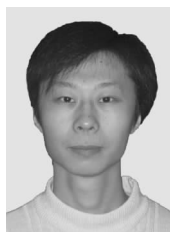


Preparation of Lignin-based Superplasticizer and Its Application in Mortar



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Abstract: Lignosulfonate-modified sulfonated melamine formaldehyde resin (LSMF) has been synthesized as a superplasticizer used in mortar, and its effects on the performance of mortar have been systematically investigated. To obtain a new superplasticizer LSMF, lignosulfonates originated from wood, straw, bamboo and bagasse were selected to react with sulfonated melamine formaldehyde through a four-step reaction. The effects of LSMF on the performances of the superplasticized mortar were studied through measuring water-reducing ratio, compressive strength, flexural strength, and accelerated carbonation depth. The result shows that straw-based LSMF with sulfonic group content of 3.663 mmol/g and intrinsic viscosity of 7.24 mL/g has the best water-reducing and reinforcement effects. When LSMF is used in dosage of 0.7% by weight of cement, water-reducing ratio reaches 21.1%. Compared with that of the control mortar, compressive strength and flexural strength of the superplasticized mortar increase 37% and 18% at 28 d, respectively. The minimum carbonation depth of superplasticized mortar at 28 d is 13 mm, while that of the control mortar is 34.5 mm. This understanding can lead to push forward the utilization of lignin with high efficiency.

Key words: lignosulfonate; LSMF; superplasticizer; durability

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木质素基超塑化剂的制备及其在砂浆中的应用

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摘 要: 来源于木材、麦草、竹子和蔗渣的木质素磺酸钠与三聚氰胺、甲醛和焦亚硫酸钠合成出磺化木质素三聚氰胺甲醛超塑化剂(LSMF)。系统研究了 LSMF 对砂浆减水率、抗压强度、抗折强度和加速碳化深度等应用性能的影响。结果表明,使用麦草基木质素磺酸钠合成出磺化度 3.663 mmol/g,特性黏度 7.24 mL/g 的 LSMF 对砂浆的减水增强性能最好。当 LSMF 掺量为 0.7% 时,砂浆减水率为 21.1%。硬化砂浆 28 d 加速碳化深度为 13 mm,空白砂浆为 34.5 mm。掺加 LSMF 后,硬化砂浆 28 d 抗压强度和抗折强度分别比空白砂浆提高 37% 和 18%。LSMF 超塑化剂为木质素高效利用提供了一种新的思路。

关键词: 木质素磺酸盐; LSMF; 超塑化剂; 耐久性

Nowadays, a new type of concrete termed high-performance concrete (HPC) has become popular in concrete construction. One key factor for successful preparation of HPC is the addition of proper superplasticizers^[1]. Sulfonated melamine formaldehyde (SMF) is used as superplasticizer in HPC, fire-endurance concrete and gypsum because of its high dispersion ability and good durability performance^[2]. However, the development of SMF is limited due to its high cost and large slump loss ratio. Recently, modified melamine

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superplasticizer has attracted much attention^[3-4]. Lignin is the main component in plants. It is a highly cross-linked, three-dimensional aromatic polymer with phenylpropane units linked together by C—C—C or C—O—C bonds. Lignin has an advantage of being cheap and abundant. Almost all lignosulfonates in China come from the sulfite processing of pulp industry, and the annual amount of lignosulfonates reached 300 000 t^[5]. Since lignosulfonate is viewed as a low value by-product, few of it is technologically utilized. Lignosulfonate has been stored as salvage, which not only causes the waste of large quantity of renewable resource, but also leads to secondary pollution of solid waste disposal. Due to the requirement of recycling economy, we should pay much attention to the utilization of lignosulfonate with high efficiency. Since lignosulfonate has many kinds of functional groups, such as sulfonate, carboxyl, phenol, and hydroxyl, it can be chemically modified as a raw material or incorporate into polymer matrix as filler to develop lignin-based materials. Through chemical modification of lignosulfonate, lignin-based materials would be widely used in the field of dye, paint, petroleum and concrete industries^[6]. In this paper, lignosulfonate-modified sulfonated melamine formaldehyde resin (LSMF) was synthesized as a superplasticizer firstly, and the effects of LSMF on the performances of mortar were studied. LSMF promotes the performance of SMF, and provides a new way to utilize lignin.

