

Preparation of montmorillonite modified phenolic resin for shell process

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Abstract: The development of montmorillonite modified phenolic resin under microwave irradiation heating was investigated. The effect of montmorillonite content and stirring time on the structure and morphology of synthetic resin was analyzed. The optimum processing procedure was found to be 45 min stirring time with 5.4% montmorillonite addition. Further, the platelet spacing increases with stirring time till montmorillonite exfoliated to nanoscale platelet. When montmorillonite is exfoliated, layered structure at nanoscale can be uniformly distributed in the resin. The overall performance of montmorillonite modified phenolic resin is improved remarkably, such as flow ability, tensile strength and toughness property of resin coated sand. However, the gelation speed decreased slightly by adding montmorillonite.

Key words: shell process; phenolic resin; montmorillonite; comprehensive performance; tensile strength
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The shell molding process is widely applied in manufacturing complicated castings of high precision with phenolic resin as binder, for it possess a number of unique properties such as good storage of cores and shells, high specific strength, good breakdown capability and high casting surface quality^[1-4]. The development of casting towards large-scale and precision production put forward higher demands for the performance of phenolic resin for shell process^[5]. Modification of phenolic resin is an effective way for improving the performance, but the current used modifier for phenolic resin, such as tung oil, cashew nut shell liquid, salicylic acid and bisphenol-A, can only provide sole and limited improvement^[6-9].

Recently, montmorillonite modified phenolic resin (i.e. phenolic resin/montmorillonite nano-composites) attracts great interest of many researchers^[10-14]. Such composite can offer highly improved comprehensive properties in both stiffness and toughness, which is difficult to attain from individual components, especially when montmorillonite is in the exfoliated structure with its characteristic nanometer size and high aspect ratio^[15]. This study mainly concerns the synthesis process of montmorillonite modified phenolic resin under microwave irradiation heating. The effect of stirring time and

montmorillonite content on the structure and morphology of montmorillonite in phenolic resin was investigated. Then the performance of montmorillonite modified phenolic resin, such as flow ability, was assessed and quantified in detail.

1 Experimental procedure

Main materials used for this research were: analytically-pure phenol, aqueous formaldehyde and oxalic acid; chemical-pure hexamine and montmorillonite (MMT) Na⁺ and octadecyl amine.

The reaction took place in a three-necked vessel. The desired amount of 98wt.% phenol, MMT Na⁺, octadecyl amine, and oxalic acid were added into the reactor. The mixture was stirred for 45 min, 30 min, and 15 min, respectively, or not stirred at all under microwave irradiation. Then the desired amount of aqueous formaldehyde and 10wt.% oxalic acid solution were charged into the reactor and the reactor was heated by microwave irradiation to reflux. After 15 min, aqueous formaldehyde and oxalic acid solution were added as supplement. The reaction was suspended after another 25 min reflux. After settling, the aqueous layer was siphoned off. Vacuum distillation (up to 185 °C) stripped the remaining volatiles off the novolac under microwave irradiation. Then the product was discharged and cooled. The synthesis period of montmorillonite modified phenolic resin under microwave irradiation was much less than that for conventional heating method, and therefore enhanced the preparation efficiency.

2 Performance tests

The morphology of the polymer was examined using X'Pert

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PRO X-ray diffractometer. The diffractometer employs a copper X-ray source that has an emission wavelength of 1.54\AA at room temperature in the range of $2\theta=0.5^\circ-10^\circ$. All samples were cured before examined by X-ray diffraction (the curing process corresponds to the preparation of resin coated sand).

Scanning electron microscope (SEM) images were obtained by a Quanta 200 with EDAX energy dispersive spectrometer (EDS). Softening point, curing time and flow distance of the resins were determined according to ZBG39005-89.

