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水泥基抗渗堵漏材料的性能及工程应用研究

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摘　要：以膨润土、甲基硅酸钠为主要成分，复掺络合组分 A、络合组分 B 和络合组分 C 制备了两种活性增强母料。通过对比研究了含活性增强母料的水泥基抗渗堵漏材料与不含活性增强母料的对照组材料、成品材料 X 的基本性能及自愈合性能，并对研制的材料进行了实际工程应用效果检验。研究结果表明：（1）研制的材料 ZSJ-M1 和 ZSJ-M2 的力学性能、抗渗性能、湿基面粘结性能和自愈合性能均优于对照组材料和成品材料 X；（2）将 ZSJ-M1 应用于实际隧道工程裂缝渗漏水的修复中，材料与基体混凝土粘结性能良好，解决了反复治理、反复渗漏的问题，渗漏水治理效果显著，具有推广及应用价值。

关键词：活性增强母料；抗渗堵漏材料；自愈合；工程应用

Research on the performance and engineering application of cement-based impermeability and plugging materials

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Abstract：Two active-enhancing masterbatches were prepared with bentonite and sodium methosilicate as the main components，and complex component A，complex component B and complex component C were compounded. The basic properties and self-healing properties of the cement-based anti-seepage plugging material containing reactive reinforced masterbatch and the control material without reactive reinforcing masterbatch and finished material X were compared and studied，and the practical engineering application effect of the developed material was tested. The results show that：(1)The mechanical properties，impermeability，wet substrate adhesion properties and self-healing properties of the developed materials ZSJ-M1 and ZSJ-M2 were better than those of the control materials and the finished materials X.（2）ZSJ-M1 is applied to the repair of crack leakage water in actual tunnel engineering，and the bonding performance between the material and the matrix concrete is good，which solves the problem of repeated treatment and repeated leakage，and the leakage water treatment effect is remarkable，which has the value of promotion and application.

Keywords：active enhanced masterbatch；anti permeability and plugging materials；self-healing；application

introduction

As a common building material，concrete will produce cracks and gradually expand and develop in the service process due to the influence of external factors，which makes the service performance of buildings decline[1]. Cement-based anti-seepage plugging material composed of cement，quartz sand and active chemical substances has the characteristics of simple operation，green environmental protection，anti-seepage and self-healing，and has been widely used in the repair and treatment of cracks and water leakage in major concrete structures[2]. In addition，this kind of material is favored by the construction industry because of its permeation and repair effect on concrete cracks，excellent performance，and significant economic and social benefits[3][4]，and has also attracted the attention of researchers at home and abroad. Zhu[5]modified the superfine ordinary Portland cement-sulfoaluminate cement composite cement material system with water-based epoxy resin emulsion to improve the material's permeation and repair of cracks. However，there are still certain engineering application limitations in terms of dosage control and operation. A large number of studies and application results show that permeable crystalline anti-seepage plugging materials have remarkable effects on the repair of concrete cracks[6][7]. Guo[8]analyzed and compared the influences of different brands of cement-based osmotic crystal waterproof materials mixed with concrete on the mechanical properties，repair rate and secondary impermability of concrete. Zhang[9]showed that cement-based permeable crystalline waterproof material coated mortar specimens and penetrated into the internal pores，forming ettringite and calcium carbonate crystals，thus refining the internal pore structure of mortar specimens and making the matrix more dense. Li[10]proposed an active chemical that permeates crystallized cement-based anti-seepage plugging material，and found that the material forms crystal accumulation in concrete cracks after permeation and reaction to repair cracks. It can be seen that the active chemical is the key factor affecting the concrete crack repair and self-healing ability of cement-based anti-seepage plugging materials with permeation crystallization repair effect，but there are few studies and discussions on the active chemical itself. Although China has been researching and developing such materials for many years from the introduction of such materials，the production has not yet realized the batch localization of core active chemicals，and the key technologies and key materials are mainly dependent on imports，and the application cost is high. Based on this，ZSJ-M1 and ZSJ-M2，two kinds of active reinforced masterbatch reinforced cement-based anti-seepage plugging materials，were developed，and compared with the control group ZSJ-1，ZSJ-2 and imported products X，the performance of cement-based anti-seepage plugging materials with excellent performance was selected for practical tunnel engineering application effect test.