1 Experimental

1.1 Materials

Sodium lignosulfonates (L) originated from wood, straw, bamboo and bagasse were provided from provinces of Jilin, Hebei, Sichuan and Guangdong, respectively; Melamine (M), formaldehyde (F), sodium pyrosulfite (S) and ammonium persulfate (A) were industrial productions; SMF (F10) was obtained from BASF Chemistry Co., Ltd., Germany; naphthalene formaldehyde sulfonation (NFS) was obtained from Dongguan Fusheng Water Reducing Admixture Mill.

Portland cement of grade 42.5 (type II) was obtained from Guangzhou Zhujiang Cement Company. River sand with a nominal grain size of 0.5–1.5 mm was gotten from Guangdong of China. To prepare mortar, the ratio of cement to sand was 1:3.

1.2 Synthesis of LSMF

Melamine was dissolved in formaldehyde in a reaction vessel equipped with a stirrer and a reflux condenser, and a 10 % NaOH aqueous solution was added to adjust pH value to 9.5. The first-step reaction was carried out at 75 °C for 30 min. Then temperature was decreased to 70 °C and sodium pyrosulfite was fed into the reactor slowly. The pH value was adjusted to 11. The second-step reaction continued at 70 °C for 90 min when the feeding of sodium pyrosulfite was finished. The third-step was low-pH value condensation-polymerization. The reaction temperature was cooled down to 60 °C and a 10 % sulfuric acid solution was added to adjust the pH value to 5. The reaction solution was stirred for 90 min. Finally, the temperature was decreased to 50 °C and a 20 % NaOH aqueous solution was added to adjust the solution pH value to 11. Lignosulfonate was fed into the solution. After lignosulfonate was dissolved, ammonium persulfate was added. The mixture was stirred at 50 °C for a given time. The prepared resin has a solid content of approximately 35 % and the final pH value is 10.

1.3 Contents of functional groups

The sulfonic group content of lignosulfonate was determined by aqueous potentiometric titration. The contents of phenolic hydroxyl and carboxylic groups in lignosulfonate were determined by a non-aqueous potentiometric titration with tetra-*n*-butylammonium hydroxide (TnBAH) in DMF^[7].

1.4 Surface tension

Surface tensions of the LSMF aqueous solution with different relative molecular weight (M_r) were

measured by a pulling ring method with an interfacial tensiometer (CSC 70545, USA). Accuracy of the tensiometer was ± 0.05 mN/m. Firstly, the prepared liquid was placed in a small beaker, and then a platinum-iridium ring was suspended in the liquid. The tensiometer was zeroed with the plank below the surface of the liquid. After that, the ring was pulled upward until it broke free of the liquid. The dial reading at the break point was recorded as the value of surface tension.

1.5 Adsorption property

Ultraviolet absorption spectroscopy has been used to research the adsorption behavior of superplasticizers with aromatic and conjugated bond groups^[8]. Six grams of cement was poured into 100 mL of prepared solution under agitation. After an adsorption equilibration of 30 min, the sample was centrifuged at a speed of 8 000 r/min until a clear supernatant was obtained. The relative concentration of LSMF in the supernatant was measured by UV spectroscopy (Shimadzu UV-2450, Japan) at 219 nm. It is worthy to mention that 219 nm is the specific absorption of LSMF. The adsorption amount of LSMF on cement particles was calculated by the concentration difference of the LSMF solution before and after adsorption.

1.6 Relative molecular mass (M_r) of LSMF

M_r of LSMF can be characterized by its intrinsic viscosity. The intrinsic viscosity of 10 % LSMF was determined by a $\varnothing 0.6$ mm Ubbelohde viscometer.

