Research on The Polycarboxylic Slump Retaining Admixture

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Abstract. The polycarboxylic slump-retaining admixture was synthesized by methyl allyl polyoxyethylene ether (TPEG) and unsaturated carboxylic acid in redox system. The factors influencing on performance of polycarboxylic slump-retaining admixture，such as temperature, reaction time, acid alcohol ratio, the amount of initiator and molecular regulator were researched. It show that the performance of slump-retaining agent is best when the ratio of acid to alcohol is 1.75:1, amount of initiator is 0.56%, molecular weight regulator dosage is 0.28%, reaction time is 1.5h, and reaction temperature 60˚C.The molecular structure of polycarboxylate slump-retaining were characterized by infrared spectroscopy.

Introduction

At present, with the large-scale development of engineering construction in our country, the polycarboxylic superplasticizer due to its non-toxic, environmental protection, water reducing rate higher characteristics has become a hotspot in the field of concrete admixture industry, the quality requirements are increasingly stringent.However, it also encountered many engineering problems in the process of polycarboxylic superplasticizer using, especially concrete slump damage is great when mixing with high efficiency superplasticizer due to cement, admixture, gravel, mud and other quality problems [1],it affects the application and development of high efficiency superplasticizer directly. Some scholars tests show that concrete slump loss is fast especially mixed with high performance superplasticizer[2,3], causes considerable difficulties to constructions.

Test materials and test equipment

Synthetic materials of slump retaining admixture. It is shown in Table 1.

Table 1 synthetic material of slump retaining admixture

materials	purity	manufacturers
Methyl allyl polyoxyethylene ether（TPEG）	industrial grade	Haian Petrochemical Plant of Jiangsu Province
acrylic acid（AA）	chemical pure	Sinopharm Chemical Reagent Co., Ltd.
hydrogen peroxide	industrial grade	Weifang Union BiochemistryCo., Ltd.
mercaptoacetic acid	industrial grade	Zhucheng Zhongxin Industry ＆Trade Co., Ltd.
TP1352	industrial grade	Shanghai Jiujie Technology Co., Ltd.
distilled water	-	Made in the lab
sodium hydroxide	analytically pure	Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd.

Cement. Changge P.O 42.5 manufactured by Hubei Junshan Cement Co., Ltd.

Superplasticizer. The superplasticizer is made in the lab.

Mixing water. The mixing water is clean tap water.

Test equipment. A glass-made reaction tank with three mouths (content:1 liter), thermometer, stirrer, dropping funnel.

Synthetisizing and testing methods of slump retaining admixture

Synthesis of slump retaining admixture. A glass-made reaction tank(content:1 liter)equipped with a thermometer, stirrer, dropping funnel, nitrogen inlet tube was charged with water and TPEG. Inside of the reaction vessel was purged with nitrogen under stirring, and heated to a certain temperature and dissolved completely. Then, a certain amount of initiator was added to the reaction vessel. Stirring for 15minutes until the initiator and TPEG stir well and fully. Keeping the temperature for a certain time. Then, AA solution and sulfhydryl acetic acid mixture solution were dropwisely added to the water in the reactor. Controlling the reaction temperature and time just well. After the completion of the dropwise addition, the system was maintained at reaction temperature for an hour. Then down to environmental temperature. PH value was adjusted to 6.0 ~ 7.0 by 30% concentration of sodium hydroxide solution.

Measurement of cement paste fluidity. The performance of slump retaining admixture was tested according to GB/T8007-2000. The condition is W/C=0.29, amount of the admixture is 0.4%, thereinto, 20% of the superplasticizer was replaced by slump retaining admixture. The cement paste was put into beaker and covered with wet cloth after each measuring. Then it was maintained a certain time and stirred well before measure the fluidity again.

Results and discussions of experiment

The copolymer performance varies with the different proportions of raw materials. On the basis of the n(AA):n(TPEG) =1.9:1,amount of initiator is 6% by weight, amount of molecular weight regulator is 0.07% by weight, the property of polycarboxylic slump retaining admixture impact on research materials and reaction conditions were researched by changing amount of each material respectively and reaction condition.

