Phosphorylated CNSL prepolymer as a foundry sand core binder

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The performance of phosphorylated cashew-nut shell liquid prepolymer (PCNSL) as a core binder in foundry applications is studied. Moulding properties such as strength and permeability and casting characteristics such as surface quality of castings, core-metal reactions, core collapsibility and anti-damping behaviour are analysed. PCNSL gave superior performance in all these factors when compared to other system of binders such as sodium silicate. Studies based on IR spectra and SEM on the nature of bonding between sand and PCNSL indicate involvement mostly of physical and mechanical interactions rather than chemical bonding. The formation (during casting) of higher content of char (due to the presence of phosphate group in the resin) with open porous structure as revealed by SEM is thought to give better collapsibility to the system.

In moulds, the cores must withstand the severest conditions of temperature and pressure. In spite of being submerged in hot metal, the core must resist erosion, thermal shock and metal penetration retaining its dimensional location with no casting defects. Nevertheless, it should not be so permanent that its removal from the casting becomes difficult. These requirements demand that cores be made of suitable materials. Not only sands but also the core binders should have versatile qualities, viz., high bonding ability till the end of solidification and collapsibility after solidification is over, appropriate viscosity and bench life for proper mixing of sand and binder, minimum gas evolution, non-corrosive nature and non-reactivity with metal and sands used.

Many inorganic and organic binders had been developed in the past, however, each has got its own limitations. Of late, cashew-nut shell liquid (CNSL) based core binders have drawn attention to foundrymen. Although some industries are already using some type of modified CNSL for core oil production, the knowhow is a trade secret. Except a few reports, data on the application of CNSL polymers for foundry use are limited.

Phosphorylated CNSL prepolymer (PCNSL, trade name: ANORIN-38) prepared by phosphorylating CNSL has properties superior to those of conventional CNSL formaldehyde. A comparison of properties shown in Table 1, clearly evidences the scope of the present investigation. This work was, therefore, undertaken with an objective of finding the feasibility of utilising PCNSL for sand core application. For a rough comparison CO₂ cores were used:

**Experimental Procedure**

**Materials** - Silica sand (obtained from Cherthala, Kerala) having the following specifications was used:

<table>
<thead>
<tr>
<th>Property</th>
<th>PCNSL polymer</th>
<th>Conventional CNSL-formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Lap shear strength between wood pieces, MN/m²</td>
<td>4.0 + 0.2</td>
<td>0.60 - 0.80</td>
</tr>
<tr>
<td>2 Viscosity, Ns/m²²</td>
<td>3600-4500</td>
<td>0.40-0.55</td>
</tr>
<tr>
<td>3 Fire-retardancy Limiting Oxygen Index (LOI)</td>
<td>38</td>
<td>21</td>
</tr>
<tr>
<td>4 Tensile strength (with asbestos), MN/m²</td>
<td>16.9-24.5</td>
<td>5-10</td>
</tr>
<tr>
<td>5 Impact strength, J</td>
<td>2.60-3.04</td>
<td>-</td>
</tr>
<tr>
<td>6 Phosphorous content, %</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

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Hexamethylenetetramine, HMTA/hexamine (Arnold Otto Meyer, Hamburg) was used as the curing agent.

Sodium silicate solution (SiO₂ 30% and Na₂O 12%) used was a product of BDH, Poole, England.

Plain carbon steel (0.19-0.02 C, 0.8-0.95 Mn, 0.3-0.5 Si & 0.03 S) was obtained from Sree Rama Krishna Steel Industries, Coimbatore and LM 4 (Al 2-4% Cu, 4-6% Si) alloy was purchased from M/s M S Metals, Bombay.

Sample preparation—Sand and powdered hexamine were mixed thoroughly in a 2.2 kg capacity laboratory type George Fisher (GF+) muller for 2 min. PCNSL was then added and mulled for further 10 min. Standard three rammed samples 0.05 m dia × 0.05 m height were prepared by a GF+ rammer. Sodium silicate binder was mixed with sand and hardened by passing CO₂ gas.