1.7 Performances of mortars

Water-reducing ratio and slump loss of mortars mixed with superplasticizers were measured out according to GB/T 8077 - 2000.

The mechanical performances of mortars mixed with superplasticizers were measured according to GB/T 17671 - 1999 (ISO). The size of specimen was 160 mm \times 40 mm \times 40 mm for testing compressive strength and flexural strength of mortar under normal consistency.

The size of specimen was 70.7 mm \times 70.7 mm \times 70.7 mm for testing carbonation resistance of mortar under normal consistency. The accelerated carbonation experiment was tested according to GBJ 82 - 1985. The specimens were demoulded after one day of preparation, and then cured at (20 ± 1) °C in 90 % relative humidity for 26 d. The specimens were placed in oven at 60 °C for another 2 d. After that, the surfaces of specimen were sealed with wax except for one side. The sealed specimens were further cured in accelerated carbonation box with (20 ± 1) % CO₂ at 20 °C for 3 and 28 d. Accelerated carbonation depth (D) was measured with phenolphthalein indicator. The accelerated carbonation depth was calculated as follows:

$$D = \sum_{i=1}^n d_i/n \quad (1)$$

where: D —accelerated carbonation depth, mm; n —the number of measured points; d_i —the accelerated carbonation depth at each selected point, mm.

2 Results and discussion

2.1 IR analysis of LSMF

Infrared (IR) analysis of LSMF was carried out on a Fourier transform infrared spectrometer (Vector 33, Germany) scanning from 4000 to 400 cm⁻¹ at room temperature. The samples were mixed with KBr and then pressed to become plates for measurements. The IR spectra are shown in Fig. 1. The vibrational wave numbers and their assignments are given in Table 1.

From all the three spectra, absorption band around 3430 cm⁻¹ is associated with stretching vibration of —NH group and —OH group; the band from 2970 to 2840 cm⁻¹ is attributed to symmetric and asymmetric stretching vibrations of —CH₃ and —CH₂^[9]. The IR spectrum of lignosulfonate shows that C=C stretching

vibration in aromatic skeleton is located at about 1600 cm^{-1} , $-\text{CH}$ stretching vibration is at 1460 cm^{-1} and $\text{C}=\text{O}$ stretching vibration in syringyl group is at 1124 cm^{-1} ^[10]. The IR spectrum of SMF shows that $-\text{CN}$ multiple stretching in the triazine ring is located around 1560 cm^{-1} , aliphatic $-\text{CN}$ stretching vibration is between 1200 and 1170 cm^{-1} and triazine ring bending is at 810 cm^{-1} ^[11].

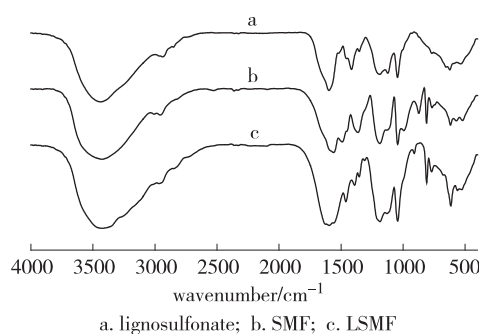


Fig. 1 FT-IR spectra of the superplasticizers

IR spectrum of LSMF has the characteristic bands locating at 1594 , 1462 and 1130 cm^{-1} , indicating the existence of aromatic rings and $\text{C}-\text{H}$ bonds in the sample. The appearance of bands locating at 1186 and 810 cm^{-1} indicate the existence of triazine ring and aliphatic $\text{C}-\text{N}$ bonds in the sample. Compared with SMF, LSMF has a stronger and broader peak at 1595 cm^{-1} , and a weaker peak at 810 cm^{-1} . These results suggest that lignosulfonate has been introduced into SMF and the synthesized LSMF has both aromatic (1595 cm^{-1}) and triazine rings (810 cm^{-1}). The peak of the $\text{C}-\text{O}-\text{C}$ bond in LSMF, which normally appears at $1010-1270\text{ cm}^{-1}$, is stronger and broader than that of lignosulfonate and SMF. The above analysis clearly indicates that lignosulfonate has reacted with SMF through polycondensation. The possible molecular structure of LSMF is shown in Fig. 2.