Impact of reaction temperature on the property of slump retaining admixture. The effect of reaction temperature was researched by changing the reaction temperature. The results is shown in Fig.1.It shows that initial cement paste fluidity changes little, after 90 minutes, cement paste fluidity loss is very large by mixing the slump retaining admixture which reaction temperature is 60˚C, with the rising of reaction temperature, the cement paste fluidity is also very large by mixing slump retaining admixture which reaction time is over 60°C from Fig.1. This is because that the reaction is incomplete and active substances are less under the condition of low temperature. With the rising of reaction temperature, copolymerization react continuously toward the ideal direction and active substances increase, cement paste fluidity become large. The reaction system is oxidation-reduction initiator system which was polymerized by free radial caused by electron transfer between reducing agent and oxidant. But decomposition activation energy of oxidation - reduction initiator system is not high， about 40 KJ/mol ~ 60 KJ/mol， so the reaction temperature should not be too high.

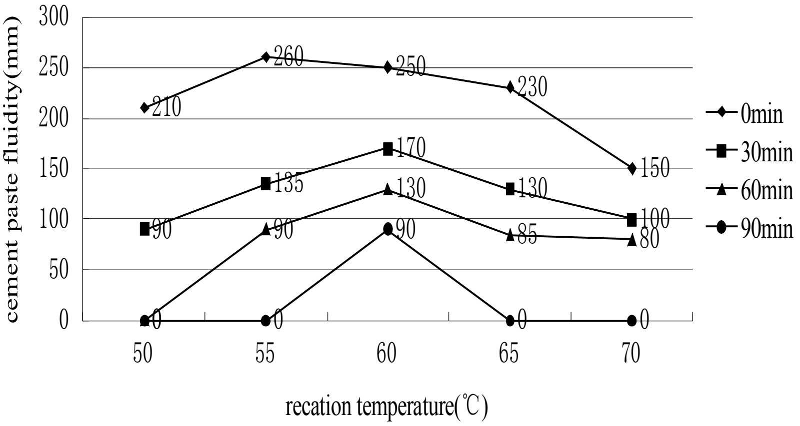

Fig.1 Impact of reaction temperature to the slump retaining admixture

Impact of reaction time on the property of slump retaining admixture. The effect of reaction time was researched by changing the reaction time based on certein reaction temperature. The result is shown in Fig.2. It shows that reaction time has significant impact on monomer conversion rate. The monomer conversion rate is low， and it found that certain monomer exists in liquor with a thick odor of unreacted monomer which has negative influence on the cement paste fluidity when polymerization time is short. It is difficult to "shielding" water reducing function group in the main chain because the number of deciduous side chain is more when reaction time is too long, which causing the decline of cement paste fluidity retention capacity.Therefore, the ideal reaction time is 1.5 h in which the slump retaining admixture reacts completely，the dispersibility and slump resistance is optimum.