Core and mould—Cylindrical samples of 0.05 m dia × 0.05 m height prepared as above were used as core. The composition of core sand mix is: PCNSL 8% based on sand, hexamine 10% based on PCNSL and cured at optimum conditions of temperature and time. Mould dimension and pattern (Fig. 1) used was as per Steel Founder’s Society of America (SFSA)⁷. In this case, all the four cores remain submerged by molten metals in a disc casting. Uncoated cores were used to find severity of reaction with metal, if any.

Casting—Melting of LM 4 alloy was done in an electrical resistance furnace using a graphite crucible. It was then poured into the mould at 750°C. Melting of steel was done in an arc furnace and poured into the mould at 1600°C.

Curing—Curing was carried out by placing the green sample in an electric air oven maintained at the required temperature. The variables studied are given below:

1. PCNSL : 3, 5, 8 and 10% based on sands
2. Hexamine : 5, 8, 10 and 15% based on resin
3. Curing temperature : 110, 150, 200 and 240°C
4. Curing time : 1, 2, 3, 4, 5, and 6 h

Measurements—Compressive and shear strengths of green samples were measured by GF⁺ universal strength machine while the same for baked samples were measured by Universal Testing Machine INSTRON 1195 and FG 100 of Veb Thuringer Industries (Germany) at a strain rate of 3.30 × 10⁻⁴ m/s. Permeability was measured by GF⁺ electric permeability meter. Average of three readings, with a percentage deviation less than 5, were taken for plotting the relationship in all the cases.

Antidamp characteristics were measured by placing 4 cores in moulds exposed to atmosphere and then by noting the change of weight of the samples over a length of time.

Assessments of mould-metal or core-metal reactions and subsurface porosity, if any, were done by metallography of the samples taken from interface region. Metalloplan (Leitz, Germany) was used for this purpose.

Scanning Electron Microscopic photographs were taken using a JEOL 35 C microscope. The samples were sputtered with gold prior to exposure.

IR spectra were recorded using KBr pellet on a Perkin-Elmer IR spectrophotometer model 882.

Results and Discussion

Selection of minimum binder content for sample preparation—Preliminary experiments showed that a minimum of 3% PCNSL was needed to hold the sand grains together so that adequate strength was obtained.
Fig. 2 - Effect of curing temperature and time on baked strength for 3% PCNSL and 5% hexamine, (a) compression, (b) shear ([△] 110°C; (●) 150°C; (□) 200°C and (○) 240°C)

Fig. 3 - Effect of curing temperature and time on baked strength for 3% PCNSL and 8% hexamine, (a) compression, (b) shear ([△] 110°C; (●) 150°C; (□) 200°C and (○) 240°C)
Strength properties

Effect of curing temperature and time—Baked strength of the core is found to vary widely with curing temperatures and time. Figs 2-5 show the variation of compressive and shear strength for four different compositions of sand core with 3% PCNSL (hexamine content 5, 8, 10 and 15%). It can be seen from these figures that the cores achieve appreciable strength only above a temperature of about 110°C and the maximum strength has been achieved after 3 h of baking at a higher curing temperature of 240°C. However, if the baking time is prolonged to 6 h, the same strength could be achieved at 200°C itself. The increase in strength with increase in temperature and time could be expected as the resin having a phenolic moiety in its structure forms a thermoset matrix holding the sand grains together. With further increase in temperature above 250°C, the strength however, registers a fall which is possibly due to thermal decomposition of the resin. The colour of the sample at this temperature changes from brown to black. It was observed that baking at a lower temperature for a longer period gave uniformity in properties.

Effect of hexamine—Fig. 6 shows the variation of strength with the amount of hexamine. It can be noted that both compressive and shear strengths increase with the increase in hexamine content till an optimum percentage (15-16%) is reached. This is expected as the hexamine contributes to the cross-link density of the cured plastic material. Earlier reports also showed an optimum hexamine content of 14-16% for phenolic resin-sand system.

Effect of amount of PCNSL—Fig. 7 shows the variation of compressive strength with the amount of PCNSL. As the content of PCNSL increases, the strength also increases and passes through a maximum after which it more or less levels off. Another interesting observation is that at higher content of PCNSL, maximum strength could be obtained at lower temperatures and times. For example with 10% PCNSL maximum strength could be achieved at a temperature of 200°C and curing time of 3 h. Thus, there is a definite curing temperature and curing time at which strength is maximum for specific compositions of PCNSL and hexamine. The ultimate strength of the resin bonded sand might depend on the strength of the...
Fig. 5 - Effect of curing temperature and time on baked strength for 3% PCNSL and 15% hexamine, (a) compression, (b) shear ([△] 110°C; [●] 150°C; [□] 200°C and [○] 240°C).