2.2 Analysis of structure characteristics

Generally, high water-reducing ability is the key property of a superplasticizer, and it is influenced by molecular structure. Lignosulfonates in China are mainly originated from bamboo, bagasse, wood and straw. Lignosulfonates from different materials have different molecular structures which are shown in Table 2.

Table 2 Functional group content of different lignosulfonates

samples	sulfonic group content	carboxy content	phenolic hydroxyl content
bamboo lignosulfonate	0.74	2.38	0.55
bagasse lignosulfonate	0.78	2.45	0.43
wood lignosulfonate	1.15	2.31	1.01
straw lignosulfonate	1.39	2.89	0.97

From Table 2, straw-based lignosulfonate has the highest content of sulfonic and carboxy group. The sulfonic group contents of lignosulfonate originated from bamboo, bagasse, wood and straw are 0.74 , 0.78 , 1.15 and 1.39 mmol/g , respectively. Though wood lignosulfonate has higher sulfonic group content than bamboo or bagasse lignosulfonates, it has the lowest carboxy content. Phenolic hydroxyl contents of 4 kinds of lignosulfonates are 0.55 , 0.43 , 1.01 and 0.97 mmol/g , respectively. Straw-based lignosulfonate shows the best chemical activity among the 4 samples.

Table 1 Vibrational wave numbers and their assignments¹⁾

items	lignosulfonate	SMF	LSMF
$\gamma_{\text{O}-\text{H}} + \gamma_{\text{N}-\text{H}}$	3435	3431	3430
$\gamma_{\text{C}=\text{C}}$	1600		1594
$\delta_{\text{N}-\text{H}} + \gamma_{\text{C}=\text{N}}$		1561	1594
$\nu_{\text{C}-\text{H}}$	1460		1462
$\nu_{\text{N}-\text{C}-\text{N}}$		1188	1186
$\gamma_{\text{C}=\text{O}}$	1124		1130
δ_{SO_3}	1045	1045	1045
$\delta_{\text{C}=\text{N}}$		811	810

1) ν : variable; γ : stretching; δ : bending

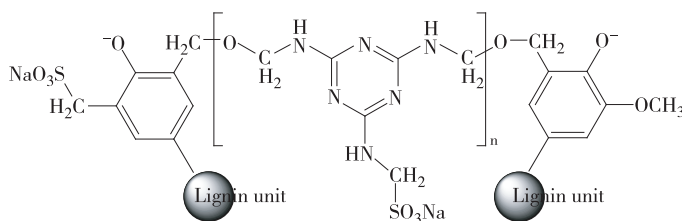


Fig. 2 Structure of LSMF

Molecular structure of LSMF, such as kinds of lignosulfonate, intrinsic viscosity and sulfonic group content, show a great effect on water-reducing ability. The effects of lignosulfonates kinds on water-reducing ratio of mortars are shown in Table 3. As expected, straw-based lignosulfonate modified sulfonated melamine formaldehyde has the best water-reducing ratio. When the dosage of straw-based LSMF is 0.7 %, water-reducing ratio of mortar is up to 21.6 %. Since straw-based lignosulfonate has the highest content of carboxy and sulfonic group, straw-based LSMF can provide more negative charges on cement surface. Therefore, cement particle can be dispersed more evenly because of stronger electrostatic repulsions generated among solid particles^[12].

