

## Effect of Polymer Grinding Aids on the Grindability and Strength of Cement

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**ABSTRACT:** In this study, different polymer grinding aids (GA) were synthesized from maleic anhydride (MA), polyethylene glycol (PEG), and acroleic acid (AA) under different process conditions, and their effects on the grindability and strength enhancement of cement were compared. The results showed that esterification was preferably conducted at a MA : PEG ratio of 1.2 : 1 at 105°C for 3 h with 1.5% catalyst; and copolymerization was preferably conducted at a MA-PEG : AA ratio of 1 : 1 at 85°C for 6 h. The number-average molecular weight of the polymer GAs was 12,964, the weight-average molecular weight was 18,156, and the polydispersity index was 1.40, respectively. The specific surface area of the samples obtained under the optimum condition increased by 32.87%, the flexural strength increased by 12.5% at 3 d and 16.67% at 28 d, and the comprehensive strength increased by 42.06% at 3 d and 22.19% at 28 d as compared with the control sample. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41153.

**KEYWORDS:** cement; molecular weight and distribution; polymer grinding aids; specific surface area; strength

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### INTRODUCTION

It has been a common practice to use low molecular grinding aids (GA) in cement manufacture to improve the grinding efficiency and mechanical properties of cement. The commonly used ethanolamine GAs include triethanolamine (TEA), diethanolamine, and monoethanolamine,<sup>1–4</sup> among which TEA is the most effective set retarder, but it produces low strength development at early and late stages of cement hydration. It has been shown that the use of triisopropanolamine (TIPA) in combination with calcium nitrate or monosaccharide results in a significant reduction in the initial and final setting times, as well as a strength enhancement at all ages of cement pastes, particularly at the very early ages.<sup>5–7</sup> Albayrak et al. showed that unsaturated fatty acids significantly reduced the compressive strength of cement.<sup>8,9</sup> This is to be expected as the double bonds in those unsaturated fatty acids can be readily oxidized by the dissolved oxygen in water during the curing period, thereby resulting in an increase in microcracks and then a decrease in compressive strength of cement. Studies on the dihydroxy-compound class GAs (ethylene glycol, propylene glycol, and polypropylene glycol) showed that propylene glycol was most effective in decreasing the specific energy consumption and increasing the specific surface area.<sup>10,11</sup> It also significantly improved the particle size distribution and flowability of cement.

Some other studies have attempted to use polymers as a GA in the grinding process,<sup>12,13</sup> and the results clearly showed that polymers had a desirable grinding effect and also played a posi-

tive role in the hydration and hardening of cement. In the use of a variety of polymer GA in the grinding process, the polycarboxylate-type polymer<sup>14,15</sup> is the most typical one. A comprehensive research was undertaken by Zhang et al.<sup>16</sup> to evaluate the optimizing effect of polycarboxylate-type GA on particle size distribution and cement strength. According to the report of Zhang et al., by applying polycarboxylate-type GA at a dosage of 0.05% of cement weight, the specific surface area increased by 19.8%, and the compressive strength increased by 10.5% at 3 d and 8.3% at 28 d. Liu<sup>17</sup> studied the synthesis and dispersibility of polymer GA, using the acrylate and methyl acrylate as the main monomers. When GA addition volume was 0.3% of the powers, Liu found that particle size decreased by 1/3 and specific surface area increased by one time. Zhang<sup>18</sup> prepared a novel grinding calcium carbonate (GCC) GA through the method of aqueous polymerization. Similarly, when the synthetic GA was used in the ultrafine wet grinding of GCC, the fluidity of the GCC slurry was enhanced remarkably. Meanwhile, the amount of GCC particles <2 μm increased by 9.3%.

As has been mentioned, TEA and TIPA are known as a component of additives and admixtures for cements and have beneficial effects on the grindability of cement clinker. However, several problems remain to be solved in the application of these low molecular GAs, such as unstable performance, sensitive to the change of amount, and high cost. In contrast, polymer GA seems to be especially promising in cement manufacture due to

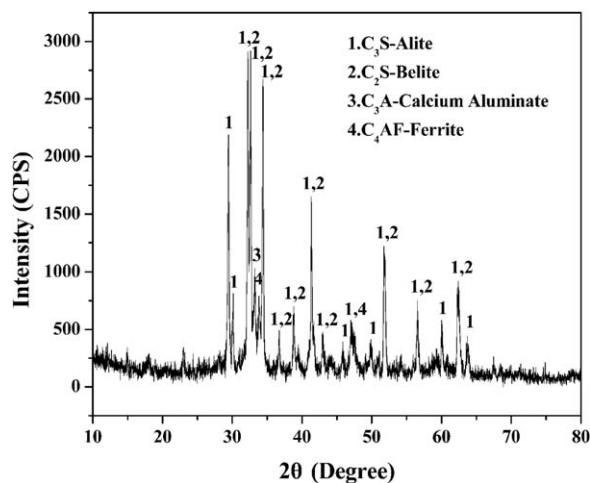


Figure 1. X-ray diffraction of the clinker used.

the following advantages: First, a polymer made from monomers makes it possible to incorporate different functional groups at the molecular level, leading to synergistic effects of these functional groups; Second, the artificially constructed molecular structure may allow for a higher proportion of effective components and a narrower molecular weight range in GA. In addition, polymer GA composed of hydrophobic main chain and hydrophilic side chain has stable performance. What makes the use of polymer GA even more desirable is that it is economically profitable on the part of the enterprise due to the low cost, as only a small amount of such GA is needed, and the changes in amount have less effect on cement performance.

