavity in the sand. The mixture of sand and nobake binder hardens with the aid of a catalyst or a coreactant to form a mold

Significance of the Study

Since the 1970s, the phenolic urethane nobake (PUNB) binders have been used to make expendable sand molds within the metalcasting industry. This process of manufacturing cores/molds has been widely accepted as a method of production, comprising 50% of the resin binders used across North America (Carey & Haugse, 1998). The PUNB chemical sand binder is produced from a variety of oil-based products. Carey (1998) characterized the binder as a three-part system comprised of (a) an oil-based polyol resin (i.e., Part 1); (b) a polymeric, methyldiisocyanate-type isocyanate (NCO; i.e., Part 2); and (c) a liquid amine catalyst (i.e., Part 3). The parts are combined in stages of calculated amounts with approximately .7% to 1.6% based on sand (BOS), 45% based on resin (BOR), and 3% to 7% on BOR, respectively. These components coat the sand to form an adhesive, which has predictable casting-specific qualities such as work time, stripping time, tensile strength, and casting performance (Schleg, 2003). The work or stripping time is determined by the speed of the initial phenolic-urethane reaction and is inversely proportional to Part 3. The reaction is temperature specific and designed to operate between the ranges of 75° F to 85° F. Temperatures below 50° F retard the polymerization process, while temperatures above 110° F prematurely accelerate the phenolic urethane reaction.

As reported by Schleg (2003), essentially every foundry using chemically bonded sand systems uses tensile strength and cure time as primary control tools measuring the quality of the process. Tensile strength must be sufficiently high to facilitate stripping from the pattern, handling or moving of the mold, and maintaining dimensional stability during the pouring stage. The cure time must be sufficiently short to accommodate moderate rates of production.

PUNB binders contain petroleum-based resin components such as phenol formaldehyde (PF) and solvents used in reducing the viscosity, which are environmentally hazardous compounds. The U.S. Department of Energy formed a coalition with the metalcasting industry to “accelerate the development of technologies and processes that will improve the industry’s energy efficiency and environmental performance” (Margolis, Jamison, & Dove, 1999, p. 1).

Hypothesis

H_o = No difference of tensile strength between PH3 and PUNB.

Compounds of PF contain hydroxyl (OH) functional groups, which are necessary for bonding with the isocyanate functional groups contained in Part 2 of PUNB system. Common agriculturally based (i.e., biobased) material containing OH groups can replace PF as a resin Part 1 in the PUNB process to match the casting characteristics of the conventional oil-based resin. A biobased replacement for the Part 1 component can be formulated from common material derived from agricultural products. The objective of this current research was to gain an understanding of the mechanisms that govern the PUNB chemically bonded binder system both in process and capability. Another aim was to link previous research focused on biopolymers to the discovery of suitable replacement material for the PUNB process. The ultimate goal was to illustrate that biobased material can replace oil-based components, such as PF, used in the production of cores/molds within the foundry industry.

Experiment

The performance of a binder is determined by its ability to produce quality castings. The step cone core is an industry-accepted method of determining the binder tendency to form penetration and veining defects, as well as the evolution of gas during the pouring stage (Tordoff & Tenaglia, 1980). Its application has evolved within the industry and the step cone core is now used to numerically evaluate penetration and veining defects within ferrous metals (Giese & Thiel, 2006). Schleg (2003) noted that the amount of gas evolving from the binder during the casting operation is an important factor of the ability of the core mold to produce a quality casting.

Limitations

The search for a biobased resin substitute was restricted to those materials derived from corn. Both primary and by-products were analyzed in this current study as potential candidates to serve as the raw material within the experimental resin. Material grown within the midwest region of the United States as “bumper crops” were widely available in many forms such as oils and syrups. Both forms are known to be heavily refined, rendering their use as a raw-material ideal. Corn syrup was selected due to its high concentration of OH groups, which are crucial in the urethane reaction. Corn syrup is available in a variety of viscosities. Highly viscous blends indicate the high concentration of OH groups with a minimum presence of water.

The foundry industry producing chemically bonded sand utilizes a wide variety of sands in the production of metalcasting, the choice of sand is determined by several factors. Sand must be compatible to metal (i.e., the binder); it must be commercially available; and engineering factors may call for a specific grain size and shape. In many cases, regional availability limits the use of specialty sand by foundries because the cost of processing and transporting the product to such facilities represents a major investment. Due to these factors, a commercially available and commonly used pure silica sand was selected in this current study. Table 1 provides a basic profile of the physical/chemical characteristics and grain distribution of this material.

The metal used in this research to evaluate binder performance was Type 35 grey iron. When selecting a metal for casting and subsequent evaluation in the performance of the binder, it was important to choose a material used by a large market share of companies currently utilizing PUNB binder systems. In addition to competing in markets dominated by PUNB binders, it was important to expose the experimental binder to a high degree of heat. When subjected to such a destructive environment, observation can determine the degree to which the experimental binders are capable of withstanding extreme temperature. If the experimental binder is found to produce favorable results in cast finish and integrity at a high pouring temperature, similar if not better results could be expected in nonferrous alloys at lower pouring temperatures.

The hand held thermocouple used for gathering melt temperatures was manufactured by Heraeus Electro-Nite™. It primary use was to measure heat loss during the duration of the Heat. The thermocouple requires time to reset between measurements. Due to this design limitation, a temperature for each casting was not be able to be captured during the experiments.

Table 1

American Foundry Society Grain Fineness and Sand Distribution

Screen	Individual retained (g)	Percentage retained	Multiplier	Product
20	0.000	0.000	0.2	0
30	1.435	2.156	0.3	0.64
40	8.935	13.424	0.4	5.36
50	16.592	24.929	0.5	12.46
70	20.560	30.890	0.6	18.53
100	12.444	18.696	0.7	13.08
140	5.788	8.696	1	8.69
200	0.694	1.043	1.4	1.45
270	.078	0.117	2	0.23
pan	.032	.048	3	0.14
Total	66.558			60.63 GFN

Note. LOI = loss on ignition = .0008%; H_2O = water = .04%; ADV = acid demand value = 4.8, GFN = grain fineness number.

Definition of Terms

A *binder* is a material, other than water, added to sand to bind particles together, sometimes with the aid of heat.

A *centipoise* is a unit of viscosity equal to 1/100 poise.

Curing time (i.e., nobake) is the period of time needed before sand mass reaches maximum hardness.

Grain-fineness number is a system developed by the American Foundry Society (AFS) for expressing the average grain size of a given sand.

Nucleophilic characteristics is an atom, ion, or molecule serving as an electron donor.

Pyrolysis refers to a chemical change induced by the action of heat.

Resorcinol is a white crystalline compound used in the production of dyes, resin adhesives, and pharmaceuticals.

Tensile strength refers to the maximum stress in the uniaxial tension testing that a material will withstand prior to fracture.

Viscosity is the property of resistance to flow in a fluid or semifluid.

CHAPTER 2

LITERATURE REVIEW

Historical Background

The use of biobased binders is a legacy science dating back to 16th-century France when sand was first introduced as a molding material (Lessiter & Kotzin, 2002). Vannoccio Biringuccio is regarded as the "father of the metal casting industry," publishing the first account of foundry practice, which recommended the use of beer and urine as sand binders (as cited in Lessitier & Kotzin, 2002, p. 76). Both materials remained in use until the 1900s.

Binder Technology

Core Oils

Agriculturally derived binders have been in use since sand molding was first introduced within the foundry industry. The first core oils were harvested by pressing the seeds of the flax plant (Lessiter & Kotzin, 2002). Without solvent or adequate mixing equipment, large quantities were used to achieve sufficient mold strength. As a result, castings suffered from gas defects. By 1770, varnish solvents, such as rosin, were added to core oils to aid in the dispersion and uniform coating of the sand grains (Brown, 1994). These solvents increased the coating efficiency while reducing the oil addition and gas-related casting defects. Scientific observation during the 1900s provided the industry with a clear understanding surrounding the curing mechanisms of core oils. Oxygen in addition to heat was needed to achieve maximum mold strength. By using oils that oxidize quickly, cure time and the energy needed to cure cores/molds was greatly reduced.

Core oils from linseed, petroleum, soy, tung, and vegetable were commercially introduced as binders during the early 1950s. Tensile strength was achieved by baking the cores/molds. Core oils add very little “green” strength during the molding process. To strengthen the cores/molds while stripping from the pattern, cereals and clays were added to the sand mix. This green strength provides stability while the molds are transported to the ovens where the liquid core oils oxy-polymerize into a crystalline solid. This method of production is limited by the long and energy-intensive cure time. Commercial use of core oils has dropped significantly as the practicality and availability of the nobake technology increased.

Shell Sand

The use of thermosetting plastic as a sand binder was introduced by a German scientist, Johannes Croning, in 1944 (Lessiter & Kotzin, 2002). Dry sand, coated in a chemically cured resin, is activated when exposed to temperatures between 350° F to 600° F. Curing the coated sand is energy intensive due to its use of heat as a catalyst. The *croning process* later became known as the *shell process,* which uses a phenolic resin as a major reactive component. A granular novalac resin is added to sand in a muller where it is heated to allow the resin to melt and coat the individual sand grains. Prior to reaching the activation temperature, the mixture is quenched with water to halt any reaction.