Table 3 Effects of lignosulfonates of different materials on water-reducing ratio of mortars %

dosage	water-reducing ratio of mortars			
	bamboo	bagasse	wood	straw
0.4	12.1	10.8	10.2	13.8
0.5	16.2	14.6	13.5	16.5
0.6	17.0	16.6	16.2	21.1
0.7	17.7	19.5	20.1	21.6
1.0	17.8	20.9	21.6	22.0

As a superplasticizer, LSMF has an optimal M_r . Generally, the M_r can be well characterized by its intrinsic viscosity. Fig. 3 shows the effect of intrinsic viscosity of LSMF on water-reducing ratio. To achieve the best water-reducing property, the optimal intrinsic viscosity of LSMF is about 7.24 mL/g. At 0.7 % dosage, water-reducing ratio of LSMF with optimal intrinsic viscosity is higher than 18 %. Water-reducing ability of LSMF with low intrinsic viscosity decreases because of the low content of lignosulfonate. Lignosulfonate generates steric hindrance by its branched group. So LSMF with few lignin units has low water-reducing ability. When intrinsic viscosity of LSMF is above the optimal value, water-reducing ratio also decreases because of the occurrence of flocculent interactions^[13].

Sulfonic group is the most important functional group of LSMF. It endows LSMF not only water solution property but also water-reducing property. Fig. 4 shows the effect of sulfonic group content of LSMF on the water-reducing ratio. Water-reducing ratio of LSMF increases with the increasing sulfonic group content when sulfonic group content is less than 3.663 mmol/g, and then decreases with the increasing sulfonic group content when sulfonic group content is larger than 3.663 mmol/g. The result shows that straw-based LSMF with sulfonic group content of 3.663 mmol/g and intrinsic viscosity of 7.24 mL/g has the best water-reducing ability.

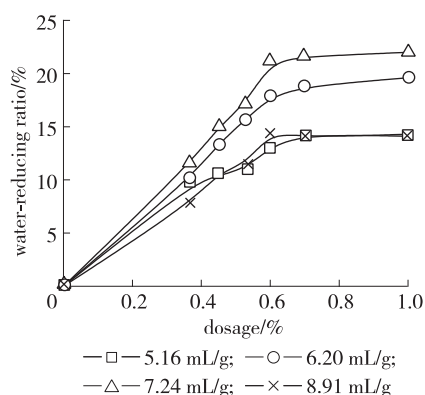


Fig. 3 Effects of intrinsic viscosities of LSMFs on water-reducing ratios

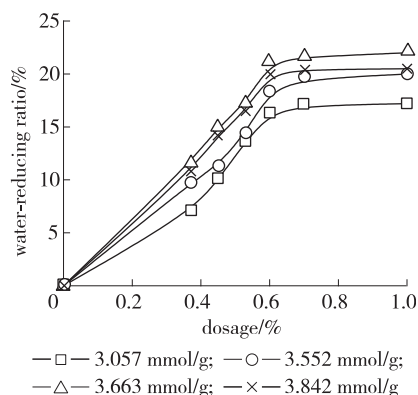


Fig. 4 Effects of sulfonation degrees of LSMFs on water-reducing ratios

2.3 Properties

2.3.1 Surface The lower the surface tension of the aqueous solution is, the easier the wetting of solid particles may be^[14]. Surface tensions of LSMF aqueous solution with different intrinsic viscosities are shown in

Fig. 5. It indicates that aqueous solution of LSMF with intrinsic viscosity of 7.24 mL/g has the lowest surface tension. At the solution concentration of 250 g/L, surface tension of LSMF with intrinsic viscosity of 7.24 mL/g is 25.6 mN/m. Surface activity of LSMF has been improved significantly compared with that of SMF.

Surface activity of LSMF aqueous solution decreases when intrinsic viscosity is more than 7.24 mL/g. This may be related to the content of lignosulfonate in LSMF which increases with the increase of molecular weight. Lignosulfonate appears spherical shape in solution, so LSMF with high lignosulfonate content cannot form a regular arrangement at the interfacial phase^[6]. Incompact adsorption layer is formed at the solution surface because of the steric hindrance between molecules, resulting in low surface activity.

