Research on High-performance Furan Urea-formaldehyde Phenol-formaldehyde Copolymer/Composite Resin

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Abstract: In response to the need for high-quality development, the foundry industry continues to demand higher performance from resin sands with wide-ranging applications. Addressing the shortcomings of furan resins currently available in the market, this study develops a resol resin that possesses both acid and heat-curing characteristics similar to traditional urea-modified furan resins. This resin is then co-polymerized and compounded with traditional urea-formaldehyde-modified furan resin under certain conditions, resulting in a multi-component resin with uniform texture and excellent stability. The advantages of the developed resin combine the high room temperature strength and good collapsibility of traditional urea-formaldehyde modified furan resin with the high-temperature strength， smooth gas evolution and no nitrogen generation of phenol-formaldehyde resin. Additionally, it exhibits low free formaldehyde content and reduces furfuryl alcohol consumption by approximately 20%, thereby significantly reducing resin costs especially during periods of high furfuryl alcohol prices. The advantages of this composite resin are particularly evident in the production of thick and large ductile iron castings.

Keywords: resol resin; copolymerization; composite; cost reduction; performance improvement

1 Introduction

There are two main types of furan resins used in casting: one is urea-formaldehyde modified furan resin, which has the advantages of high ordinary temperature strength, fast curing speed, and good collapsibility, but has high nitrogen and formaldehyde content, produces a large amount of smoke, and makes castings prone to nitrogen porosity. The other type is phenolicmodified furan resin, which does not contain nitrogen, can effectively reduce the risk of nitrogen porosity in castings, and has higher high-temperature strength but has the drawback of low ordinary temperature strength in sand cores. Both types of resins share common shortcomings: their modification components are singular and in small quantities, and the high proportion of furfuryl alcohol leads to abnormally high product costs when the price of furfuryl alcohol is elevated.

2 Experimental procedure

1. Reducing furfuryl alcohol and improving performance is the main direction

Since the main material of furan resin, furfuryl alcohol is derived from furfural extracted from corn cobs and then reduced, it cannot currently be produced through chemical synthesis. Therefore, the supply of furfuryl alcohol is sometimes hard to secure, resulting occasional price spikes. In the long term, its price has an upward trend which increases the cost of furan resins and significantly undermines its application advantages. Hence, to promote better and wider application of furan resin, reducing the consumption of furfuryl alcohol and improving its performance are the keys.
There are three common methods to reduce furfuryl alcohol consumption: urea-formaldehyde modification, phenolic modification, and the addition of other modification materials that are less expensive than furfuryl alcohol. All these methods have shortcomings.

2. Furan-urea-formaldehyde-phenolic copolymer/ composite resin

2.1 Resin synthesis mechanism

The synthesis mechanisms of urea-formaldehyde, phenolic, and their modified furan resins are well-known. The mechanism of composite resin is as follows: if two different resins can maintain a uniform texture for a long time after mixing and have the same or similar curing characteristics (such as thermosetting and acid-setting), or even complement each other (e.g. one having lower thermal strength and the other higher thermal strength), then compounding can potentially achieve the goal of complementing strengths and improving performance. If the other resin involved in the compounding is significantly cheaper, it can improve performance while reducing costs. Phenolic resin, with its widely available raw materials and stable prices, is generally cheaper than furfuryl alcohol and is therefore an ideal material for composite resins.

2.2 Study on phenolic resin for compounding

2.2.1 Property requirements for composite phenolic resins

To enable the phenolic resin to be compounded with traditional urea-formaldehydemodified furan resin, it is crucial to ensure that the compounded resin can maintain a uniform texture over time and not separate. Using a weak acid as a catalyst to control the degree of polymerization of the phenolic resin, it kept the resin's average molecule amount small, and its degree of polymerization low. This forms a resole phenolic resin liquid with a good water solubility, a water dilution ratio of about 50%, a solid content of about 70%, numerous active groups, and highly active with a low degree of polymerization. This resin, when copolymerized/ compounded with traditional urea-formaldehyde-modified furan resin under suitable conditions, exhibits good compatibility.

2.2.2 Copolymerization/compounding conditions

Extensive experiments have determined the optimal process conditions for copolymerization/compounding: a pH value of 5.5-6.5, a temperature of 55-60°C, and a duration of 30-40 minutes. If the pH value is too low, the compounding temperature is too high, or the compounding time is too long, the viscosity of the compounded resin will become too high due to excessive copolymerization. Conversely, if the two resins are mixed only at room temperature, minimal copolymerization occurs, leading to an unstable final product prone to separation. The experiments show that with a phenolic resin content lower than 20%, the viscosity changes very little within three months. However, if the phenolic resin content reaches 30%, the viscosity starts to increase after one month.

2.2.3 Study on curing characteristics

Because the phenolic resin used for compounding has a low degree of polymerization and is rich in active groups such as -OH, it rapidly polymerizes into a highly polymerized resin in an acidic environment, achieving a curing effect. This is similar to the curing characteristics of traditional acid-cured self-hardening furan resin. By controlling the degree of polymerization of the synthesized phenolic resin liquid, the two resins can have almost synchronous curing.

2.3 Performance of composite resin

2.3.1 High-temperature resistance

Numerous research findings have shown that phenolic resin has better high-temperature resistance than furan resin. When phenolic resin constitutes 20-30% of the composite resin, the composite resin's high-temperature resistance is superior to that of urea-formaldehyde-modified furan resin, while also retaining the good collapsibility characteristics of urea-formaldehyde-modified furan resin.

2.3.2 Gas emission performance

Experiments have demonstrated that phenolic resin emits gas more smoothly and in smaller quantities than furan resin, particularly not producing nitrogen. Since the composite resin contains 20-30% phenolic resin, its gas emission is significantly lower than that of traditional urea-formaldehyde-modified furan resin, and emits at a smoother rate.

2.3.3 Reduction of free aldehydes and harmful substances, significant reduction in furfuryl alcohol consumption

Comparing the composite resin ZFP801 with a nitrogen content of ≤3.0% used for large ductile iron parts with the non-composite resin ZF801, the experimental results showed that the consumption of furfuryl alcohol per ton of product decreased by 34.0%, free formaldehyde decreased by 46.4%, and the tensile strength increased by 13.5%. It indicates that the composite resin can significantly reduce the consumption of furfuryl alcohol and free formaldehyde while improving the tensile strength.

3 Result and discussion

(1) Exceeding 20% of phenolic resin in the composite will lead to a rapid increase in its viscosity. Further research is required to enable greater composite proportions.

(2) Composite resin isn't just a simple mixture; it requires copolymerization/compounding to ensure uniformity of the resin after blending. The mechanisms and conditions for copolymerization/compounding require further research.

4 Conclusion

(1) The proportion of phenolic in the composite resin should optimally be around 20%, with a shelf life of up to 4 months. If the proportion exceeds 30%, the viscosity of the resin will increase rapidly, and the shelf life will be limited to one month.

(2) The composite resin leverages the complementary advantages of the two resins, enhancing high-temperature resistance and improving gas emission performance, effectively reducing the occurrence of porosity defects in castings while maintaining good collapsibility.

(3) The composite resin can achieve lower nitrogen content. Urea and other aldehyde removers can be added during compounding, reducing free formaldehyde which is more environmentally friendly.

(4) The composite resin can significantly reduce the dependency on furfuryl alcohol, with a reduction of over 30%. When the price of furfuryl alcohol is significantly higher than that of phenol, it can substantially reduce the costs.

References

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