1　Laboratory test

1.1 Test material

The raw materials used in the test are：（1）gelling components（ordinary Portland cement + sulfoaluminate cement）；（2）70-110 mesh quartz sand；（3）ISO standard sand；（4）Industrial grade 800 mesh white powder talc powder；（5）Industrial grade 400 mesh white powder heavy calcium carbonate；（6）Industrial grade cellulose ether；（7）Industrial grade yellow powder bentonite；（8）Reagent grade complex component A，complex component B，complex component C，are white crystalline powder；（9）Industrial grade white powder sodium methylsilicate；（10）An imported well-known brand of anti-seepage plugging material finished X；（11）tap water.

1.2 Test method

The combination of cementer-based anti-permeability and leak-blocking ZSJ-M1 and ZSJ-M2 and their undoped active reinforcement masterbatch in the blank test control group ZSJ-1 and ZSJ-2 is shown in Table 1，wherein the composition and proportion of the active reinforcement masterbatch of the two formulations are as follows：（1）The active reinforcement masterbatch M1 of ZSJ-M1：Bentonite：complex component A：Complex component B：sodium methylsilicate =105：6：22：20；（2）The activity of ZSJ-M2 enhanced masterbatch M2：Bentonite：complex component C：sodium methylsilicate =105：15：10.

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Table 1 ZSJ-M1 and ZSJ-M2 and corresponding blank test group formulations（Unit：g）

Ingredients	ZSJ-M1	ZSJ-1	ZSJ-M2	ZSJ-2
Gelling component	260	260	265	265
Quartz sand	170	170	170	170
Talc powder	12	12	20	20
Heavy calcium carbonate	35	35	25	25
Active enhanced masterbatch	24	0	24	0

According to the mix ratio in Table 1, each raw material is added to the mortar mixer to prepare ZSJ-M1, ZSJ-M2, ZSJ-1 and ZSJ-2 materials. The four kinds of materials prepared and the finished product X of the contrast material were used to prepare the clean pulp specimen and the mortar specimen respectively. Water in clean pulp test specimen: formula material =1: 3, water in mortar test specimen: formula material: standard sand =0.5: 1: 3. Use a mixer to pour the evenly mixed slurry into a triple mold of 40mm × 40mm × 160mm for molding, and put it into a standard curing box for curing to the corresponding age after demudding.

1.3 Performance testing and characterization

The compressive strength and flexural strength of the specimens are tested according to the standard 《Cement mortar Strength Test Method (ISO method)》GB/T 17671-2021. The impermeability test and wet base bond strength test were tested with reference to the standard 《cement-based permeable crystalline waterproof material》 GB 18445-2012.

In the self-healing performance test, ZSJ-M1, ZSJ-M2, ZSJ-1 and ZSJ-2 mortar specimens and finished products were X-shaped and cured at 14d and 28d. First, the mortar specimens were folded in half by the bending test method, and one half was randomly selected to test the ultimate compressive strength P_0 of the mortar specimens of different curing ages of 5 materials; the other half was prepressed 60% P_0 and then further cured, and the corresponding experimental groups of different secondary curing ages (7d, 14d, 28d) were tested for their compressive strength P_R. The strength recovery rate is taken as the main basis for evaluating the self-healing properties of materials, and the calculation formula of strength recovery rate is shown in equation 1.

$$K = \frac{P_R}{P_0} \times 100\% \qquad (1)$$

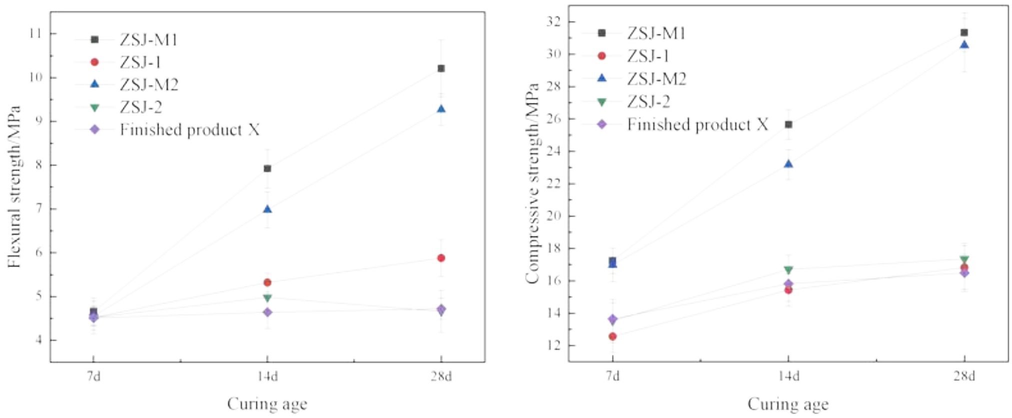
In the formula, K is the recovery rate of compressive strength; PR is the compressive strength test value, MPa; P0 is the reference value of the ultimate compressive strength of the specimen, MPa.