As shown in Fig. 5 (a), surface tension of LSMF aqueous solution decreases continuously with the increasing concentration, without exhibiting equilibrium. This phenomenon indicates that surface tension behavior of LSMF aqueous solution differs from that of the low-molar-mass surfactants. Gamier et al^[14] also find the same phenomenon in amphiphilic diblock copolymers. Through dynamic light scattering (DLS) measurement, they observe micelles in diblock copolymers. So they think the continuous decreases of surface tension with increasing concentration due to those polymeric micelles of slightly surface active. In this case, LSMF shows some characteristic of polymeric surfactants, so surface tension continuously decreases with increasing concentration of LSMF aqueous solution.

2.3.2 Adsorption It is generally accepted that superplasticizer is firstly adsorbed onto the surface of cement grains, and then shows its water-reducing property and dispersing effect. Fig. 5 (b) shows the adsorption curves of LSMF with different intrinsic viscosities on surface of cement grains. The adsorption isotherms of LSMF on surface of cement grains follow the Langmuir type. When intrinsic viscosity of LSMF is 5.16 mL/g, saturation adsorption amount is 12.3 mg/g. As comparison, saturation adsorption amount of SMF is measured to be 13 mg/g. LSMF with low M_r has almost the same saturation adsorption amount as SMF. Plank et al have mentioned the adsorption process of SMF on cement particles. They consider that superplasticizer with negative charge can easily be adsorbed on the early-age cement hydration products such as ettringite (AFt)^[12]. Since AFt shows a highly positive zeta potential, SMF with negative charge can be strongly adsorbed onto AFt to form a loose SMF layer. With the hydration process continuing, a new cement hydration layer can cover the SMF layer, and then the new cement hydration layer will adsorb SMF again. Therefore, SMF appears a high adsorption amount. The structure of LSMF with low M_r is similar to SMF, and thus the two superplasticizers have a similar adsorption behavior on cement grain surface.

With the increase of intrinsic viscosity of LSMF, adsorption amount of LSMF decreases quickly. This phenomenon can be explained as follows. The adsorption process of LSMF is similar to that of SMF as mentioned by Plank et al LSMF with negative charge can also be strongly adsorbed onto AFt to form a loose LSMF layer. With the hydration process continuing, a new cement hydration layer can cover the LSMF layer. However, LSMF with high M_r can form a three-dimensional structure with many lateral chains because of the branched groups of lignin units. These lateral chains of LSMF can penetrate through the new cement hydration layer and extend in the solution. At this stage, the new cement hydration layer will adsorb superplasticizer again. Actually the new cement hydration layer can not completely cover the formerly adsorbed LSMF layer, so it is hard for the new cement hydration layer to adsorb LSMF again. As a result, the adsorption amount of LSMF with high M_r is less than that of the LSMF with low M_r . As expectation, although the adsorption amount of LSMF with high M_r is low, cement particles with the adsorbed LSMF layer can be dispersed effectively because of electrostatic repulsion and steric hindrance.

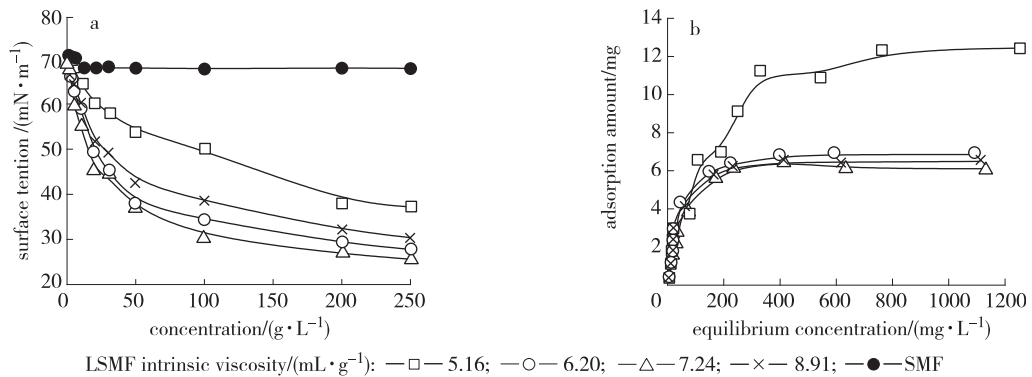


Fig. 5 Surface tension (a) and adsorption amount (b) of LSMF with different intrinsic viscosities