The great advantage of using shell sand is that it only cures sand exposed to heat, allowing foundries to achieve the same production with less sand than would be required to produce solid cores/molds. The casting finishes of the materials produced through this process are known to be of high quality. The shell-sand process remains a vital method of producing intricate cores with high tensile strength. Emissions from this binder include phenol and formaldehyde, which are released during the coremaking, pouring, and shakeout stages. Additional emissions include benzene and toluene (see Appendix A), all of which have been flagged as Hazardous Air Pollutants by the American Foundry Society (AFS) and the Environmental Protection Agency.

Phenolic Urethane Nobake

The next evolutionary step in the use of polymers as a sand binder was introduced during 1958 with the phenolic nobake system (Lessiter & Kotzin, 2002). The acid-cured method of catalyzing the resin and NCO components greatly reduced the energy needed to harden the molds and cores. The process was also known as an *air set* because the binder cures at room temperature without the aid of heat.

In 1970, the PUNB process was further engineered and classified as a three-part system. As seen in Figure 1, Part 1 of the PUNB system involves a phenolic resin containing OH groups. Part 2 uses a diisocyanate containing NCO groups. When the two components are combined, a reaction occurs that “is essentially a nuclephilic attack of the oxygen atom of the phenol on the carbon atom of the di-isocyanate group” (Lytle, Bertsch, & McKinley, 1998). This reaction is accelerated in the presence of a tertiary amine catalyst. The reaction and curing of the cores/molds is dependent upon an array of variables including ambient temperature, sand temperature, binder temperature, moisture content, binder percentage, catalyst percentage, and the acid demand value of the sand.

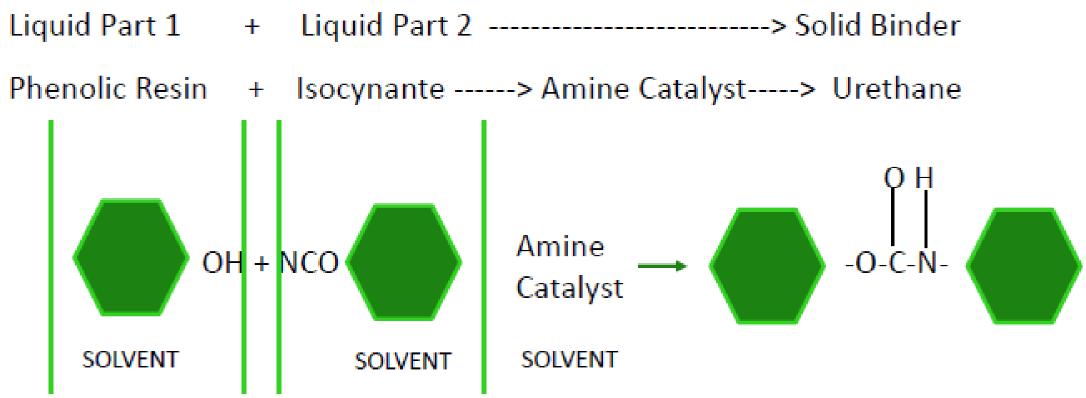

Figure 1. Urethane reaction flow diagram.

A predictable cure rate can be attained in the PUNB system by adding a specific percentage of a catalyst based on resin (BOR). This method of core/mold production is widely used in both ferrous and nonferrous applications due to its versatility. Alterations to the binder and catalyst levels, in addition to an array of additives that enhance specific casting characteristics, have allowed this process to gain widespread acceptance and use within the industry. The extensive advantages with implementation of the PUNB process include ease of use, high production capability, predictability, excellent surface finish, versatility, and dimensional accuracy when used correctly. This binder system although robust, is sensitive to moisture. Sand and individual binder components must be kept dry even from atmospheric moisture as water not only reacts with the isocyanate but it also retards the urethane reaction.

During the introduction of molten metal to molds manufactured with the PUNB process, the binder decomposes rapidly at the elevated temperatures within the mold environment (McKinley, Jefcoat, Herz, & Frederick, 1993). The rate of decomposition is dependent upon temperature and pressure from metal and other gas species such as atmospheric moisture. The emission of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) increases as mold temperature increases (Lytle et al., 1998, p. 128). To better understand the thermal profile of phenolic-urethane binders, Lytle et al. (1998) conducted a range of pyrolysis experiments. These researchers determined that phenolic-urethane resin began to emit the majority of volatiles at 840° F, while sand coated with phenolic urethane still possessed a large portion of volatiles at 1110° F. This apparent discrepancy indicates the high heat capacity of the sand and its ability to absorb heat prior to its transmission to the resin. The PUNB binder system contains chemicals that are released during the core making, pouring, and shakeout stages of production. The emissions released during pouring and shakeout are a result of the thermal decomposition of the binder exposed to elevated temperatures. The specific emissions are presented in Appendix A.

Furan

The furan nobake systems were introduced for commercial use during the same era as the phenolic nobakes. They were classified as a two-part system composed of a resin Part 1 and a catalyst Part 2. The major reactive ingredient is furfuryl alcohol, which is derived from agricultural by-products, such as corn husks, and serves as the raw material of the Part 1 component (Carey & Lott, 1998). A strong acid catalyst is needed to counteract the condensation reaction. During the reaction, water is expelled in the form of vapor, which slows the cure rate (Tordoff & Tenaglia, 1980). Furan binder systems are classified as thermosetting and are extremely reactive at room temperature. Care must be taken to select the correct catalyst. Both excessive and insufficient quantities of catalyst will result in a loss of tensile strength in the cores/molds.

Furan binders have proved to be attractive alternatives to PUNB binders because they do not contain free phenol, formaldehyde, or high levels of harmful HAPs and VOCs. They also do not emit an unpleasant odor during production, which is common with PUNB binders. There are a number of production characteristics that have limited their successful use. They do not cure as rapidly as PUNB binders. Additionally, furan binders are referred to as *deep-set* binders, indicating that the centers of the cores/molds are the last to cure. This slow cure rate presents problems with transportation and handling prior to pouring.

Although Furan binders do not emit unpleasant odors, they do contain a limited number of VOCs including phenol, toluene, and benzene. These are released during the molding, pouring, and shakeout stages. A complete list of emissions is provided in Appendix A.

Low Volatile Organic Compound

Sodium silicate. In 1952, the sodium-silicate binder system was commercially introduced within the foundry industry (Lessiter & Kotzin, 2002). When dry, it is classified as a water-soluble glass. As a binder, it is comprised of silica (SiO_2), soda (Na_2O), and water. The binder can be cured through a number of different methods including dehydration or polymerization. Dehydration is achieved with the addition of powders such as di-calcium silicate or by drying with heat. Polymerization is achieved with the addition of weak acids such CO_2 gas or an organic ester (Brown, 1994). The most common form of curing utilizes gassed CO_2 and was the first gas-hardened binder used within the foundry industry. The cured sodium silicate forms a glassy film or matrix, binding the individual sand grains together. When exposed to molten metal at temperatures above 752° F, the silicate fuses with the sand grains, rendering shakeout difficult in small- and medium-sized ferrous casting. The sodium-silicate binder system possesses excellent environmental characteristics, emitting zero VOCs. It is an easy process to maintain and remains in use as a method for producing cores.

GM Bond™. The future of sand molding is dependent upon the reduction and elimination of hazardous emissions from the molding and pouring processes. Several sand systems have been released since 1994 that advertise zero VOCs. One on the most prominent systems is GM Bond™, which utilizes collagen protein in the form of flakes that resemble the material used in the shell-sand processes.

With use of GM Bond™, the sand grains are first heated in a sand muller where dry flakes are mixed into the sand (Eastman, 2000). Water is then added to the batch to aid in coating. While the sand is being mulled, it is exposed to a dehydration process to coat the sand with a thin layer of protein. Prior to the production of cores, the dry sand is subsequently conditioned with water and blown into the heated core box. The core is exposed to a second dehydration process as the moisture is driven from the core. As the sand mixture dries, it strengthens. If maximum binder strength is needed, the cores proceed through a final drying stage to ensure the binder is fully crystalline. The emissions of GM Bond™ have been reduced by 90% compared to those emitted by PUNB binders (Siak, Whited, Schreck, Biederman, & Datte, 1996). This renders these binder systems attractive to manufacturers seeking compliance with emission standards set forth in clean-air regulations.

Phenolic-urethane nobake. Other binder companies have followed suit in offering low emission and binders. A 1998 patent outlined alterations to the formulation of the PUNB process, which was similar to that of the PUNB binder system in terms of the reactive chemicals used and the reaction itself (Teodorczyk, 1998). Low VOC PUNB binders are three-part systems involving a resin, an isocycanate, and a catalyst. The major difference is that alkyl resorcinols are used as a solvent substitute for those solvents found in PUNB, which contain phenol, formaldehyde, benzene, toluene, naphthalene, and cyanide compounds—all of which are noted in the Clean Air Act Amendment of 1990 as sources of VOCs and commercially regulated.