2 Laboratory test results and discussion

2.1 Basic performance test

2.1.1 Mechanical property

Mechanical tests were conducted on clean pulp specimens of ZSJ-M1, ZSJ-M2, ZSJ-1, ZSJ-2 and finished product X at different curing ages, and the test results of mechanical properties were shown in Figure 1.



(a) (b)

Fig. 1 Mechanical properties of ZSJ-M1, ZSJ-M2, ZSJ-1, ZSJ-2 and finished product X: (b) flexural strength; (a) compressive strength

As shown in figure 1, compared with the mechanical properties of finished X material, the compressive strength and folding strength of ZSJ-1 and ZSJ-2 without active reinforcement masterbatch increased less with age, while the compressive strength and folding strength of ZSJ-M1 and ZSJ-M2 with active reinforcement masterbatch increased significantly. Since complex components A, B and C in the active enhanced masterbatches M1 and M2 contain abundant carboxylic acid groups, carboxylic acid groups can be complexed with free calcium ions to form metastable calcium ion complexes, which can enrich dispersed free calcium ions[11]. The enrichment behavior of calcium ion complex accelerates the hydration process of cement and produces more C-S-H gel, which is conducive to the improvement of mechanical properties. Sodium methylsilicate also has a certain degree of micro-expansion, and can also play a role in increasing the density of the specimen. Therefore, under the synergistic action of the above substances, the mechanical properties of ZSJ-M1 and ZSJ-M2 are significantly improved compared with the corresponding control group ZSJ-1 and ZSJ-2 at different curing ages of 7 days, 14 days and 28 days.

The mechanical properties of ZSJ-M1 are generally higher than those of ZSJ-M2, indicating that the mechanical properties enhancement effect of active enhanced masterbatch M1 on cement-based anti-permeability plugging materials is better than that of active enhanced masterbatch M2. Among the two active masterbatch components, the proportion of complex components A, complex components B and sodium methylsilicate in M1 is higher. Therefore, M1 has a stronger effect on promoting the hydration process of cement and a better effect on improving the mechanical properties of specimens. The 28d compressive strength and flexural strength of ZSJ-M1 clean pulp specimen are 31.34MPa and 10.21MPa, respectively, and the 28d compressive strength and flexural strength of ZSJ-M2 clean pulp specimen are 30.55MPa and 9.27MPa, respectively. The mechanical properties of the two materials are more advantageous than those of the currently commonly used finished product X.

2.1.2 Impermeability

The mortar impermeability and concrete impermeability of ZSJ-M1, ZSJ-M2, ZSJ-1, ZSJ-2 and finished product X were tested, and the test results were shown in Table 2 and Table 3.

Table 2 Test results of impermeability of mortar

Group	28d impermeability (benchmark mortar specimen impermeability pressure 0.3MPa)			
	With coating impermeable pressure/MPa	Tape coating Permeability resistance pressure ratio /%	Remove coating impermeability pressure/MPa	Remove the coating impermeability pressure ratio /%
ZSJ-M1	1.2	400	0.9	300
ZSJ-1	0.9	300	0.8	267

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ZSJ-M2	1.1	367	0.9	300
ZSJ-2	0.8	267	0.7	233
Finished product X	0.8	267	0.7	233

Table 3 Test results of concrete impermeability

Group	Impermeability（reference concrete specimen impermeability pressure 0.4MPa）				
	With coating impermeable pressure/MPa	Tape coating Permeability resistance pressure ratio/%	Remove coating impermeability pressure/MPa	Remove the coating impermeability pressure ratio /%	Secondary impermeable pressure/MPa
ZSJ-M1	1.5	375	1.2	300	1.1
ZSJ-1	1.2	300	0.9	225	0.8
ZSJ-M2	1.4	350	1.1	275	0.9
ZSJ-2	1.2	300	0.9	225	0.8
Finished product X	1.1	275	0.9	225	0.8