2.3.3 Dispersing Slump loss in concrete is defined as the decrease in slump with increasing time. The most conspicuous manifestations of slump loss in concrete include difficulty in handling and manipulation during placement and compaction, reduced ultimate strength, and worse durability^[15]. To estimate slump loss of mortar with LSMF, commercial superplasticizers, such as SMF and NFS, are selected to mix with mortars for comparison. Fig. 6 shows slump loss of mortar mixed with 0.7 % superplasticizers, such as LSMF, SMF and NFS. Slump loss ratio of mortar with LSMF is much less than that of mortar with SMF and NFS at the same initial slump. Within 90 min, slump loss ratio of mortar with LSMF is 42 %, but that of mortar with SMF or NFS is 70 %. Therefore, LSMF shows better slump retention than SMF and NFS. LSMF can form a three-dimensional structure with a lot of lateral chains because of branched groups of lignin units. Therefore, LSMF with the three-dimensional structure has a large steric hindrance which provides slump retention ability.

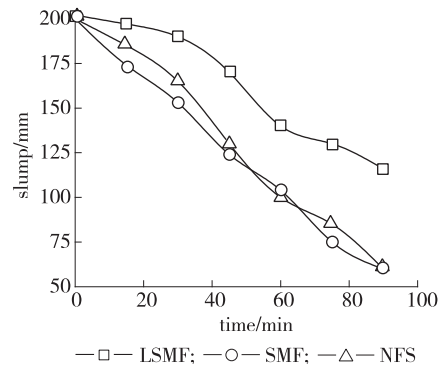


Fig. 6 Slump loss of mortars mixed with superplasticizers with time elapsed

2.4 Mechanical performances of mortars

Mechanical performances include flexural strength and compressive strength. Table 4 shows the effect of intrinsic viscosity of LSMF on mechanical performances of superplasticized mortar under normal consistency. It is apparent that mechanical performances of mortars with different M_r of LSMF are higher than those of control mortar due to the dispersing ability of LSMFs. The optimal intrinsic viscosity of LSMF achieving the maximum compressive and flexural strength values is about 7.24 mL/g. Compared with control mortar, compressive strength of mortar with LSMF with intrinsic viscosity of 7.24 mL/g increases 62 % at 3 d and 37 % at 28 d, and flexural strength of mortar increases 29 % at 3 d and 18 % at 28 d. Superplasticizer such as LSMF has good dispersing ability. It can reduce the amount of water to achieve the same workability as control mortar, and thus cement hydration product with more compact structure is achieved, and the mechanical performances of mortar increase.

Table 4 Effect of intrinsic viscosity of LSMF on mechanical performances of superplasticized mortar

mass concn. of LSMF/(mL·g ⁻¹)	3-day strength/MPa		7-day strength/MPa		28-day strength/MPa	
	flexural	compressive	flexural	compressive	flexural	compressive
plain	3.8	18.9	4.6	24.9	6.2	32.7
5.16	4.5	25.8	5.7	31.2	6.8	41.5
6.20	4.7	28.4	5.9	34.7	7.2	44.5
7.24	4.9	30.6	6.3	37.5	7.3	44.9
8.91	4.5	26.1	5.8	33.3	6.9	42.2

2.5 Durability performance of mortars

Carbonation resistance became more and more important durability performance of concrete because of serious greenhouse effect. Atmospheric carbon dioxide (CO_2) can interact with the alkaline products of cementitious matrix^[16]. When all the available alkaline products had been reacted, the pH value fell to a level below 11 which accelerated the corrosion of steel in concrete.