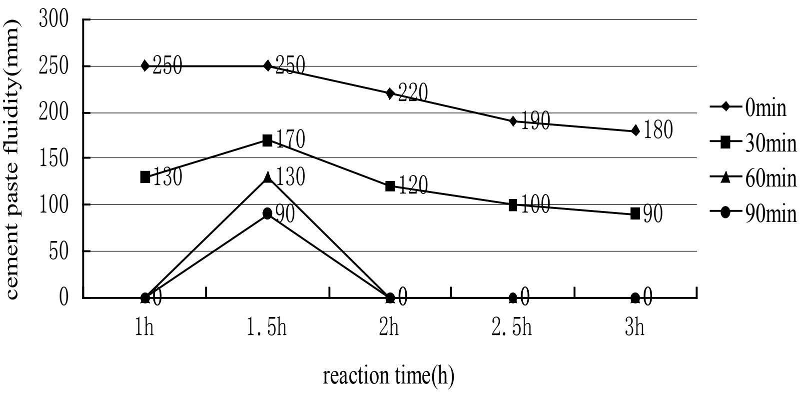

Fig.2 Impact of reaction time to the slump retaining admixture

Impact of acid alcohol ratio on the property of slump retaining admixture. The effect of mole rate of TPEG and AA was researched by changing the the mole rate of TPEG and AA at certain reaction time and temperature. The result is shown in Fig.3.It shows that the cement paste fluidity is optimum when mixing the slump retaining of acid alcohol ratio is 1.75:1, cement paste fluidity increases with the acid alcohol ratio raising after 90 minutes. But cement paste fluidity decreases with the acid alcohol ratio reach a certain mole ratio because that main chain increases with the rising of AA weight, but it is easy to produce flocculation phenomenon and influence charge effect of carboxylic acid function group， which lead to reduce the cement paste fluidity[4] cause by polymer molecular when the AA weight over a certain value.

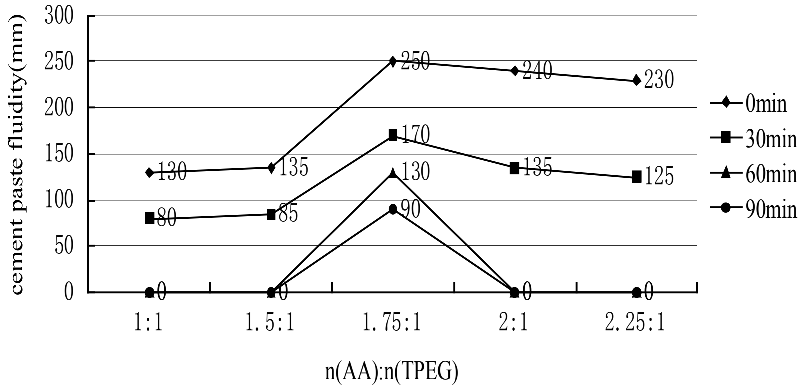

Fig.3 Impact of acid alcohol ratio to the slump retaining admixture

Impact of initiator on the property of slump retaining admixture. The effect of initiator was researched by changing the amount of initiator at certain reaction time and temperature. The result is shown in Fig 4.It shows that cement paste fluidity firstly increases then decreases with the amount of the initiator from 0.28% to 1.12% by weight. The slump retaining admixture performance is optimum when the dosage is 0.56%. The initiator not only play role of initiating reaction, but also adjust the product molecular weight in the polymerization reaction.

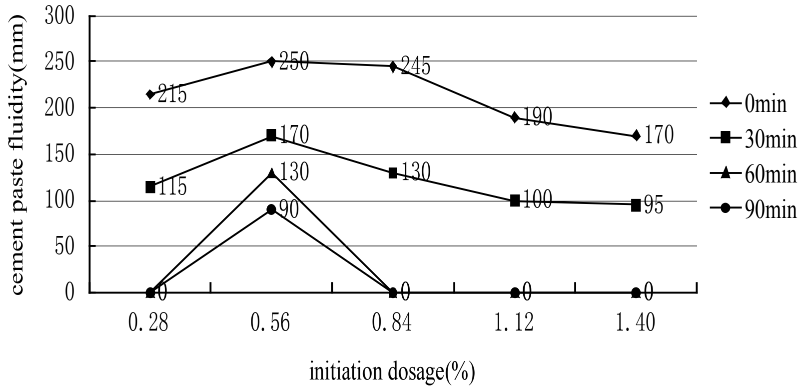

Fig.4 Impact of initiator to the slump retaining admixture

In the free radical copolymerization reaction, kinetic chain length is inversely proportional to the square root of initiator concentration [5], and is presented by the following formula(1):

$$g = \frac{k_p}{2(fk_d k_t)^{\frac{1}{2}}} \bullet \frac{[M]}{[I]^{\frac{1}{2}}} \quad (1)$$

In the formula (1)：

g ——kinetic chain length ;

k_p ——chain propagation rate constant;

f ——initiator efficiency;

k_d ——The initiator decomposition rate constant;

k_t ——The initiator termination rate constant;

$[M]$——Monomer concentration;

$[I]$——Initiator concentration.