It can be seen from the table that the impermeability pressure ratio of mortar specimens and concrete specimens of 5 kinds of materials meets the requirements of GB 18445-2012（impermeability pressure ratio ≥ 250% with coating， impermeability pressure ratio ≥ 175% without coating）in cement-based permeable crystalline waterproof Materials. The activity enhanced the complex components in the masterbatch M1 and M2 accelerated the cement hydration reaction process， generated more C-S-H gels and continuously enriched to form calcium ion complexes. Calcium ion complexes can also react with free acid ions such as SiO_3^{2-}、CO_3^{2-}和 HCO_3^- in the matrix of the specimen（concrete）to form insoluble crystal substances such as calcium carbonate and fill gaps to improve the compactness of the specimen[12][13]. Sodium methicosilicate contained in the active enhanced masterbatch has a good osmotic crystallization effect， which can cross-link with silicate materials to seal cracks， improve structural densification， and reduce the water absorption performance of specimens or concrete[14]， so as to improve the impermeability. In addition， bentonite can also fill the pores and reduce the number of connected pores[15]. Its viscosity and water absorption can also better inhibit the entry of water molecules， enhance the compactness and hydrophobicity of the test pieces， and thus improve the impermeability of the test pieces. Therefore， when applying mortar or concrete as a coating material， the improvement effect of ZSJ-M1 and ZSJ-M2 on the impermeability of reference specimens is higher than that of ZSJ-1， ZSJ-2 and finished X materials.

2.1.3 Wet base bonding properties

The wet base bonding performance of ZSJ-M1，ZSJ-M2，ZSJ-1 and ZSJ-2 with finished product X was tested，and the test results were shown in Figure 2.

As shown in figure 2， the wet base bonding strength of ZSJ-M1， ZSJ-M2 and finished product X is 1.5MPa， 1.4MPa and 1.4MPa， respectively， while the wet base bonding strength of ZSJ-1 and ZSJ-2 without active reinforcement masterbatch is lower. The bentonite in the active enhanced masterbatch M1 and M2 has good viscosity and water absorption， which can enhance the hydrophobicity of the specimen and inhibit the entry of water molecules. Bentonite and sodium methicosilicate work together to ensure the bond and compactness between cement particles， hydration products and inorganic fillers（talc and heavy calcium carbonate）. The complex components in the active enhanced masterbatch M1 and M2 promote the formation of more cementing materials in the hydration process of cement， and further improve the bond strength between ZSJ-M1 and ZSJ-M2 and the wet base of the matrix.

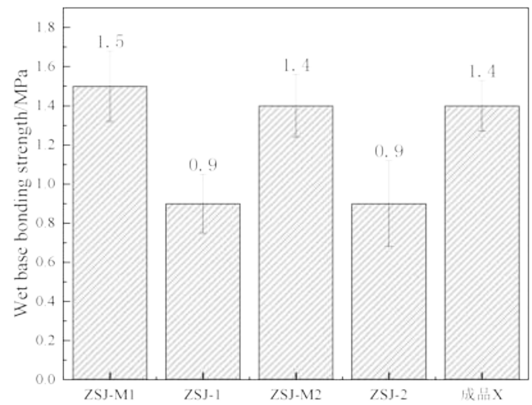


Fig. 2 Wet base bond strength

2.2 Self-healing performance test

The self-healing ability of cement-based anti-seepage plugging material is reflected by the recovery efficiency of compressive strength of the specimens through preloading test. Five kinds of materials were used to prepare molded mortar specimens，and after curing to 14d and 28d，the damaged specimens were cured to the specified age to test their compressive strength and calculate the strength recovery rate. The compressive strength and strength recovery rate of each material at different ages are shown in Table 4.

Table 4 Compressive strength and strength recovery rate of prepress-curing mortar specimens

Early curing age	Group	Compressive strength P_0/MPa	Pre-pressure - curing for 7 days		Pre-pressure - curing for 14 days		Pre-pressure - curing for 28 days	
			Compressive strength P_R/MPa	Strength recovery rate K/%	Compressive strength P_R/MPa	Strength recovery rate K/%	Compressive strength P_R/MPa	Strength recovery rate K/%
14d	ZSJ-M1	11.88	14.35	120.79	15.32	128.96	16.02	134.85
	ZSJ-1	9.76	9.56	97.95	11.88	121.72	12.12	124.18
	ZSJ-M2	11.42	12.98	113.66	13.95	122.15	14.54	127.32
	ZSJ-2	9.31	8.45	97.76	10.34	111.06	10.97	117.83
	Finished product X	9.66	8.35	86.44	10.75	111.28	10.85	112.32
28d	ZSJ-M1	17.01	18.64	109.58	19.21	112.93	20.21	118.81
	ZSJ-1	10.96	10.33	94.25	10.98	100.18	11.17	101.92
	ZSJ-M2	16.21	16.97	104.69	17.88	110.30	19.75	121.84
	ZSJ-2	10.44	9.54	91.38	10.24	98.08	10.88	104.21
	Finished product X	9.91	8.37	84.46	9.48	95.66	9.97	100.61