Table 5 shows the effect of intrinsic viscosity of superplasticizer on accelerated carbonation depth of superplasticized mortar under normal consistency. It is observed that carbonation depth of mortar with superplasticizer is much lower than that of the control mortar. When mortar is superplasticized by LSMF with intrinsic viscosity of 7.24 mL/g, the minimum carbonation depth at 28 d is only 13 mm, while carbonation depth of control mortar is 34.5 mm. Mortar with LSMF can significantly decrease carbonation depth. Obviously, carbonation resistance ability of mortar increases because of adding LSMF.

Carbonation depth of mortar decreases with the increasing dosage of LSMF from 0 to 0.7%. If the dosage increases right along, the increasing extent of carbonation depth is obvious. This phenomenon is caused by airentraining action of LSMF being aggravated in high dosage. Air entraining action can bring in the open pore. Lots of open pores accelerated the diffusion of CO_2 and the reaction rate of carbonation.

Table 5 Effect of intrinsic viscosity of LSMF on carbonation depth of the superplasticized mortar under normal consistency

mass concn. of LSMF/(mL·g ⁻¹)	accelerated carbonation depth at 3 d/mm			accelerated carbonation depth at 28 d/mm		
	0.5 %	0.7 %	0.8 %	0.5 %	0.7 %	0.8 %
5.16	6.5	4.8	6	19	15	17
6.20	5.5	4.5	5.5	16.5	14	15.8
7.24	5	4	4.5	15	13	13.5
8.91	7	6	7	21	17	19
plain		10.5			34.5	

The life-times of carbonation resistance can be estimated by accelerated carbonation depth. Accelerated carbonation of concrete is associated with concentration of CO_2 . Relationship between accelerated carbonation depth and carbonation depth under atmospheric condition is as follows:

$$D_z/D_k = \sqrt{(t_z C_z)/(t_k C_k)} \quad (2)$$

where: D_z —mortar protective layer thickness, here it is defined as 35 mm; C_z —atmospheric CO_2 concentration, here it is 0.04%; t_z —life-times for carbonation resistance under atmospheric condition, d; D_k —accelerated carbonation depth, mm; C_k — CO_2 concentration under accelerated carbonation condition, here it is 20%; t_k —curing time under accelerated carbonation condition, here it is 28 d^[17].

As discussed above, under optimum dosage, the lowest accelerated carbonation depths of mortars with LSMF 5.16, 6.20, 7.24 and 8.91 mL/g are 15, 14, 13 and 17 mm, respectively. According to equation 2, life-times for carbonation resistance of mortars with LSMF 5.16, 6.20, 7.24 and 8.91 mL/g are calculated to be 208.8, 239.7, 278 and 162.6 years, respectively. For comparison, life-time of carbonation resistance of mortar mixed with LSMF with intrinsic viscosity of 7.24 mL/g is about 8.6 times as that of the control mortar. It is obvious that LSMF increases the life-time for carbonation resistance of mortar.

3 Conclusions

This work studied the effect of a new superplasticizer LSMF on the performances of mortar, such as water-reducing ratio, compressive strength, flexural strength, and accelerated carbonation depth. Lignosulfonates originated from wood, straw, bamboo and bagasse were selected to react with SMF to obtain LSMF, and straw-based LSMF with sulfonic group content of 3.663 mmol/g and intrinsic viscosity of 7.24 mL/g has the best

water-reducing and reinforcement effects. When LSMF is used in dosage of 0.7 % by weight of cement, water-reducing ratio reaches 21.1 %. Compared with that of the control mortar, compressive strength and flexural strength of the superplasticized mortar increase 37 % and 18 % at 28 d, respectively. The minimum carbonation depth of superplasticized mortar at 28 d is 13 mm, while that of the control mortar is 34.5 mm. The life-time of carbonation resistance can be estimated by accelerated carbonation depth. The life-time of carbonation resistance of the superplasticized mortar is about 8.6 times as that of the control mortar. LSMF promotes the performance of SMF, and provides a new way to utilize lignin.

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