Along with 189 HAPs, standards for the maximum achievable control technology have encouraged the use of low or zero VOC binders within the foundry industry (McKinley et al., 1993). New low-emission binders offer the industry comparable physical and casting performance to the conventional PUNB binder systems with the added benefit of reducing the airborne emission from the molding, pouring, and shakeout stages. The reduction or elimination of emissions from material and processes used by the foundry industry were listed as a priority by the American Foundry Society.

Biobased Polymers

The focus of those within the foundry industry has shifted toward renewable polymers both in modifying existing polymers and developing new biobased material that is comparable to or better in performance than conventional polymers in physical properties (Parulekar, 2007). Biopolymers are classified into two categories. The first are those polymers produced by living organisms such as microorganism, plants, and animals. The second category consists of those synthesized from biological materials such as sugars, proteins, fats, and oils.

Building Blocks

The focal point of this current research centers on polysaccharides and corn syrup. Corn syrup is classified as a disaccharide containing glucose and fructose, the latter of which is produced using cornstarch as a feedstock. Corn syrup possesses many of the OH functional groups needed in the Part 1 component of the PUNB binder system to bond with the isocyanate NCO groups in the Part 2 component in the presence of an amine catalyst. According to the U.S. Congress, Office of Technology Assessment (1993), “Starch has attracted considerable attention as a biodegradable additive or replacement in traditional oil-based commodity plastics” (p. 36). As much as 75% of industrial, nonfood-grade cornstarch is consumed in the production of the adhesives needed within the various paper industries.

Cornstarch contains approximately 10% to 20% amylose and 80% to 90% amylopectin, depending upon the starting material. Amylose molecules are comprised of long chains of glucose, typically ranging from 200 to 20,000 units (Zamora, 2005). Amylopectin contains significantly more units of glucose than amylose and also possesses side chains numbering approximately 30 units per chain. Amylopectin molecules may contain as many as 2 million units of glucose and are not soluble in water.

Hydrolysis is a method used to transform starches into commercially useful products. By using acids or other catalysts, such as enzymes, water can be added to the molecules to break the long chains into smaller chains and simple sugars. The degree to which water is added to the individual molecules is measured by the dextrose equivalent value, which ranges on a scale between 1 and 100 (Zamora, 2005). A value of 100 indicates that the molecules are completely hydrolyzed starch, yield pure glucose, and are completely water soluble. Corn syrup, which is made for a number of applications, may possess a dextrose equivalent value from 20 to 91, indicating that it can contain long-chain molecules and single units of glucose. By adding specific enzymes, the long chains can be broken into fructose, as is the case in high-fructose corn syrup, which is a widely used commercial sweetener.

Plastic Intermediate

The list of feedstocks available to produce biopolymers is growing. Sugars continue to be increasingly manipulated to produce important polymer intermediates, which will eventually replace oil-based plastics (Zhao, Holladay, Brown, & Zhang, 2007). Zhao et al. (2007) have investigated the possibility of alleviating pressure on the steadily depleting oil reserves by creating a sustainable future for the chemical industry based upon renewable resources. Several researchers have demonstrated that, by converting five- and six-carbon carbohydrates, such as glucose and fructose, into 5-hydroxylmethylfurufural, a vital link "between biomass-based carbohydrate chemistry and petroleum-based industrial organic chemistry" can be produced (as cited in Biello, 2007, para. 4). Zhao et al. have produced a 90% transformation of fructose and 70%

transformation of glucose to 5-hydroxylmethylfurufural with the addition of metal chlorides such as chromium chloride ($CrCl_2$). By using carbohydrates as building blocks, literally hundreds of chemicals can be produced from the renewable 5-hydroxylmethylfurufural platform.

Reaction With Isocyanate

Biopolymers like as those produced from biological starting materials such as sugar have potential application in virtually all sectors of the economy (Zhao et al., 2007). The majority of research on bioplastics has been conducted with a focus on the discovery of a complete replacement of current plastics, which are formulated from oil. Very few researchers have addressed the topic of partial replacement; that is, using biopolymers as a substitute for one component in a system comprised of multiple components. Replacing the oil based part 1 resin component with polysaccharide represents a unique research pathway.

The isocyanate component contains NCO functional groups. The reactive relationship between part 1 resin and isocyanate can be seen in Figure 1. Research suggests that polysaccharide based resins and isocyanate will form bonds in the presence of a catalyst. Simple tests can be conducted in order to determine the reactivity.

CHAPTER 3

METHODOLOGY

The primary experimental objective of this research was to investigate the use of corn syrup as a partial or total replacement for the phenol formaldehyde of the Part 1 resin component within the phenolic urethane nobake binder process. American Foundry Society testing procedures were employed to evaluate the physical and casting performance of the Part 1 resin replacement compared to a conventional PUNB binder. Physical performance was measured by determination of the work time and stripping time, the tensile strength of the two nobake binder systems, and their resulting casting performance when introduced to molten metal. The casting performance was measured by the occurrence and severity of casting defects in step cone castings of Type 35 grey iron. A method of numerically ranking the step cones was employed to gain greater understanding of the casting performance of the two nobake binder systems (Giese & Thiel, 2006).

Raw Materials of Biobased Resin

In the search for a suitable raw material to serve as a resin for the total replacement of the Part 1 component of the PUNB binder system, four criteria were selected. The material must (a) be readily available, (b) have good environmental characteristics, (c) be low in cost compared to the conventional Part 1, and (d) contain OH functional groups. Materials derived from the agricultural industry, such as corn syrup, proved to be valuable in meeting all four criteria, in addition to providing a total elimination of phenol formaldehyde.

To determine the raw-material compatibility with isocyanate and the amine catalyst, a gel test was performed. The raw material was combined in a cup with equal additions of isocyanate and 15% amine based on resin (BOR). A stopwatch was used to time the start and duration of the reaction. The mixture was stirred vigorously with a plastic pipette. If the raw material was compatible, an exothermic reaction would ensue and the mixture would subsequently harden. If the raw material was not compatible, no reaction would occur and the constituents would remain in their liquid form.

Solvents

Chemical sand binders generally possess a viscosity below 250 cps at room temperature. It is vital that binders meet this standard to ensure adequate coating of the sand grains and aid the production of a homogenous binder mixture. The raw materials used in the production of nobake binders generally have a viscosity in excess of 200 cps, which renders proper coating difficult in high-speed production applications. Consequently, solvents are added to the binders to thin the mixture to lower its viscosity, thus improving the coating of the sand grains.

Corn syrup used within the food industry has a relatively wide array of viscosities within the range of 160 to 4200 cps, depending upon the formulation and water content. Viscosities were determined using a Brookfield™ Digital Viscometer Model DV-E. Compatible solvents were needed to lower the viscosity of the chosen material, which was light corn syrup with a viscosity of approximately 840 cps. The method of choosing compatible solvents was performed by first looking for solvents with OH groups and then by trial and error. Additionally, solvents were chosen on the basis of their exclusion from classified VOCs.

Potential solvents were mixed by hand with the corn syrup to determine their solubility. Of the many available solvents found to be soluble with the corn syrup, the testing of tensile strength further narrowed the choice of optimal solvents. Resins containing propylene carbonate (PC) and ethylene glycol (EG) yielded the highest tensile-strength values, in addition to allowing a curing duration that matched those of the baseline PUNB. It was determined that both PC and EG are reactive solvents and, as a result, were consumed in the reaction. When PC was combined with an amine, it formed a carbonate, which is a hard material and, as a result, aided the generation of tensile strength (Broekaert, 2001). When EG was combined with isocyanate, the isocyanate groups bonded with the EG OH groups, forming long-chain polymers. By including reactive solvents in the resin, which are consumed during the polymerization process, vapors emitted by the cores/molds should be minimal.

Baseline Phenolic Urethane and Sand-Sample Preparation

The baseline binder system was selected in this study due to its wide use within the foundry industry. It is known for its effective casting performance in ferrous alloys. The PEPSET™ package of resins, isocyanates, and catalysts can meet specific industrial needs. PEPSET™ X1000 served as the resin Part 1, PEPSET™ X2000 served as the Part 2 isocyanate, and the PEPSET™ X3500 catalyst accelerated the reaction between Parts 1 and 2. A complete instruction of mixing procedures can be found within Appendix C “AFS 3333-00-S Sand-Mixture Preparation.” The total binder percentage was set at 1.5%

based on sand (BOS) which was centered upon accepted industrial use. Binder levels can be tailored to meet an array of industrial applications. Small castings, which require easy shakeout, may use lower than 1.0% binder BOS. Large castings, which may experience high metalstatic pressure during solidification, require a more than 1.5% binder BOS for the mold to remain dimensionally stable.