After preheated to 160°C , 1,000 g of standard sand was charged into a laboratory muller. The sand was allowed to equilibrate to 135°C , then 20 g of novolac resins was added, the sand and resins were muller till $110^\circ\text{C}-105^\circ\text{C}$, and HTMA solution, accounting for 10%–15% of resin was added. The 1.5 g of calcium stearate was added thereto, mulling continued until the mixture was crumbled, and the coated sands were then discharged. Finally, the tensile and bending tests were performed on the resin coated sands in accordance with JB/T8834-2001.

Fracture deformation was measured during bending test. The displacement transducer was reclined on the sample and was initially set to zero, then loaded the specimen until fractured, final reading from the displacement transducer was defined as fracture deformation.

3 Results and Discussion

3.1 Preparation of montmorillonite modified phenolic resin

Montmorillonite monocrystal layer consists of a 2:1 layered structure of a dioctahedral aluminum sheet sandwiched between two silica tetrahedral sheets of about 1 nm thick, and the crystallographic structure of montmorillonite is schematically showed in Fig. 1. Montmorillonite crystal is stack of the monocrystal layers which are linked by Van der Waals force, and the distance of layers is called platelet spacing (as d_{001} in Fig. 1). The platelet spacing can be calculated by Bragg equation $2d\sin\theta = \lambda$ (d is the platelet spacing, θ is the half incident angle and λ is incident rays wavelength)^[16]. Montmorillonite's platelet spacing is about 0.96 nm in aggregate structure^[15]. The platelet

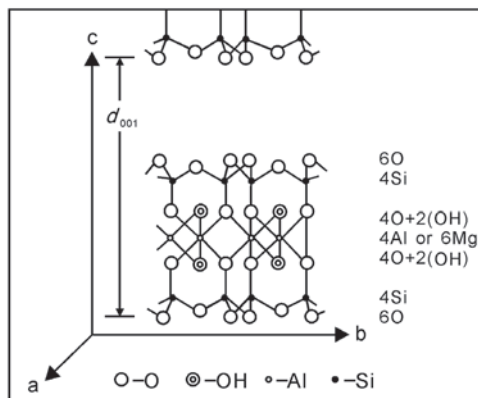


Fig. 1 Schematic diagram of ideal crystal structure of montmorillonite

spacing can be increased and the incident angle of diffraction peak decreases accordingly when polymer intercalated into the interlayer, or the monomers polymerization in the interlayer, then montmorillonite is called in intercalation structure. When the platelet spacing further increases or randomly till the platelet escaped the influence of Van der Waals force, the montmorillonite dispersed in separate sheets entirely in resin, then the diffraction peak disappears and montmorillonite is now in its exfoliation structure. The performance of montmorillonite modified phenolic resin is optimum when montmorillonite is in its structure of exfoliation and uniformly disperses in resin at nanoscales^[14].

In order to obtain the optimum process, the effect of stirring time and montmorillonite content on the structure and morphology of phenolic resin was analyzed respectively. By varying the stirring time while keeping the montmorillonite content constant, it was found that the platelet spacing increased monotonically with the stirring time. Figure 2 shows intercalation and exfoliation for the phenolic resin with 5.4% montmorillonite that was stirred prior to polymerization for 15 min, 30 min, 45 min, or not stirred at all under microwave irradiation. X-ray diffraction analysis shows that the platelet spacing is 1.3 nm for not stirred sample, the platelet spacing increased to 1.6 nm for the samples with 15 min stirring, and 1.75 nm when stirring for 30 min, and there is no peak in the state of stirring 45 min, which implies that the montmorillonite is completely in its structure of exfoliation. When the stirring time is no longer than 30 min, montmorillonite is mainly in intercalated structure. Montmorillonite is mainly in exfoliated structure when stirring longer than 40 min.