The molecular weight of the polymerization products decreased with the increase of initiator under the same other conditions. The molecular weight of copolymer is bigger, the aqueous solution dispersed uniformity when amount of initiator is less. On the other hand, macromolecules are conformation of no rules clew. It has big branched chains and shield groups in the main chain lead to the less adsorption positions and small space steric hindrance which cause the fluidity reduced. Copolymer molecular weight decreases, each perssad monomer copolymerizes perfectly,the dispersion ability strengthens when the amount of initiator increased. However, the system has high polymerization speed which cause gelling effect easily, the dispersion ability drop considerably when initiator dosage still increases, At the same time, It shows that air-entraining performance of polymerization increase with amount of initiator increase and then affect the strength of concrete according to the research made by Zheng pingSun[6].

Impact of to the slump retaining admixture. The effect of molecular weight regulator was researched by changing the amount of initiator at certain reaction time and temperature. The result is shown in Fig.5.It shows that cement paste fluidity loss decreases gradually with the increasing weight of molecular weight regulator. The property of slump retaining admixture is optimum when the amount of molecular weight regulator is 0.28%.The propertywill weaken if still increasing weight of molecular weight regulator.

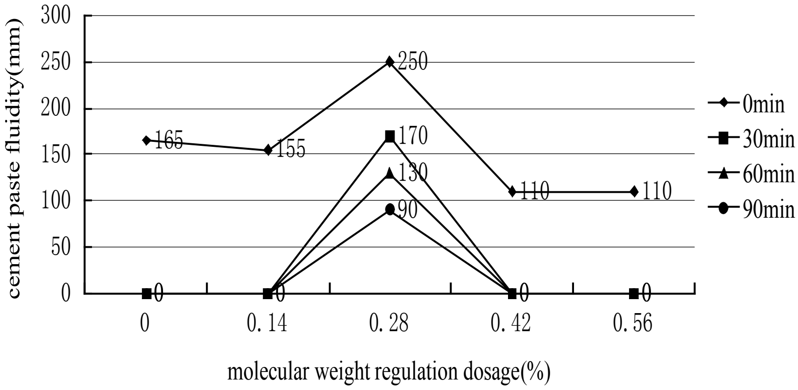

Fig.5 Impact of molecular weight regulator to the slump retaining admixture

Polycarboxylic slump retaining admixture named ZBT was synthetized under optimum conditions according to the results above.

Contrast test of slump retaining admixture. Adopting blank control group and control group mixed with the commercial admixture named Tai Jie in order to test the performance of the admixture which synthetized under optimum conditions, the dosage of admixture is 0.4%, thereinto, 20% of superplasticizer is replaced by slump retaining admixture. Water-cement ratio is 0.29. testing cement paste fluidity after 0 minute, 30minutes, 60minutes and 90minutes respectively. The results are shown in Table 2.It shows that cement paste fluidity loss is great when mixed with no admixture. Compared with Tai Jie slump retaining admixture, ZBT can enhance cement paste initial fluidity to some extent and maintain a relatively high fluidity after 30 minutes. The performance is optimum.

Table 2 Result of slump retaining admixture contrast test

serial number	Category ofslump retainingadmixture	Cement paste fluidity/mm			
		initial	30min	60min	90min
PC-1	n（PC）:n（BT)=10:0	190	80	0	0
PC-2	n（PC）:n（BT)=8:2	230	210	190	95
PC-3	n（PC）:n（ZBT)=8:2	250	235	150	90

IR test of the polycarboxylic slump retaining admixture

The molecular structure of the polycarboxylic slump retaining admixture was analyzed By Infrared spectrum（IR）as shown in Fig.6. It shows that the larger intensity broad aborption peak at 3392.31cm^{-1} shows that the bands of —OH vibrations of the admixture molecular are observed in the spectra and strong symmetrical H bonds are synthetized. The aborption peak at 2880.21 cm^{-1} is sharp and strong attributed to vibreations of the C—H in the Polyoxyethylene chain. Themedium and sharp peaks at 2880.21 cm^{-1} is the aborption of C=O. The abortption peak at 1470.78cm^{-1} is the characteristic peak of —CH_2.The peaks of C—H deformation vibration around 1358.35 $cm^{-1}$and C—O flexural vibrations around 950.94 cm^{-1}. There is strong spiculate peak at 1120.91 cm^{-1} attributed to antisymmetric absorptionof the C—O—C groups of the admixture.