The mixture of corn syrup, PC and EG that was tested is referred to as Polyhybrid 3 (PH3). Physical evaluations of the PUNB baseline binder and biobased PH3 binder were conducted in this current study following the basic procedures outlined in the *Mold & Core Test Handbook* (American Foundry Society [AFS], 2001). For tensile strength testing, dog bones of both binder materials were prepared under similar environmental conditions of approximately 72° F to 82° F and relative humidity between 60% and 85%. The baseline PUNB data provided a range of tensile strength values that served as a benchmark. Performance of the PH3 biobased binder was measured against the values collected for the baseline PUNB binder. Binder percentages between binder types were matched as closely as possible; however, the ratios of Part 1 and Part 2 deviated from the industrial standard operating procedure. Once data were collected and evaluated following the series of tensile-strength tests, formulations with the highest tensile-strength values were chosen to test the casting performance using the step cone method.

Commercially available foundry sand was used to evaluate the binder performance in the following areas: tensile strength, cure time, casting defects in ferrous metals, and feasibility. The sand chosen is a commercially available, four-screen silica sand with an acid demand value of 4.84 and neutral pH, rendering it ideal for use with nobake binders. Following the test procedures provided by the AFS, the sample was split from a 3000 lb super sack. Using a 16:1 sand reducer, 4000 g samples were bagged. The sand distribution and average grain-fineness number were reported in Table 1.

Step Cone Castings

According to Tordoff and Tenaglia (1980), the step cone test casting is considered the optimal choice to evaluate overall casting performance. The step cone is a cylindrical, bottom-gated casting, which reduces the effect of turbulence, with a 5 in. outside diameter and a height of 7 in. The steps within the test casting simulate a wide range of casting sizes and sand-to-weight ratios, which range from 4:1 to 1:4. Tordoff and Tenaglia suggested conducting a series of step cone test castings to determine a clear indication of binder performance. In terms of a calculation the sand-to-weight ratio of 4:1 is represented by step number 1. Within step number 1 the core material is exposed to the least amount of abuse. At the other end of the spectrum the sand-to-weight ratio of 1:4 is represented by step number 6 and is exposed to the most abuse.

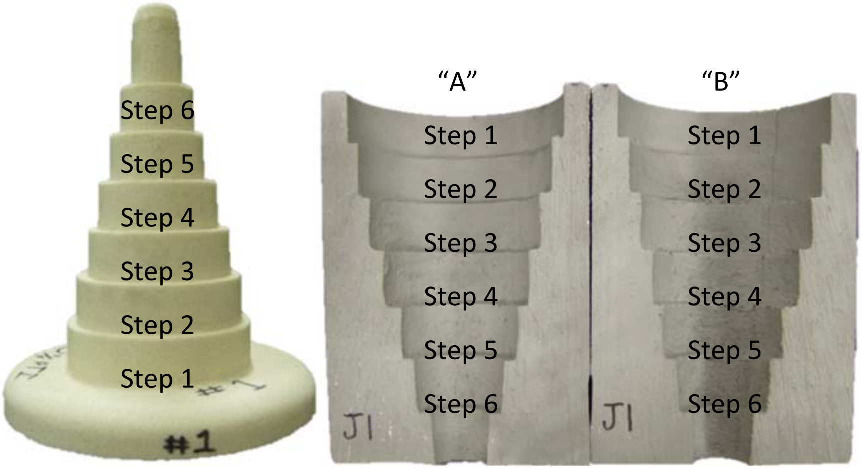

Figure 2: Step cone level identification. Above left – step cone. Above right – step cone casting.

A series of 16 step cone test castings were made in this current study, with both the baseline PUNB binder and the PH3 biobased binder. Four step cone cores were produced in this study using baseline PUNB binder and 12 were produced using the PH3 binder at three different binder ratios. For the investigation of the PUNB cores, the total binder level was 1.5% at a 55:45 ratio of Part 1 to Part 2. For the investigation of the PH3 cores, the total binder level was 1.5% with ratios of part 1 to part 2 of 20:80, 30:70 and 40:60 ratio between Part 1 and Part 2. Table 2 provides the complete list of core identification. The step cones were poured during two heats of Type 35 grey iron with similar starting and ending temperatures. Chemical analyses of the grey iron, as well as the chill wedges, were collected for verification of the casting material. The castings were subsequently evaluated with coded casting numbers to limit researcher bias. The evaluation of casting performance was conducted using the numeric ranking of step cones test castings, as outlined by Giese and Thiel (2006). This method allows the assessment of veining and penetration defects stemming from the generation of gases during the thermal decomposition of the binder when exposed to liquid metal. The location and severity of the defects determine to the casting quality.

Once step cone castings had been poured and allowed to solidify, they were subsequently removed from their cores/molds and halved along the core parting line. Figure 2 provides an example of the casting orientation and the resulting halves when cut.

They were then lightly cleaned of the carbon buildup and ranked by a minimum of two evaluators. Using an index for veining (i.e., v-index) and an index for penetration (i.e., p-index), each evaluator in this current study assigned a number between 0 and 4 to each individual step within the respective casting for both categories. A step value of 0 indicates no sign of defect, while a step value of 4 indicates a severe presence of either penetration or veining, depending upon the index. The ratings for each step in each half of the casting were entered into the equation below to calculate the index value for that defect. After the index values were obtained from all evaluators, they were summed to obtain a total score. From the list of total scores, the lowest sum was assigned Number 1, indicating the lowest occurrence of defects within that particular test series. The next lowest sum was assigned Number 2 and so on until all castings have been ranked from best to worst overall performance.

(step 1A + step 1B) x 1 = individual step value
(step 2A + step 2B) x 2 = individual step value
(step 3A + step 3B) x 3 = individual step value
(step 4A + step 4B) x 4 = individual step value
(step 5A + step 5B) x 5 = individual step value
\+ (step 6A + step 6B) x 6 = individual step value

Index value = Sum of individual step values /

CHAPTER 4

RESULTS AND DISCUSSION

Factors involved in these trials include the choice of raw materials, solvents, isocyanates, liquid amine catalysts, total resin addition, and the Part 1 to Part 2 ratios. Upon formulation of the various polyhydric samples, success was gauged on the tensile-strength development and cure rate. Once tensile strengths met or surpassed those of the baseline phenolic urethane nobake, the track of the research shifted to casting trials.

Raw Materials

Based upon the criteria of readily available raw material, good environmental characteristics, low cost compared to the baseline Part 1, and OH functional groups, the polysaccharides were chosen as potential candidates. Materials such as molasses, corn syrup, high-fructose corn syrup, and table sugar were selected for preliminary testing. From that grouping, the materials already in liquid form were determined to be more suitable as a resin. Additionally, table sugar proved to be a challenge in terms of locating a solvent within which a sufficiently high quantity of the material could be dissolved to reach the level of concentration needed for a resin.

A gel test was performed using 20 grams of the polysaccharide, 20 grams of the isocyanate Part 2 component, and 2 grams of various amine catalysts. Corn syrup, molasses and table sugar reacted to form hard substances when in the presence of an isocyanate and catalyst. From the gel test, it was found that some materials performed more favorably than others. During the reaction, molasses samples formed large foam bubbles, which would be an unfavorable characteristic when molding in sand. Complete polymerization was also difficult to achieve. The samples prepared with molasses contained areas that had not reacted with the isocyanate and remained in a liquid state. The sample prepared with corn syrup preformed much better. The percentage of the material that had polymerized appeared to be significantly higher than that of molasses. With molasses the resulting material was not uniform and contained semi solids. From this series of gel tests, corn syrup clearly proved to be the most reactive with foundry grades of isocyanate.

Solvent Package

The ultimate goal of this research was to discover a replacement for conventional PUNB-binder resins. Toward this end, it was necessary for the physical characteristics of these materials to be as closely matched as possible. Corn syrup was selected as a preliminary candidate but the viscosity was not appropriate for use as a foundry resin. The material viscosity of the base corn syrup was 840 cps at approximately room temperature, which required reduction to meet industrial sand-coating and mixing needs. The baseline PUNB part 1 resin has a viscosity of 200 cps. The viscosity of corn syrup is dependent upon its water content. Water is already used as a solvent to reduce the viscosity of the corn syrup and must be minimized as much as possible due to its retarding effects on the urethane reaction. Small quantities of moisture can be tolerated, although tensile strengths will be reduced.

A solvent package that is environmentally compatible and soluble with corn syrup was needed. Compatibility was determined regardless of whether a reaction occurred. Only a few solvents were potential candidates. The decision to use propylene carbonate was based upon its current industrial use as a green or environmentally friendly solvent. Similarly, ethylene glycol was selected based upon its OH groups, which classified it as a reactive solvent. It was surmised that during the reaction, EG was incorporated into the bonding of the resin and isocyanate.

To determine the percentages of solvent needed for addition to the corn syrup, viscosity was used as a stop point with the goal of 200 cps. Initially EG and PC were used individually as solvents to form Polyhybrid 1 and 2. Using the solvents individually proved to yield poor tensile strengths in comparison to the conventional PUNB. After 24 hours of stripping time, the ultimate tensile strengths were approximately 125 psi, which is far below the 220 psi goal. Small amounts of both EG and PC were added in 20 g and 10 g increments, respectively, until the goal point was reached. Starting with a corn syrup base of 450 g it was found that 110 g of EG and 60 g of PC were required to bring the viscosity range of the resin between 195 and 200 cps. The PH3 yielded a resin content of 73% with 17% EG and 10% PC. Appendix B provides the precise mixing instructions.

