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Comparison of a new, green foundry binder with conventional foundry binders

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ABSTRACT

Metalcasting within the United States aims to meet ever-more stringent environmental standards as new process technologies are developed. Conventional foundry core binders are responsible for up to 70% of a foundry's volatile organic compound (VOC) emissions. New core binder technologies are essential for environmental sustainability within foundries. Herein, conventional and novel foundry core binders were appraised using thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), hot distortion testing (HDT), and (Pilot-scale) molten iron erosion tests. Inherently, these tests cannot replace full-scale casting trials to evaluate binder effectiveness, however, these tests were performed to more fully elucidate binder properties that might cause casting defects or other unwanted behaviors at high temperatures. During each of these lab protocols, the combination of collagen plus alkali silicate as binders exhibited properties that matched or exceeded those of conventional phenolic urethane. Also, in iron erosion testing, the collagen/alkali silicate binder exhibited the same low erosion as conventional phenolic urethane. In hot distortion testing, the collagen–alkali silicate binder exhibited longer resistance to thermal bending, and comparable thermal flexibility to conventional phenolic urethane.

1. Introduction

Metalcasting is integral to American industry as castings are employed in nearly 90% of manufactured durable goods. Within recent years, the metal casting industry has sought to meet ever-more stringent environmental standards. However, conventional core binders emit up to 70% of a foundry's volatile organic compound (VOC) emissions [1,2]. A number of foundry managers have expressed an interest in replacing these conventional core binders with novel low-emission core binders—if they can offer the same physical and mechanical properties at high temperatures. This paper describes the thermal and thermomechanical stability of novel, low VOC binders as an alternative to traditional binders. Inherently, these tests cannot supersede casting trials to evaluate binder effectiveness, but they can certainly elucidate nuances useful for understanding full-scale behavior.

Cores are important components of metalcasting molding operations. In the conventional casting process, a mold is shaped to form the geometry for a desired object, and molten metal is poured into the mold. Upon metal solidification, the mold is shaken-apart and the cast object is removed. Conventional foundry casting processes utilize green sand to create the outer geometry of the casting mold, and this is composed of a sand, coal, water, and clay mixture. However, the sand, coal, and clay mixture is not suitable for creating molds for the more complex metal casting that contain hollow cavities. The hollow cavities are created using cores, as in the cylinders in an engine block. Cores are composed of two components: sand and binder. Sand acts as a filler, comprising 97–99% of a core. The sand is held together with 1–3% binder, or 'core binder' as is common foundry nomenclature. Herein, 'binder' will refer to the chemical mixture, which adheres the filler (i.e. sand) to form a core. Additionally, 'core' will refer to the solidified 'binder' and 'filler' composite. These cores must have adequate strength at room temperature and also maintain structural integrity when exposed to molten metal. During metal pouring, the maximum temperatures experienced by cores range from 1510 °C at the molten iron interface, down to 50–300 °C several inches away from this interface; temperature exponentially declines from the metal interface through the core [3]. Paradoxically, after withstanding molten metal exposure and subsequent cooling, the binder must then disintegrate during shake-out, so that the sand can be easily removed from the cast

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product cavities. Subsequently, this shaken-out sand provides the filler for the next cycle of green sand exterior molding.

Several conventional petroleum-based binder systems, such as phenolic urethanes and furans provide structural integrity, shake-out propensity, and casting quality. However, these phenolic urethanes and furan binders will thermally decompose after metal exposure, emitting as much as 30–70% of a foundry's VOCs and hazardous air pollutants (HAPs) [1,3]. For the paper herein, "VOCs" are defined as the VOCs with C6–C16 hydrocarbon length, per foundry nomenclature [2]. It is these C6–C16 VOCs that may be considered a health concern. As expected, VOC and HAP emissions increase proportionately with an increase in core-loading [4,1,5]. Recent work has determined that C6–C16 VOC emissions for a collagen core binder are 70–90% less than for conventional phenolic-urethane binders [2,6]. Specifically, lab scale pyrolysis determined that collagen emits 41.5 mg VOC/g binder in the C6–C16 hydrocarbon range, compared to phenolic urethane's 107.8 mg VOC/g binder in the C6–C16 range. Further, collagen emits 7.7 mg HAP/g binder, compared to phenolic urethane's 32.1 mg HAP/g binder [2]. Instead of VOC and HAP emissions, collagen releases more C1–C5 hydrocarbons than conventional phenolic urethane [2].