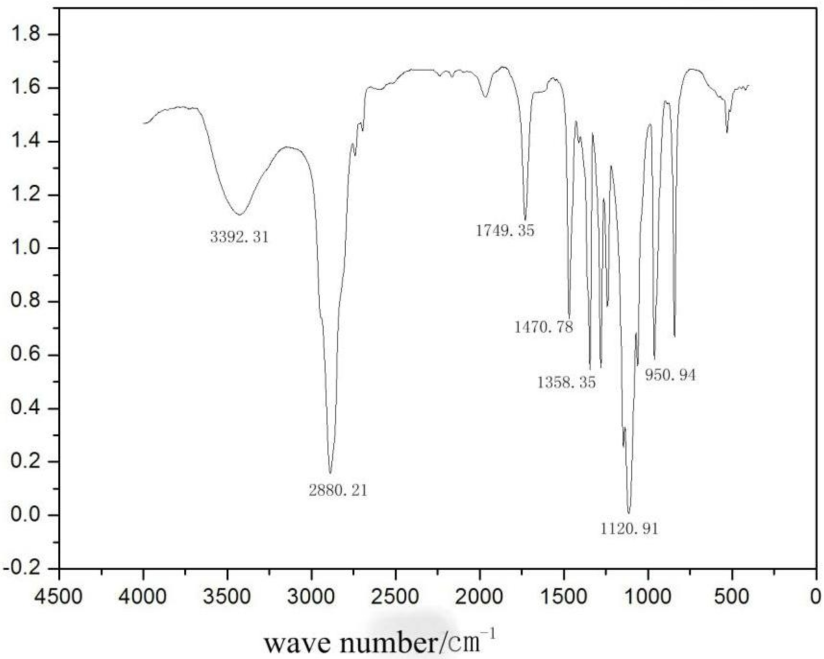

Fig.6 IR test of the polycarboxylic slump retaining admixture

Conclusions

The slump-reatining admixture which has good slump performance was synthesized in the conditions that reaction temperature is 60˚C, reaction time is 1.5 hours, acid alcohol ratio is 1:1.75,dosages of initiator and molecular regulator are 0.56% and 0.28% by weight.

Acknowledgements

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Reference

[1]Yu XIAO.Research on polycarboxylic high performance slump retaining admixture[D].Wuhan: Wuhan University of Science and Technology, 2013(In Chinese)

[2]Juan CHENG, Xiang-yang GUO. Research on the gradual loss and control in slump of the ready-mixed concrete[J]. Concrete, 2005(1):64-68 (In Chinese)

[3]Jiang XU, Hong-guang CHEN, Fu-jun WANG, Jing-liang CUI. Analysis on causes for slump loss of fresh concrete and countermeasures[J]. Tunnel construction,2010,30(6):652-655 (In Chinese)

[4]Zhi-yong ZHANG, Qian-ping RAN, Yong YANG, Yong-lin MAO, Dongliang ZHOU. Study on preparation and performance of polymaleic water reducer based on allyl polyethylene glycol[J], New building materials, 2011,38(6):40-43 (In Chinese)

[5]Zi-ming WANG. Polycarboxylate hight performance uperplasticizer—preperation·performance a nd application[M]. Beijing: China architecture＆building press, 2009 (In Chinese)

[6]Zhen-ping SUN, Xiong-rong HUANG. Study on Allyl Polyethylene Glycol Based Polycarboxylate Superplasticizer[J]. Journal of Building Materials, 2009,12(4):407-412 (In Chinese)