Biobinder and Material Testing

Once the PH3 resin was ready for material testing, and reactivity with isocyanate was observed in the presence of an amine by means of a gel test, this research progressed to the next experimental phase involving sand. How the resin would react in the presence of sand was unknown. Early dog bone trials were made with a 50:50 Part 1 to Part 2 ratio, which resulted in poor tensile-strength values. Consequently, Part 1 to Part 2 ratios of 20:80, 30:70, and 40:60 were used. The decision to exclude a trial of a 10:90 Part 1 to Part 2 was made because that ratios containing greater than 80% isocyanate are not cost effective. Large amounts of isocyanate increases the risk of encountering nitrogen pinholing defects within ferrous castings.

The baseline binder system was made with a Part 1 to Part 2 ratio of 55:45. For equal comparison between test subjects and the baseline PUNB binder system, the industrial protocol for total binder-to-sand additions was followed. A total binder of 1.5% was used for each of the 20 dog bone batches of silica sand; however, the choice of the Part 3 catalyst differed between the PUNB and PH3 resin.

A large number of catalysts were used for the nobake binder systems. The Part 3 catalyst directly influenced the cure rate and development of tensile strength. During the early stages of development, a catalyst was needed that was compatible with the biobased resin. A number of catalysts were considered; however, a “hot,” or stronger tertiary amine, demonstrated the best performance. The catalyst chosen for the PUNB is a weaker catalyst. All PH3 samples were prepared using 9 g of the stronger tertiary amine PEPSET™ 307. All PUNB samples were prepared using 4.5 g of PEPSET™ X3500.

Tensile Strength

Dog bone trials were performed and compared using PH3 and a conventional PUNB (see Table 2). To compare the performance of PH3 to that of the PUNB binder, tensile strength and cure rate in work time and stripping time were measured. Following the AFS test procedures outlined for sand preparation, cure rate, and tensile-strength specimens, a series of 20 batches of sand were created and evaluated. Table 2 outlines the ratio of Part 1 to Part 2 and the binder material. All dog bones and step cones were prepared using 1.5% total binder based on sand.

Table 2

Tensile-Strength Specimens and Step Cones

Material	Phenolic-urethane nobake	Polyhybrid 3	Polyhybrid 3	Polyhybrid 3
Part 1:Part 2	55:45	20:80	30:70	40:60
Dog bone batches	5	5	5	5
Step cones	4	4	4	4

Once the individual sand batches were mixed and packed into the dog bone mold, samples were observed to determine work time and stripping time. Upon reaching the stripping time, the time was recorded and tensile strength was recorded at 10 minutes, 1 hour, 3 hours, and 24 hours after the stripping time. The tests were run over a 2-day period during the late summer with laboratory conditions between 72° F and 82 ° F and a relative humidity between 60% and 85%. Because of the large effect of relative humidity on the tensile strength, the data shown in Figures 3 and 4 below represent a humidity range of 62% to 67% and a temperature range of 79° F to 82° F. Performance of various binder ratios were evaluated using PUNB as a baseline at 1.5% binder BOS and a catalyst of 20% BOR. The tensile-strength values of 100 psi at 10 minutes, 160 psi at 1 hour, 200 psi at 3 hours, and 220 psi after 24 hours represent the typical performance of PUNB binder systems at the stated binder percentages and ratios.

The average tensile strength values at the three binder percentages are shown in Figure 3. The best-performing set of dog bones were PH3 at 20% Part 1 and 80% Part 2. PH3 at 20% differed from the baseline in tensile-strength development in that it reached 80% of its 24-hour strength just 10 minutes after reaching the stripping time.

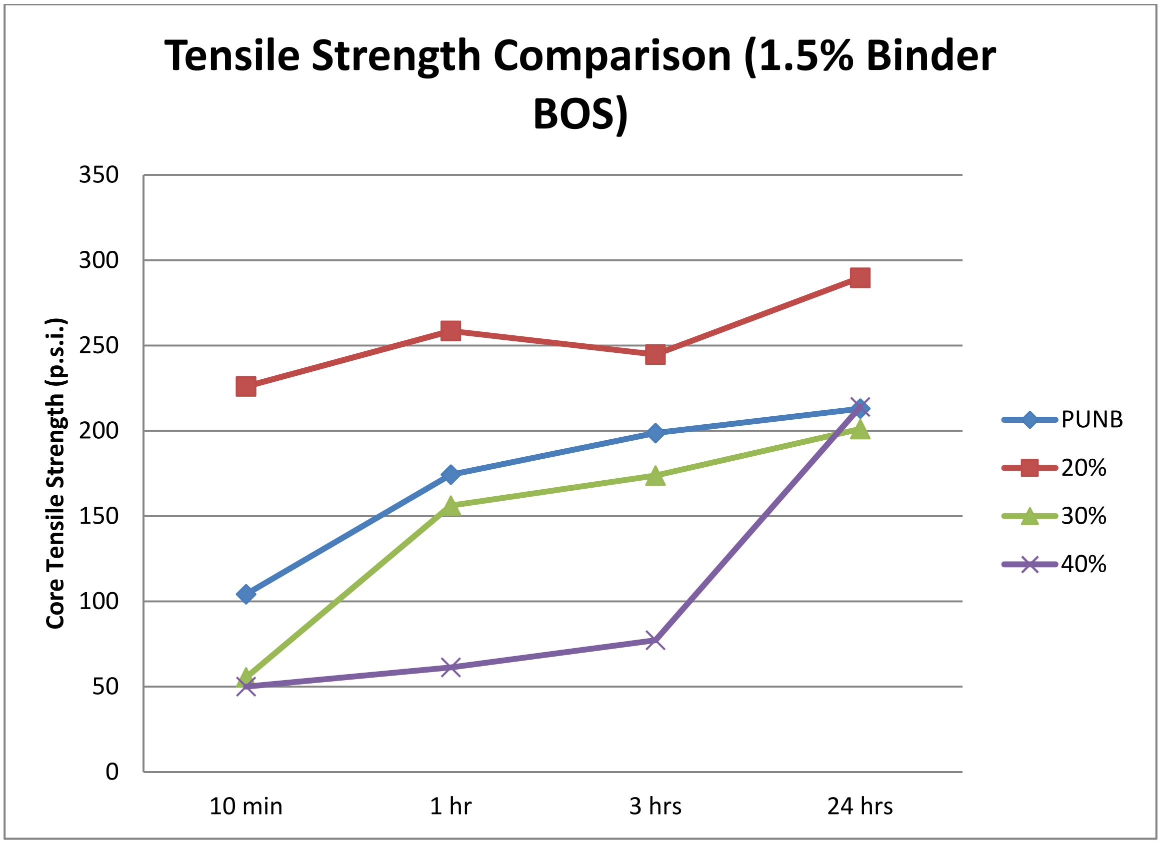

Figure 3. Tensile strength development of PUNB and PH3. PUNB = phenolic urethane nobake; PH3 = Polyhybrid 3. PH3 percentage is shown in the legend.

Conventional PUNB reaches an average 45% of its 24-hour strength within that short time frame. PH3 at 30% Part 1 and 70% Part 2 appeared to be the most similar to PUNB in the development of strength over time. However, it achieved tensile strengths below the 10-minute, 1 hour, 3 hour, and 24-hour values of the PUNB measurements.

Curing Profile

To meet the industrial production demands of current nobake technology, a hot catalyst was chosen for the PH3 binder. At the current binder percentage and catalyst level, the baseline PUNB was the most rapid performer. Work time was achieved within 3 minutes and 20 seconds; stripping time was reached within 4 minutes and 10 seconds. The next-fastest curing profile was PH3 at 40% Part 1 and 60% Part 2 with 9 g of PEPSET™ 307. Work time was achieved within 4 minutes and stripping time was reached within 5 minutes and 20 seconds. A comparison of curing profiles is provided in Figure 4.

Step Cone and Heat Preparation

From the promising results of tensile-strength development and curing profile, it was hoped that the PH3 series would perform comparably to PUNB when used to produce ferrous castings. A series of 16 step cones were produced under similar laboratory conditions to those of the tensile-strength specimens. Samples of 4000 g of sand were collected while adhering to the procedure outlined by the AFS (see Appendix C). To treat each sample equally, each of the 16 batches of sand were mixed with binder, following the same procedure. Precise mixing instructions are provided in Appendix C.