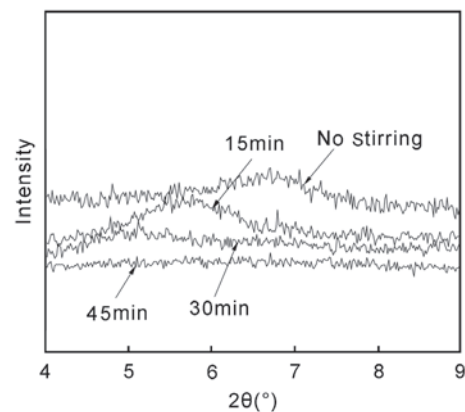


Fig. 2 XRD profiles for montmorillonite (content 5.4%) in phenolic resin with different stirring times

Figure 3 shows the XRD profiles of montmorillonite in phenolic resin with different montmorillonite contents (after stirred for 45 min). For 2.7% and 5.4% montmorillonite content, there is no particular peak on the XRD profiles, so the montmorillonite were exfoliated completely which can also be confirmed in SEM observation (Fig. 4). For 8.1% and 9% montmorillonite, the peak location is the same and the platelet spacing is 1.6 nm, which indicates that the average

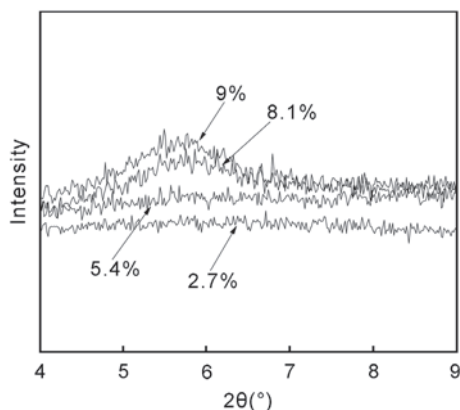


Fig. 3 XRD profiles for montmorillonite in phenolic resin with different montmorillonite content (stirring for 45 min)

montmorillonite platelet spacing does not depend on the montmorillonite content once the content exceeds the limit. Montmorillonite can only be intercalated structure when the montmorillonite content is less than 5.4%. Therefore, the optimum process under microwave irradiation is stirring for 45 min and the montmorillonite is 5.4%.

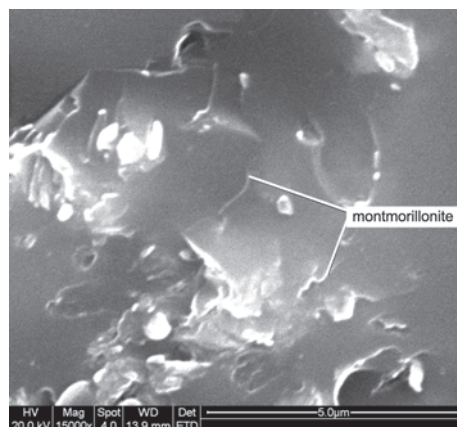


Fig.4 SEM images of montmorillonite modified phenolic resin (stirring for 45 min, montmorillonite is 5.4wt.%)

3.2 Performance of montmorillonite modified phenolic resin

(1) Softening point

The performances of montmorillonite modified phenolic resin were tested, and the data is summarized in Table 1. It was found that the overall performances were improved significantly except for a slight decrease in gelation speed.

Table 1 Comprehensive performance of montmorillonite modified phenolic resin*

Montmorillonite content wt.%	Softening point °C	Average molecular weight	Flow ability mm	Curing time s	Thermal tensile strength MPa	Cold tensile strength MPa
0	85	559	73	60	1.12	2.62
2.7	80	531	98	65	1.85	3.82
5.4	76	486	119	66	2.13	4.20
8.1	72	412	97	68	1.96	3.76

* The molar ratio of formaldehyde to phenol is 0.82.