As can be seen from Table 4, the longer the early curing period, the more cementified material products generated by the cement hydration reaction, and the higher the compressive strength of the mortar specimen. When the specimens were prepressed and cured to different ages, the strength recovery rate of the specimens increased with the prolongation of the curing ages after prepressing. After curing, the strength recovery rate of most specimen groups is higher than 100%, indicating that ZSJ material specimens can still repair and close the crack damage through hydration reaction to generate new cementation material. The hydration reaction time of specimens aged 28 days in the early curing period is longer and the compressive strength P_0 is higher. After the damage caused by the prepressing of specimens, the crack repair speed of specimens after the damage is slowed down due to the decrease of the hydration reaction rate in the later stage. Therefore, the strength recovery rate of specimens aged 28 days in the early curing period is lower than that of specimens aged 14 days in the early curing period. It shows that curing age has a great influence on the self-healing ability and efficiency of the specimen.

From the perspective of formulation, the strength recovery rates of ZSJ-M1 and ZSJ-M2 at different ages were higher than those of ZSJ-1 and ZSJ-2 without active reinforcement masterbatch and finished product X. This is due to the fact that under the curing condition of the active enhanced masterbatch, the calcium ion complexes generated by the concentration and consumption of free calcium ions of the complex components will migrate to the matrix cracks with the water, and then replace the acid ions around the cracks to form stable and insoluble calcium carbonate crystals to repair the cracks. The consumption of calcium ion complex will also accelerate the hydration reaction rate of unhydrated cement particles around the damaged cracks, and form C-S-H gel to repair and fill the cracks and improve its strength.

2.3 Field application test

In order to investigate and verify the practical application effect of the developed material, after the indoor test of the material, ZSJ-M1 material with better performance was selected and applied to the water leakage treatment of an intercity railway tunnel in China and the crack leakage repair of the main structure of a station in the open-cut section of a railway tunnel in China respectively according to different application scenarios of tunnel structural diseases. The effect of field application is shown in figure 3 and figure 4.

(a)

(b)

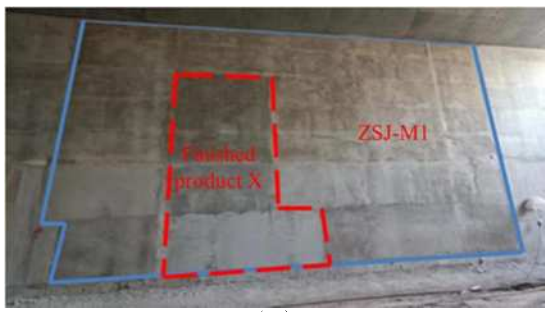
(c)

(d)

Fig. 3 Field application test: (a) Water leakage from bolt holes of segments; (b) 8 months after treatment of water leakage from the bolt holes of the segment; (c) Leakage of concrete from the side walls; (d) 8 months after the side wall concrete seepage treatment

As shown in figure 3 (a) and (b), there is leakage in the bolt holes of the pipe segments. Evenly apply ZSJ-M1 slurry to the leaking base surface. The complex components of the active enhanced masterbatch in ZSJ-M1 slurry migrate to the internal cracks of the matrix through the seepage water of the matrix, and repair and seal the cracks on the surface of the matrix under the synergistic action of bentonite and sodium methicilicate. The cement slurry reacts to form C-S-H gelling and other substances to form a second anti-seepage water plugging layer on the surface of the matrix. After 8 months of follow-up observation, it was found that the base surface of the brushing material remained dry, indicating that the moisture leakage of bolt holes was effectively improved after brushing ZSJ-M1 material. In figure 3 (c) and (d), it can be seen that there is leakage on the side wall of the station, accompanied by a small amount of clear water flow, and the leakage gap is large. Two coats of ZSJ-M1 slurry material were applied to the seepage point. As there was clear water leakage at the seepage point, ZSJ-M1 dry powder was applied to the coating after brushing to avoid excessive dilution of ZSJ-M1 slurry coating with water seepage. The complexing components of the active enhanced masterbatch in ZSJ-M1 migrate through water leakage and complexing calcium ions in the concrete matrix, which plays a complexing and precipitation role. Since the complex component only plays the role of "porter" in this process, it is not consumed, and the calcium ion complex enters a dry and dormant state after the water leakage sealing, forming a relatively stable substance and providing a certain strength for the concrete matrix. When water leakage occurs again, calcium ion complexes and complex components will be reactivated and play a role in crack repair[16]. Follow-up observation for 8 months, the coating base surface has been kept dry, there is no repeated leakage, to achieve excellent water leakage treatment effect.