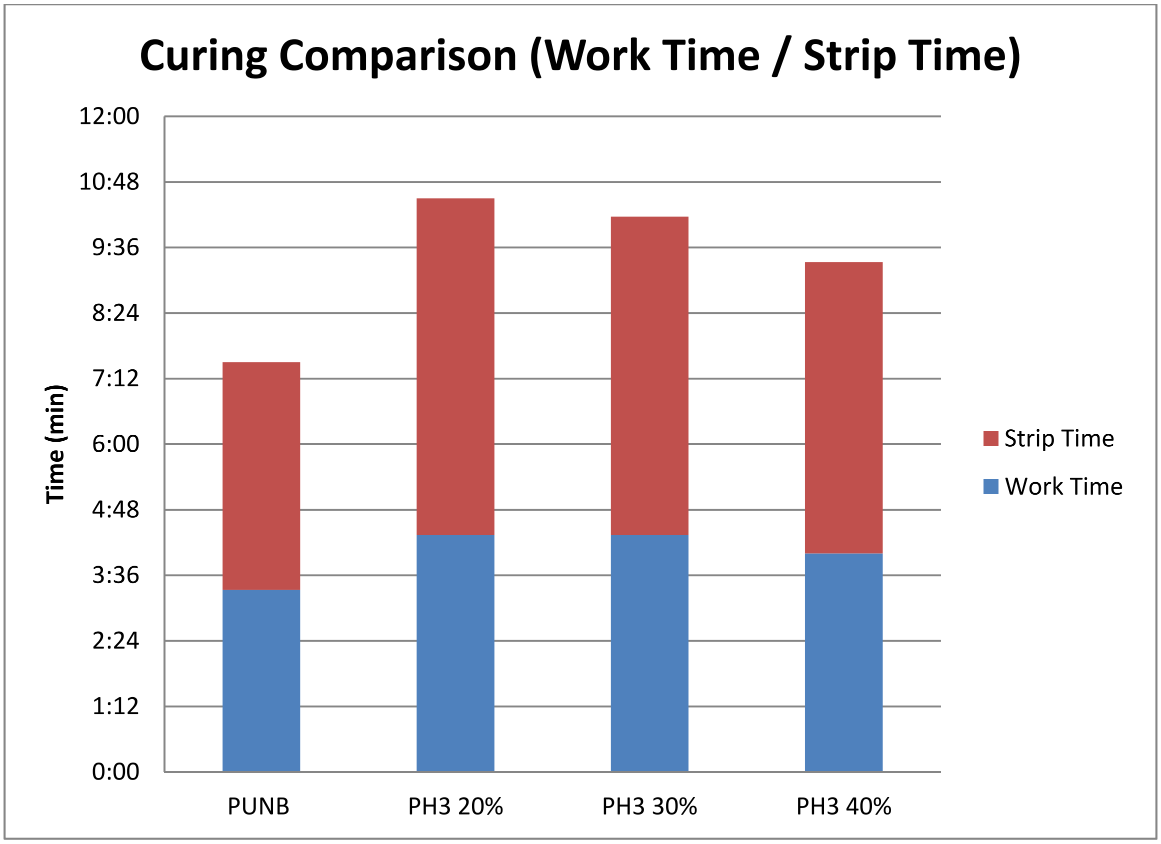

Figure 4. Cure-rate development and comparison between phenolic-urethane nobake and Polyhybrid 3.

After the step cones were made, they were allowed to cure for 24 hours prior to placement into molds. The core number was carved into the back of the step cone mold for identification after shakeout. The cores were placed into the molds and weights were placed over the cores to prevent them from floating during introduction of the Type 35 grey iron. Due to the limitations of the furnace melt capacity, the 16-step cones and molds were divided into two heats of eight cones. The pouring order was based upon the exposure to the heat extremes (see Tables 4 & 5). Each of the two binder types and four binder ratios were exposed to the highest and lowest pouring temperatures during the course of the two heats. Using an optical emission spectrometer, preliminary and final chemistries were taken of the Type 35 grey iron. The final chemistry for the first and second heats is described in Tables 3 and 4.

Table 3

Pouring Order and Spectrometer Analysis of Heat 1

Pouring order	Casting number	Core identification Part 1 (%)	Pouring temperature (^{0}F)
1	2	20	2595
2	5	30	Not recorded
3	1	55 / 45 PUNB	2579
4	6	30	Not recorded
5	4	40	2574
6	3	20	Not recorded
7	12	40	Not recorded
8	8	55 / 45 PUNB	2569

Note. Final chemistry of Heat 1 and pouring temperature (%C = 3.21; %Si = 1.96; %Mn = 0.44; %P = .071; %S = .075). PUNB = phenolic-urethane nobake; C = carbon; Si = silicon; Mn = manganese; P = phosphorous; S = sulfur.

Numeric Ranking of Step Cone Castings

Once the castings solidified, they were broken out of the molds and sprue and gating removal were performed. The core parting line was then cut with a band saw and lightly cleaned of the lustrous carbon buildup with a sand blaster. The castings were numbered and displayed on a large sturdy table for numeric ranking with both the p-index and v-index. The two individuals selected to evaluate the castings were unaware of the relation between the casting numbers and specific binder system or binder ratio.

Table 4

Pouring Order and Spectrometer Analysis of Heat 2

Pouring order	Casting number	Core identification Part 1 (%)	Pouring temperature (^{0}F)
1	10	55 /45 PUNB	2593
2	13	40	Not recorded
3	11	20	2582
4	7	30	Not recorded
5	16	20	2572
6	14	40	Not recorded
7	15	55 / 45 PUNB	Not recorded
8	9	30	2552

Note. Final chemistry of Heat 2 and pouring temperature (%C = 3.26; %Si = 2.16; %Mn = 0.40; %P = .089; %S = .069). PUNB = phenolic-urethane nobake; C = carbon; Si = silicon; Mn = manganese; P = phosphorous; S = sulfur.

Upon completion of the numeric ranking of the step cones, the raw data were incorporated into a spreadsheet to determine casting performance (see Table 5). Of the 16 samples of step cones, the four prepared with PH3 at 40% Part 1 ranked within the top six for low incidence of veining and penetration. Of the four cores prepared with the baseline PUNB binder system, all ranked within the lowest six castings for low incidence of veining and penetration. The four step cones prepared with the PH3 at 20% Part 1 were found to either have a tensile-strength development greater than those of the baseline PUNB or matched or outperformed the PUNB in casting performance. As shown in Table 2, the castings prepared with PH3 at 20% Part 1 were ranked between 7 and 14, whereas the baseline PUNB cores were ranked between 11 and 16.

Hypothesis Test

H_o = No difference of tensile strength between PH3 and PUNB.

H_a = There is statistical difference of tensile strength between PH3 and PUNB.

A single-factor nova table was constructed to further analyze the statistical difference between PH3 at 20% part 1 and PUNB. The ANOVA table is listed in Table 6. As the P-value (1.59%) in the ANOVA table is less than 5%, this means that there are some significant difference among the four averages. Out of the three different concentrations of bio-based binders, 20% turned out the best result in tensile strength. The tensile strength was better than the petroleum based binder.

Table 5

Results of Numeric Ranks in Step Cone Castings

			Penetration index		Veining index		
Rank	Casting number	Core identification Part (1%)	Evaluator 1	Evaluator 2	Evaluator 1	Evaluator 2	Sum of indexes
1	4	40	9	0	22	27	57
2	6	30	0	6	32	33	70
3	12	40	10	13	23	33	78
4	7	30	17	25	16	26	83
5	13	40	23	14	23	27	87
6	14	40	23	26	24	29	102
7	11	20	20	29	26	29	104
8	9	30	29	28	19	31	107
9	5	30	17	11	39	46	113
10	3	20	34	29	26	37	126
11	8	55 / 45 PUNB	20	20	40	51	130
12	16	20	32	32	37	39	139
13	1	55 / 45 PUNB	19	18	45	61	142
14	2	20	36	38	24	45	143
15	15	55 / 45 PUNB	30	26	41	55	151
16	10	55 / 45 PUNB	27	27	41	62	156

Note: PUNB = phenolic-urethane nobake.

Table 6

Single-Factor Nova Test Summery

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	4	690.16	172.54	2331.56
Column 2	4	1019	254.75	721.26
Column 3	4	586.3	146.57	4036.23
Column 4	4	402.6	100.65	5838.19

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	50158.63	3	16719.54	5.173	0.0159	3.49
Within Groups	38781.78	12	3231.81			
Total	88940.41	15				

Note: 20% PH3 and the PUNB.

Using the statistical analysis, with an alpha value of 5% the least significant difference (LSD) was found to be 87. The average difference between the PH3 at 20% and the PUNB was 82 (=254-172). The average difference is slightly smaller than the LSD, suggesting that there is not a significant difference between them, but at least it performed equivalently well. Similar comparisons were not needed to determine the statistical difference between the other PH3 ratios because there was a significant difference between their tensile strength values.