Softening point is taken as critical assessment to differentiate the license tag of the phenolic resin for shell process. Figure 5 shows that softening point decreases with the increase of montmorillonite content. When the montmorillonite content exceeds 5.4%, the decrease of softening point becomes faster. The softening of polymer corresponds to the increased motion freedoms of the molecular chain, and the energy of molecular chain's movement increase with lengthening of molecular chain^[17]. Therefore, the softening point is the characteristics of average molecular weight (\bar{M}_n) of resin, and the decrease of softening point is attributed to the reduction of \bar{M}_n . The \bar{M}_n of resin was measured and calculated by gel permeation chromatography (GPC), as listed in Table 1, which confirms that the \bar{M}_n of resin decreases with the increase of montmorillonite content. The reduction of \bar{M}_n can be attributed to the concentration of montmorillonite platelet, which restrains the motion of long molecular chain and decreases the probability of the growth of long molecular chain, thus the \bar{M}_n of resin decreases. When the montmorillonite content exceeds 5.4%, montmorillonite has mainly intercalated structure and aggregates, which makes the long molecular chain moving more difficult, therefore the decrease of softening point

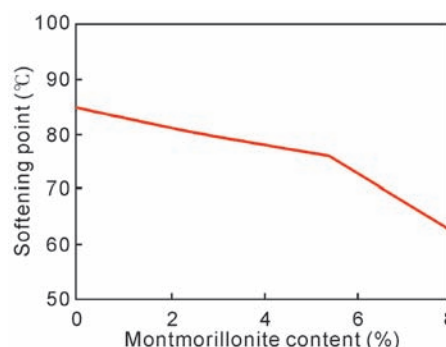


Fig. 5 Effect of montmorillonite content on the softening point of modified resin

becomes faster.

(2) Flow ability

Flow ability of phenolic resin is a key parameter for preparing resin coated sand. The flow ability of montmorillonite modified phenolic resin is improved remarkably, especially when the montmorillonite content is 5.4%. Figure 6 shows that the flow ability of montmorillonite

modified phenolic resin increases with the increase of montmorillonite content. As the montmorillonite content exceeds 5.4%, the flow ability begins to decrease. There are two reasons to cause this phenomenon. First, the decrease of \overline{M}_n of resin leads to an improvement of flow ability. Secondly, the nanoscales platelet dispersed in resin increases the distance of long molecular chains and damages the polarity connection of molecular, therefore the Van der Waals force of molecular is decreased and the flow ability of modified resin is improved. When the montmorillonite content is more than 5.4%, the intercalated structure and aggregate absorbs long molecular chain, therefore the Van der Waals force of molecular chain increases and, adversely the flow ability of resin decreases.

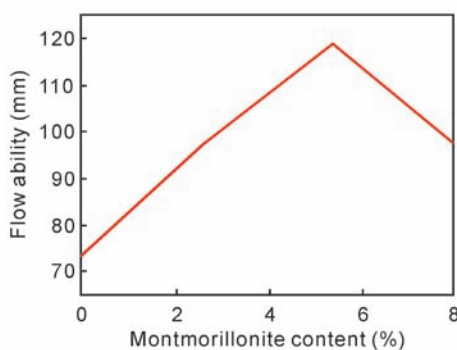


Fig. 6 Effect of montmorillonite content on the flow ability of modified resin

(3) Gelation speed

Gelation speed is defined as the time required from softening to melting, flowing and until the gelation of phenolic resin that blended with curing agent. It is used for measuring the curing time of resin, fast gelation means short curing time. The gelation speed of montmorillonite modified phenolic resin decreases slightly with the increase of montmorillonite content. This is due to low molecular weight (which needs more reaction time for cure) and montmorillonite platelet structure (which hinders the collision of resin and curing agent).

(4) Strength and toughness of resin coated sand

The tensile strength of coated sand prepared by modified phenolic resin is showed in Fig. 7. It was found that both hot and cold tensile strength increased with increasing montmorillonite content at first, and started to decrease once montmorillonite content is more than 5.4%. When the montmorillonite content is less than 5.4%, montmorillonite is completely in exfoliated structure and uniformly disperses in resin, so the tensile strength increased with the increase of montmorillonite content. When montmorillonite content is more than 5.4%, montmorillonite is mainly in intercalated structure and aggregate, which lead to uneven distribution of montmorillonite in resin and weak boundary layer. Thus, the tensile strength of resin coated sand begins to decrease.