Despite the significant and necessary emission reductions enabled by collagen, it is only marginally employed in foundries. The inability of collagen (alone) to withstand significant temperatures imparted by molten iron (1290 °C–1510 °C) at the molten metal and sand interface is the key reason that collagen is not implemented ubiquitously through the industry. Specifically, this inability incurs erosion when molten iron pours onto the collagen (alone)-adhered core, and this produces costly casting defects. Collagen, which is available in large quantities as a by-product of the meat-packing industry, is the fibrous protein that strengthens skin, tendon and bones, and at ambient temperature, this triple-helical material has a tensile strength equivalent to steel [7]. The individual collagen strands are 200–500 nm long, and each polypeptide strand is comprised of a three amino acid repeating sequences. These typically include a repeating sequence similar to X–Y–Glycine, where Glycine comprises about 34% of collagen, while the "X" and "Y" include proline (12%), alanine (10%), hydroxyproline (10%), glutamic acid (7%) or other amino acids [8,9].

When collagen is used as an adhesive, the triple helical structure is denatured in water. Then as the adhesive dries, the polypeptide strands randomly re-align and bond through Hydrogen Bonds [10]. Hydrogen Bonds between the polypeptide strands are numerous, yet each bond is 'weak', with bond energy less than 25 kJ/mole and are at least an order of magnitude less than covalent bonds [11–13]. The authors sought to increase the adhesive integrity at high temperatures by increasing the bond energy [14] in a collagen binder system by utilizing well-documented covalent intermolecular organic cross-linking to increase the mechanical integrity and stability of collagen [15–24]. Cross-linking also increases resistance to water solubility [25,26], which would improve core storage when exposed to humidity. Of the types of cross-linking that could be employed, it has been the inorganic silicate cross-linking that we found achieved more favorable results than organic cross-linking under the thermal duress imposed.

Specifically, the authors sought herein to include alkali–silicates in conjunction with collagen to produce a 'hybrid' organic/inorganic binder. The crosslinking formation between collagen and silicates has been studied by Coradin and others for biological application [27–32]. This cross-link has the potential to increase the binding strength at both room temperature [33,27], and high temperature. Further work has been performed by Gelinsky et al. [34] creating a mineralized collagen, which was made by precipitating amorphous calcium phosphate from a collagen solution as the collagen fibrils were reassembling. Over time, the amorphous mineral phase transformed to nanocrystalline hydroxyapatite, which then precipitated onto collagen fibrils. Yet, the utilization of collagen and silicates for use in foundry applications is novel. The authors hypothesized that the alkali–silicates will provide strength when exposed to molten metal, while the low-VOC emitting collagen will gradually decompose after thermal exposure, as is conventionally desirable in the foundry industry, so as to provide easy sand removal after metal solidification.

Alkali–silicates, specifically sodium silicates, are widely used as adhesives and are also commonly used as core binders in the metalcasting industry [35–38]. Despite their many favorable characteristics, unmodified sodium silicate binders have one key problem—difficulty in shakeout or the inability to breakdown after metal solidification [38]. Other forms of alkali–silicates are potassium and lithium silicates; most importantly lithium silicates are the most insoluble following curing [36,37], which is attributed to the smaller ionic radius of lithium than that of sodium or potassium [37]. Additionally, a blend of potassium and lithium silicates provides a similar level of moisture resistance as lithium silicate [37]. The increased moisture resistance provided by lithium silicates is favorable for foundry core storage.

The objectives of the work herein were to (1) develop a novel low-emission foundry core binder, (2) benchmark the relevant physical as well as mechanical properties for both conventional binders and novel binders that could influence casting quality, and (3) provide a practical lab-scale test framework that can be utilized as a pre-cursor to full-scale molten metal tests that predict foundry binders' ability to withstand molten metal erosion. The driving hypothesis for this work is that collagen is a low-emission adhesive that when used alone cannot provide the physical and mechanical properties necessary to withstand the high temperatures imparted at the molten metal interface experienced by cores, however when collagen is coupled and cross-linked with alkali–silicates the 'hybrid' binder can provide the necessary physical and mechanical properties for use in metal casting.

2. Materials and methods

2.1. Materials

Sodium silicate was a modified sodium silicate provided by J.B. DeVenne INC. (Berea, OH). This modified sodium silicate formulation contained 42.5% by weight of dry solids. Collagen was provided by Entelechy (Plymouth, MI), and came as a dry powder. The phenolic urethane binder that was heat-set and cured by triethylamine (TEA) was provided by Ashland Chemical Company (Columbus, OH), and came as a two-part binder that cured when mixed and heated. The blended potassium/lithium silicate was provided by PQ Corporation (Malvern, PA), and came as a liquid with 29% solids content. Silica sand was provided by Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67 to 73.

2.2. Sample preparation overview

Samples for thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and hot distortion testing (HDT) were prepared as described in respective test sections. In general, DMA and HDT samples were prepared by coating filler with binder, and the mix was molded into gum-stick sized core samples (12.00 ± 0.30 mm $\times$ 5.00 ± 0.15 mm $\times$ 35.00 ± 0.00 mm) for DMA, or candy bar sized samples (15.24 cm $\times$ 2.54 cm $\times$ 1.27 cm) for HDT. The samples for DMA and HDT experiments contained the typical percentages of sand (98–99%) and binder (1–2%) that