Using alpha level of 5%, the LSD calculation is as follows.

$$LSD = t_{\alpha/2,k(n-1)}\sqrt{s_p^2}\sqrt{\frac{1}{n}+\frac{1}{n}}$$

$$= t_{0.05/2,3(4-1)}\sqrt{3231.81}\sqrt{\frac{1}{4}+\frac{1}{4}}$$

$$= 2.179\sqrt{3231.81}\sqrt{\frac{1}{4}+\frac{1}{4}}$$

$$= t_{0.05/2,3(4-1)}\sqrt{3231.81}\sqrt{\frac{1}{4}+\frac{1}{4}}$$

=87.59

If the statistical test standard is relaxed and the alpha value is increased to 10%, the resulting LSD is 71. The average variance is larger than the LSD, suggesting that there is a significant difference between the PH3 at 20% and the PUNB. Using alpha level of 10%, the LSD calculation is as follows.

$$LSD = t_{\alpha/2,k(n-1)}\sqrt{s_p^2}\sqrt{\frac{1}{n}+\frac{1}{n}}$$

$$= t_{0.10/2,3(4-1)}\sqrt{3231.81}\sqrt{\frac{1}{4}+\frac{1}{4}}$$

$$= 1.782\sqrt{3231.81}\sqrt{\frac{1}{4}+\frac{1}{4}}$$

=71

CHAPTER 5

CONCLUSION

Summary of the Findings

This investigation found that polysaccharides are suitable as substitutes for petroleum-based raw materials within nobake binder systems. Early observation found that green solvents, such as ethylene glycol and propylene carbonate, are compatible with the formation of urethane bonding which is the bonding mechanism for phenolic urethane nobake binder systems. The quantitative evidence, which supports the hypothesis of this study, demonstrates that biobased binders formulated from raw materials such as corn syrup can match the tensile strength and casting performance of PUNB binder systems.

The development of tensile strength in PH3 surpassed the performance of the PUNB. At 1.5% total binder and a Part 1 to Part 2 ratio of 20:80, tensile strength reached 226 psi or 80% of its 24-hour tensile strength within 10 minutes after stripping time was attained. When compared with the tensile results of PUNB, the tensile-strength development exhibited by PH3 can support moderate production rates.

An analysis of the step cones found that the PH3 met and surpassed the casting performance of those prepared with PUNB binders at equal total-binder percentages. Reviewing the numeric ranking of the 16 step cone cores, the PUNB cores were found to have the least resistance to veining and metal-penetration defects. Comparing the PUNB to the PH3 samples made with a 20:80 binder ratio, the PH3 performed only slightly better than the PUNB binders. Step cone cores made with a PH3 40:60 binder ratio yielded the best resistance to veining and penetration of all the sample tests; however, their tensile-strength development was the lowest of all tested. This observation suggests that strength alone does not dictate casting performance. Nevertheless, the purpose of a binder system is to provide a sand mold with sufficient strength to facilitate stripping of the mold from the pattern and maintain dimensional stability of the mold wall during solidification. The use of polysaccharides in the nobake binder method has proven to be comparable with the binder technology implemented within the contemporary foundry industry.

Recommendations

Use of the PH3 Part 1 replacement in nobake binders has proven to be possible under the conditions outlined; yet questions remain for future study. Areas recommended for further research are cost savings, resistance to humidity, environmental emissions, other potential solvents, casting performance in other ferrous and nonferrous metals, application to similar binder technology, and the addition of materials that increase casting performance. The decision to investigate the use of polysaccharides as a nobake resin was made for this current study based upon their market share. Of the chemically bonded sands on the market, 50% use urethanes. Similar systems may yield comparable results with PH3. Investigation of the phenolic-urethane, cold-box binder system is recommended to increase its application with use of the biobased-binder technology.

Corn syrup and its accompanying green solvent package have proven useful as a replacement for synthetic resins. Consequently, it is recommended that further research be conducted into the reduction of hazardous emissions during the molding, pouring, and shakeout stages of production. In the worst case scenario, the overall reduction in emissions is hypothesized to reach 20% with a PH3 20:80 binder ratio. A complete elimination of phenol and formaldehyde would be expected because it is only found within the Part 1 resin the corn syrup can replace. However, environmental testing at each stage of production must be conducted to support these claims.

REFERENCES

American Foundry Society. (2001). *Mold & core test handbook* (3rd ed.). Des Plaines, IL: Author.

Biello, D. (2007, June 15). Turning plants into plastic and replacing oil in the process. *Scientific American.* Retrieved from http://www.sciam.com/artical.cfm?id=turning-plants-to-plastic-replacing-oil

Broekaert, M. (2001). *Modified MDI-prepolymers improve the initial physical properties and reduce the in-service time of aromatic polyurea coatings.* Retrieved from http://www.huntsman.com/pu/Media/Nurnberg_paper_final.pdf

Brown, J. R. (1994). *Foseco foundryman's handbook: Facts, figures, and formulae* (10th ed.). Boston, MA: Butterworth-Heinemann.

Carey, P. R. (1998) Practical aspects of resin binder processes. *Foundry Management Technology, 123,* 3-7.

Carey, P. R., & Haugse, L. (1998) Sand binder systems – Part 3: Urethane binders. *Foundry Management Technology, 123,* 13–16.

Carey, P. R., & Lott, M. (1998). Sand binder systems – Part 5: Furan no-bake. *Foundry Management Technology, 123,* 22–26.

Clean Air Act Amendments of 1990, S. 1630, 101s Cong. (1989). Retrieved from http://www.govtrack.us/congress/bills/101/s1630

Eastman, J. (2000, October). Protein-based update: Performance put to the test. *Modern Casting,* 32–34.

Giese, S. R., & Thiel, G. (2006) Numeric ranking of step cone test castings. *American Foundry Society Transactions, 115,* 401–410.

Lessiter, M. J., & Kotzin, E. L. (2002, September). Timeline of casting technology. *Engineered Casting Solutions,* 76–80.

Lytle, C. A., Bertsch, W., & McKinley, M. D. (1998, February). Determination of thermal decomposition products from a phenolic urethane resin by pyrolsis-gas chromatography-mass spectrometry. *Journal of High Resolution Chromatography, 21*(2), 128–132.

Margolis, N., Jamison, K., & Dove, L. (1999). *Energy and environmental profile of the metalcasting industry.* Washington, DC: Government Printing Office. Retrieved from http://www1.eere.energy.gov/industry/metalcasting/pdfs/profile.pdf

McKinley, M. D., Jefcoat, I. A., Herz, W. J., & Frederick, C. (1993). Air emissions from foundries: A current survey of literature, supplies and foundrymen. *American Foundry Society Transactions, 105,* 979–990.

Parulekar, Y. (2007). Modified biobased materials from polyhydroxyalkanoates for packaging and engineering applications. *Dissertation Abstracts International:* Section B-68.

Schleg, F. P. (2003) *Technology of metalcasting.* Schaumburg, IL: American Foundry Society.

Siak, J.-S., Whited, W., Schreck, R., Biederman, S., & Datte, M. (1996, October). GM develops a breakthrough green binder for core sand. *Modern Casting,* 24–26.

Teodorczyk, Zygmunt. (1998). US Patent No. US5847058 A. Chicago, IL: US Patent Office

Thomas-Sadowski, S. (Ed.). (2005). *Metalcasting dictionary* (2nd ed.). Schaumburg, IL: American Foundry Society.

Tordoff, W. L., & Tenaglia, R. D. (1980). Test casting evaluation of chemical binder systems. *American Foundry Society Transactions, 88,* 149–158.

U.S. Congress, Office of Technology Assessment. (1993). *Biopolymers: Making materials nature's way.* Washington, DC: U.S. Government Printing Office.

Zamora, A. (2005). *Dr. Z on biochemistry.* Retrieved from http://www.zenitech.com/documents/new%20pdfs/articles/Dr%20Z%20on%20Biochemistry%20Part%203.pdf

Zhao, H., Holladay, J. E., Brown, H., & Zhang, Z. C. (2007, June 15). Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science, 316,* 1597–1599.

APPENDIX A

POTENTIAL HAZARDOUS AIR POLLUTANT PRODUCTS

Binder Material	Major Reactive Chemicals	Use Level (BOS)	Core Making	Pouring	Shakeout
Shell Sand	Phenolic, Hexamethyltetramine	4-5%	Formaldehyde, Methanol, Phenol	Benzene, Cresole/ cresylic acid, Phenol, Toluene, Polycyclic-organic matter	Benzene, Cresole/ cresylic acid, Formaldehyde, Phenol, Toluene, Polycyclic-organic matter
PUNB	Phenolics, Isocyanates, Triethylamine	0.4-1.2%, 0.4-1.2%, 0.1%	Formaldehyde, MDI, Phenol	Benzene, Cresole/ cresylic acid, Formaldehyde, Naphthalene, Phenol, Toluene, Polycyclic-organic matter, Cyanide compounds	Benzene, Cresole/ cresylic acid, Formaldehyde, Naphthalene, Phenol, Toluene, Polycyclic-Organic matter, Cyanide compounds
Furan	Furfuryl-Alcohol, Benzene-Sulfonic-Acid	0.9-2.0%, 0.3-0.9%	Benzene, Methanol, Phenol, Toluene	Benzene, Cresole/ cresylic acid, Formaldehyde, Phenol, Toluene, Polycyclic-organic matter, Cyanide compounds	Benzene, Cresole/ cresylic acid, Formaldehyde, Phenol, Toluene, Polycyclic-Organic, matter, Cyanide compounds

From "Air Emissions From Foundries: A Current Survey of Literature, Supplies and Foundrymen," by M. D. McKinley, I. A. Jefcoat, W. J. Herz, and C. Frederick, 1993, *American Foundry Society Transactions*, p. 988. Copyright 1993 by American Foundry Society. Adapted with permission.