The phenolic resin after curing is brittle, and the coated sand core often cracks during pouring. This is closely related to the toughness property. In this study, hot flexural strength and

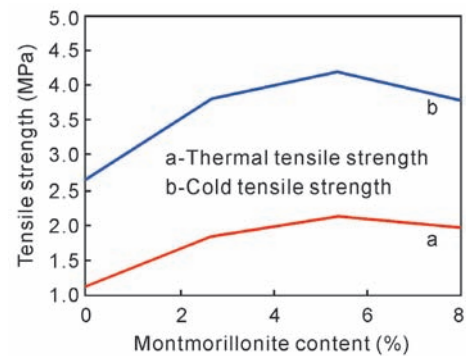


Fig. 7 Effect of montmorillonite content on the strength of resin coated sand

fracture deformation were used to characterize the toughness property^[18]. The high hot flexural strength and large fracture deformation correspond to good toughness. The effect of montmorillonite content on the toughness properties of resin coated sand is shown in Fig. 8. It can be seen clearly that the thermal flexural strength and fracture deformation of montmorillonite modified phenolic resin coated sand were improved remarkably compared with those of resin without modification. The maximum toughness was achieved when montmorillonite content is 5.4%.

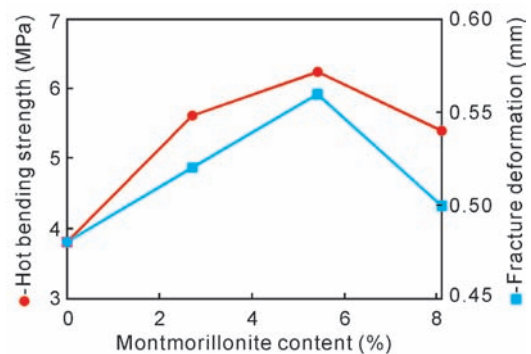


Fig. 8 Effect of montmorillonite content on toughness properties of resin coated sands

The reason for the increase of tensile strength and toughness property of coated sand prepared by modified phenolic resin is due to the exfoliation of montmorillonite in the resin. Although the montmorillonite cannot absorb strain well, it can increase the material's toughness by roughening. Examination of the fracture surfaces reveals a substantial increase in the area of fracture via roughening. The implication is that the high strength of the smectite platelets prevents their fracture when the polymer fails. The bonding between the montmorillonite and the polymer is substantial enough to transmit stress through the interfacial area and spread the effective area of deformation, due to the large surface area of the inorganic phase and the corresponding limited mobility of the polymer in the interfacial region. Cracks must propagate around the montmorillonite in a tortuous path that requires more energy. Because the bonding is better in montmorillonite modified

phenolic resin, the crack must overcome a more significant barrier to move along the interface when comparing with traditional composites.

4 Conclusions

(1) Montmorillonite modified phenolic resin can be easily prepared under microwave heating. X-ray diffractions of montmorillonite in phenolic resin showed that the platelet spacing increases with stirring time till exfoliation of montmorillonite. Montmorillonite can only exist in intercalated structure when the montmorillonite content is more than 5.4%. Therefore the optimum process is stirring for 45 min and the montmorillonite addition is 5.4%.

(2) The softening point and flow ability of modified phenolic resin are improved remarkably by montmorillonite, especially the montmorillonite in its structure of exfoliation, except for a slightly decreased gelation speed.

(3) The tensile strength and toughness property of montmorillonite modified phenolic resin are significantly improved with montmorillonite addition in its structure of exfoliation. When montmorillonite in exfoliated structure, it can improve tensile strength of resin coated sand by roughening mechanism and prevents brittle fracture.

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