(a)



(b)

Fig. 4 Comprehensive treatment of joint sealing and waterproof + honeycomb surface at the station leakage: (a) apply along the roof direction; (b) Overall application effect

As shown in figure 4, the side wall of the main structure of the tunnel adopts the developed ZSJ-M1 and the finished product X to apply waterproof repair treatment to the entire cracking and seepage wall of the leakage site. After coating, the tracking observation shows that the ZSJ-M1 material coating has no peeling, cracking or falling off phenomenon, and no repeated leakage occurs, which has a good sealing effect on the seepage point. The finished X coating also had no peeling, cracking, or peeling phenomenon, but there were two multiple leaks after 4 months of brushing.

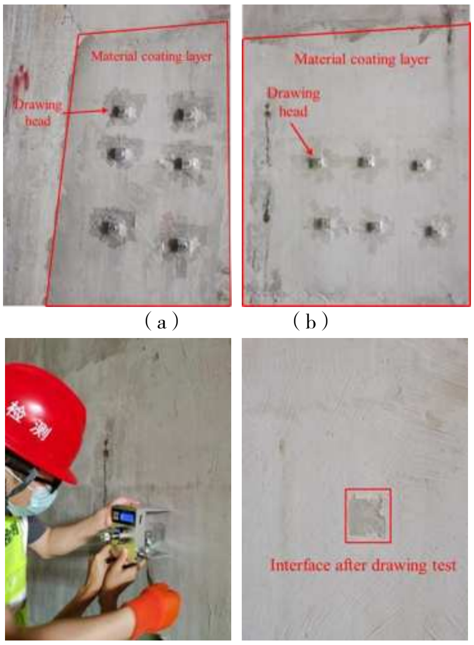


Fig. 5 Interface bond strength test: (a) ZSJ-M1 coating; (b) Finished X coating;
(c) In-situ testing; (d) Pull-out interface

As shown in figure 5, in order to further investigate the bonding effect of ZSJ-M1 material and finished X with matrix concrete, in-situ bonding strength test was conducted on ZSJ-M1 coating and finished X coating with bond strength puller after 4 months of painting. The interfacial bond strength of ZSJ-M1 and finished product X is 1.44MPa and 1.08MPa, respectively. It can be seen that ZSJ-M1 has better compatibility with the matrix concrete, and its bonding effect is better than that of the imported similar product X. It can achieve more excellent seepage and water leakage control effect through the dual effect of permeation repair on the leakage site and bonding and sealing on the matrix surface.

3 Conclusion

(1) The 28d compressive strength and flexural strength of ZSJ-M1 clean pulp specimen are 31.34MPa and 10.21MPa, respectively, and the 28d compressive strength and flexural strength of ZSJ-M2 clean pulp specimen are 30.55MPa and 9.27MPa, respectively. The two materials have excellent impermeability, good compatibility with matrix and high wet base bonding strength, and their properties are superior to those of control group ZSJ-1, ZSJ-2 and imported similar products X.

(2) The self-healing properties of ZSJ-M1 and ZSJ-M2 are excellent, and the highest recovery rate of preloaded strength can reach 134.85% and 118.81%, respectively. The active enhanced masterbatch M1 and M2 can promote the hydration reaction process of cement through the complexation precipitation reaction, and accelerate the formation of insoluble substances such as C-S-H gel. Under the synergistic action of bentonite and sodium methicosilicate, they have the effect of long-term repair of specimen cracks and improve the density and strength.

(3) ZSJ-M1, with its excellent impermeability, bonding performance and self-healing performance, can effectively repair the cracks and water leakage in the actual tunnel engineering, solve the problem of repeated treatment and repeated leakage, and has a wide range of promotion and application value.

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