APPENDIX B

FORMULATION OF POLYHYBRID 3 BIOBASED RESIN

Purpose: To prepare a resin for the total replacement of phenol formaldehyde Part 1 resin in the PUNB binder system.

Equipment/Materials Needed:

- NALGENE®–500 ml bottle or equivalent, sealable container
- BROOKFIELD™ DIGITAL VISCOMETER–(Model DV-E) or equivalent viscometer
- BROOKFIELD™ LV SPINDEL SET–Spindle #61
- GARDEN CLUB™ LIGHT CORN SYRUP–450 g
- Fisher Scientific® Ethylene Glycol–110 g
- HUNTSMAN JEFFSOL® Propylene Carbonate– 60 g
- Suitable containers for weighing chemicals
- Balance with sensitivity of 0.1 g
- Hard, flat surface

Procedure

1. Weigh 450 g of GARDEN CLUB™ light corn syrup into 500 ml bottle.
2. Weigh 60 g of polycarbonate into container and add to 500 ml bottle.
3. Place cap securely on 500 ml bottle and shake vigorously for 2 minutes.
4. Weigh 110 g of ethylene glycol, remove cap, and add to 500 ml bottle.
5. Place cap securely on 500 ml bottle and shake vigorously for 2 minutes.
6. Allow 500 ml bottle to rest on hard, flat surface while air bubbles rise and dissipate.

7. Prepare BROOKFEILD™ digital viscometer by appropriately placing spindle #61 on sensing element. Power viscometer on and select #61 from choice of spindles. Select a rotation speed of 6.0 rpm.

8. Remove cap from 500 ml bottle, place it under the viscometer, and lower the spindle at an angle that will not trap air pockets underneath the spindle. After the spindle is lowered to the manufacturer specifications, power on the viscometer.

9. Allow sensing element to rest on a consistent centipoise reading for 30 seconds and record value.

10. Turn motor off. Centipoise value should be approximately 195–200 cps. Lift viscometer from 500 ml bottle and replace cap securely.

11. Part 1 resin replacement of PH3 formulation is complete.

APPENDIX C

AMERICAN FOUNDRY SOCIETY TESTING PROCEDURES

American Foundry Society (AFS) 1122-00-S Reduction of Dry Sand, 16:1 Reducer

Purpose: To reduce the weight of a sample for testing and analysis.

Equipment/Materials Required:

- 16:1 reducer and stand with a minimum of three appropriately sized pans.

Procedure:

1. Place the sample evenly into the dispensing pan.
2. Place two receiving pans under the 16:1 reducer at the front and rear.
3. Set the control gate to provide uniform flow of all material.
4. Pour the sample from the dispensing pan into the center of the hopper. The pan must be horizontal.
5. Gently tap and brush reducer to ensure that all material has flowed.
6. Further reduction of the sample is performed by repeating Steps 2 through 6 of the procedure until the 3000 g sample size is achieved.

AFS 3333-00-S Sand-Mixture Preparation

Purpose: To prepare a mixture of sand, acid catalyst, and binder for use in the various testing procedures.

Equipment/Materials Required:

- Suitable container for weighing dry sand
- Suitable containers for weighing binder (e.g., resin and isocyanate)
- Suitable container for weighing catalyst
- One Kitchen-Aid™ mixing bowl
- Balance with sensitivity of 1 g for weighing sand
- Balance with sensitivity of 0.1 g for weighing binder chemicals
- 50 lbs of dry silica sand, UNIMIN IC55™ with a grain-fineness number of 55
- Catalyst (ASHLAND PEPSET™ 3500)
- Binder (i.e., resin [ASHLAND PEPSET™ 1000] and Polyhybrid 3
- Isoycanate (ASHLAND PEPSET™ 2000) and HUNTSMAN RUBINATE 1780™
- Kitchen-Aid mixer or appropriate laboratory mixer

Procedure:

1. Record sand, ambient temperature, and relative humidity.
2. Pour appropriate amount of sand into container.
3. Charge sand into mixer.
4. Weigh recommended amount of Part 3 catalyst into the container. The percentage is based upon the weight of the binder.

5. Pour recommended amount of Part 1 resin into the container. The percentage is based upon the weight of the sand.

6. Pour recommended amount of Part 2 isocyanate into the container. The percentage is based upon the weight of the sand.

7. Create a pocket in the sand. Pour the measured amount of catalyst-to-sand into the Kitchen-Aid™ mixer. Ensure the catalyst does not touch the mixing blades or side of the bowl.

8. Power on the mixer and use a No. 2 speed setting. Mix for 45 seconds, stop the mixer, remove the mixing bowl, and flip the sand mixture, bringing the dry sand to the top. Replace the mixing bowl and mix for 45 seconds to ensure uniform distribution is attained.

9. Create a pocket in the sand. Pour the measured amount of Part 1 resin-to-sand into the Kitchen-Aid™ mixer. Ensure the Part 1 does not touch the mixing blades or side of the bowl.

10. Power on the mixer and use a No. 2 speed setting. Mix for 45 seconds, stop the mixer, remove the mixing bowl, and flip the sand mixture, bringing the dry sand to the top. Replace the mixing bowl and mix for 45 seconds to ensure uniform distribution is attained.

11. Create a pocket in the sand. Pour the measured amount of Part 2 isocyanate-to-sand into the Kitchen-Aid™ mixer. Ensure that the Part 2 does not touch the mixing blades or side of the bowl.

12. Power on the mixer and use a No. 2 speed setting. Mix for 45 seconds, stop the mixer, remove the mixing bowl, and flip the sand mixture, bringing the dry sand to the top. Replace the mixing bowl and mix for 45 seconds to ensure uniform distribution is attained.

13. Stop the mixer and remove the mixing bowl.

Dog bone Specimen Preparation, 1 in.-Thick Tensile Specimen

Purpose: To prepare nobake tensile specimens using a multicavity core box.

Equipment/Materials Required:

- Multicavity tensile core box, meeting AFS 1 in.-thick specifications
- Sample for testing
- Butt rammer of equivalent
- Strick-off bar
- Timer

Procedure:

1. Clean and assemble core box according to manufacturer recommendations.
2. Dump the prepared sand onto the core box and start timer.
3. Level the sand over the box, hand tucking the sand into the individual cavities using the index and middle fingers of both hands.
4. Using a butt rammer, compact the sand into each cavity.
5. Using the strike-off bar, remove excess sand.
6. Using excess sand, complete Steps 2 through 9 of work time/stripping time, nobake sand mixture, hardness method.
7. After reaching the stripping time, turn the box over onto a clean, flat surface.
8. Carefully remove the specimens, as well as those from the core box.
9. Store the specimens on their edge prior to testing.
10. For subsequent test, repeat Steps 1 through 9 of the tensile strength, 1 in.-thick tensile specimen test method.

AFS 3180-00-S Work Time/Stripping Time, Nobake Sand Mixture, Hardness Method

Purpose: To determine the work/ stripping time of a chemically bonded sand mixture. This test method was conducted congruently with AFS 3333-00-S Sand-Mixture Preparation.

Equipment/Materials Required:

- Freshly prepared sand mixture
- B-scale, “green” hardness tester
- Stopwatch
- Molding frame
- Hand rammer and strike-off bar
- Flat, hard surface
- Thermometer and relativity humidity gauge or wet-bulb/dry-bulb thermometer

Procedure:

1. Obtain a freshly prepared sand mixture from the sand-mixture preparation procedure.
2. Place the frame on one of the core plates and fill it with the sand mixture.
3. Hand ram the sand and strike off the excess sand.
4. Place the other core plate on top of the frame and turn the assembly over.
5. Measure and record the ambient temperature; mixed-sand temperature, using the excess sand from Step 3; and relative humidity.
6. Remove top core plate. Holding the hardness tester perpendicularly to the sand surface, press the B-scale, green hardness tester to the reference plane. Record the time and maximum reading on the hardness tester.

7. Repeat Steps 5 and 6 at appropriate intervals. Record each time and maximum hardness reading. Do not test the same spot.

8. When a hardness reading of 45 is reached, the time is recorded as the end of the work time for the sand mixture.

9. Repeat Steps 5 and 6 until a hardness of 90 is achieved. This is recorded as the stripping time for the sand mixture.

AFS 3301-00-S Tensile Strength, 1 in.-Thick Tensile Specimen

Purpose: To determine the tensile strength of 1 in.-thick tensile specimens.

Equipment/Materials Required:

- Tensile tester with grips for specimen
- Balance with sensitivity of 0.1 g
- Tensile specimens

Procedure:

1. Set up tensile-testing machine according to manufacturer instructions.

2. Begin testing 10 minutes after stripping time has been reached.

3. Obtain three tensile specimens.

4. Weigh each specimen and record.

5. Break specimen according to manufacturer instructions. Record all tensile strengths.

6. Repeat Steps 3 and 4 at intervals of 1 hour, 3 hours and 24 hours after stripping time has been reached.

7. Calculate the average of the three specimens.