Fig. 6 - Effect of amount of curing agent on baked strength, (a) compression, (b) shear ([△] 1 h; [●] 2 h; [□] 3 h and [○] 4 h).
cured resin, the strength of the bridges (or interfaces) between the resin and the sand and the size and number of these bridges. Therefore, it is important to find out correctly the optimum amount of resin that gives adequate coverage to the grains so that sufficient number of bridges are formed. Tests with 8% sodium silicate bonded sample (CO₂ gasing time 1 min) showed that the maximum strength attainable was only 1.75 MN/m² against a value of 6 MN/m² obtained with 8% PCNSL (10% hexamine at 240°C, 3 h baked).

Green strength—The compressive strength of the green samples was found to be extremely low with values in the range of 0.16-0.30 MN/m². So heat curing is essential to attain enough strength.

Permeability—A permeability number of 285 was obtained for 3% PCNSL cured with 15% hexamine samples against 260 of 5% sodium silicate bonded samples.

Bench life—PCNSL bonded core sand showed improved bench life of around 24 h compared to the 30 min bench life of silicate core sand. This higher bench life makes working easy for the preparation of the core.

Antidamp characteristics—The percentage change in weight (taken at different time intervals) of PCNSL bonded cores was only negligible (0.001%) compared to 0.05% for the sodium silicate cores. This indicates that PCNSL bonded cores could be stored for a longer period than silicate bonded cores.

Casting characteristics
Surface finish—Actual aluminium casting is shown in Fig. 8. The surface finish obtained along the core metal interface was found to be better with PCNSL core than with sodium silicate core.

Collapsibility—The collapsibility of the PCNSL core was found to be much superior to that of the silicate cores. This is possible because of the formation of char from the organic resin at the pouring temperature of the molten metal (750°C for aluminium). PCNSL is known¹⁴,¹⁵ to give a higher char content of 41% than that (13%) of conventional CNSL-formaldehyde resin. The higher level of char content in the core after casting helps to retain the integrity of the core and at the same
Fig. 11 - Microstructures of steel casting at core-metal interface

seen from Fig. 12 that uniform coating cannot be achieved by mixing alone. However, on heating the resin flows and forms a uniform coating over the grains. Inter-granular bridge of resin is also formed.

IR spectroscopic studies did not show any evidence of chemical reaction between sand and PCNSL. Therefore, the increase in strength observed could probably be due to either mechanical or physical (Fig. 12c shows a neat coating of cured resin around sand granules) interactions between sand and PCNSL.

It could also be noted from Fig. 9 that the whole structure gets opened up and becomes porous after casting due possibly to the formation of char as discussed earlier. This porous structure helps in making the material collapsible.

Conclusion

1 Phosphorylated CNSL resin with hexamine as curing agent develops higher strength than sodium silicate binder. There is a definite curing temperature and time at which strength is maximum for specific compositions of PCNSL and hexamine. For example, with 3% PCNSL and 5% hexamine the maximum strength was attained at 240°C and 3 h. In general, for most of the working compositions, the curing temperature is in the range of 200-240°C and baking time 2-3 h. Room temperature curing is not at all effective.

2 Collapsibility of PCNSL bonded core after casting is superior to that of sodium silicate bonded core.

3 Bench life of PCNSL bonded sand mix is much higher than that of sodium silicate bonded sand mix.
4 Antidamp character of PCNSL bonded cured core is also better compared to sodium silicate bonded core.

5 No core-metal reaction of PCNSL binder was observed. Also there are no indication of reaction between PCNSL and sand.

6 Phosphorylated CNSL resin is found to be promising for foundry use.

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References

7 AFS sand Division Committee 8-T, in Moulding methods and materials (The American Foundrymen Soc., Des Plaines, Illinois), 1962, 142.

Fig. 12—SEM of the surfaces of (a) sand alone, (b) PCNSL bonded green sample at intergranular boundary before curing, (c) same sample (b) after curing at optimum condition as described in experiment