In this study, a variety of polymer GAs were synthesized from maleic anhydride (MA), polyethylene glycol (PEG), and acroleic acid (AA) by altering the conditions of esterification and copolymerization.<sup>16</sup> The molecular weight and distribution were measured by gel permeation chromatography, and the grindability and strength properties were compared between cement with and without the use of polymer GA, based on which the optimum molecular weight distribution was determined.

## EXPERIMENTAL

### Experimental Raw Materials

MA, PEG-400, AA, toluene-*p*-sulfonic acid, and ammonium persulfate were obtained from Lingfeng Chemical Industry

Table I. Chemical Analysis of the Portland Cement Clinker Used

Chemical analysis	wt %
CaO	66.3
SiO <sub>2</sub>	19.8
Al <sub>2</sub> O <sub>3</sub>	4.4
Fe <sub>2</sub> O <sub>3</sub>	3.5
MgO	3.3
K <sub>2</sub> O	1.1
SO <sub>3</sub>	0.81
Na <sub>2</sub> O	0.14
Loss in ignition	0.77

(Shanghai, China), cement clinker and plaster from Zhonglian Dengfeng Cement (Henan, China), and standard sands from China ISO Standard Sand (Xiamen, China), respectively. The cement clinker was analyzed by XRD and XRF, and the mineral and chemical compositions were shown in Figure 1 and Table I, respectively.

### Experimental Methods

**Esterification.** MA and PEG with a given molar ratio were weighed. MA and toluene-*p*-sulfonic acid were placed into a 4-mouth flask and deaerated with nitrogen gas. Then, the flask was heated until MA was melted, and PEG was added uniformly and stirred at 105°C for 3 h.

The esterification rate was determined by measuring the acidity of the reaction mixture. The esterification product of 0.7–1.0 g was dissolved with 30 mL distilled water in an Erlenmeyer flask and then placed in a boiling water bath for 5 min to accelerate dissolution, then phenolphthalein indicator was added into the solution. The sample was titrated by adding 0.5 mol/L NaOH solution from a burette drop by drop, and stirred constantly until 1 drop turned the sample faint pink.

$$\text{Acid Value} = \frac{V \times C_{\text{NaOH}} \times 40}{M}$$

where  $V$  is the volume of NaOH solution (mL),  $C_{\text{NaOH}}$  is the molality of NaOH solution (mol/L), and  $M$  is the sample weight (g), respectively.

$$\text{Esterification Rate} = \frac{\text{initial acid value} - \text{termination acid value}}{\text{initial acid value}} \times 100\%$$

**Copolymerization.** The esterification product was dissolved in water to a 50% solution, and a certain amount of AA and ammonium persulfate were weighed and then dissolved in 50 mL water. The esterification product solution was added into a 4-mouth flask, deaerated with nitrogen gas, stirred uniformly, and heated up to 85°C. The AA and ammonium persulfate solution were dropped uniformly within 2 h, and left for reaction for 4 h. The reaction product was neutralized using 8 mol/L NaOH solution.

### Sample Preparation and Performance Test

The esterification product was washed with water and alkali, and then subjected to silica gel column chromatography with dichloromethane as the eluent. The second fraction was further purified in the same way. Then the eluent was removed, and the final product were analyzed by Fourier infrared spectroscopy.

The copolymerization product was transferred to the beaker, precipitated repeatedly with tetrahydrofuran, washed, filtered, and redissolved. The residual tetrahydrofuran in the product was evaporated in a vacuum oven at 40°C. The final product was analyzed by Fourier infrared spectroscopy and gel permeation chromatography.

Raw materials (95% cement clinker, 5% plaster, and 0.05% GA) were mixed, and steel balls of about 2.5 times the amount of raw materials were added as grinding media. They were then ground in a ball mill for 40 min. Cement mortar samples were

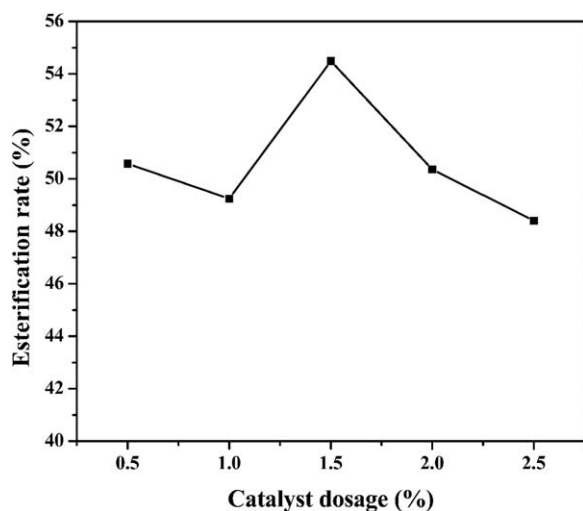


Figure 2. The influence of catalyst dosage on esterification rate.

prepared by mixing 450 g cement with 1350 g standard sand and 224 mL water for comprehensive and flexural strength test.

## RESULTS AND DISCUSSION

### Esterification

The effect of different amounts of catalyst on the esterification rate was studied at a MA to PEG ratio of 1.2 : 1 and a reaction temperature of 85°C. Figure 2 showed that changes in the amount of catalyst had only a marginal effect on the esterification rate. The esterification rate reached a maximum of 54.49% when 1.5 wt % catalyst was used, and further increasing or decreasing the amount of catalyst would decrease the esterification rate. Thus, the optimum amount of catalyst was determined to be 1.5%.

The effect of different reaction temperatures on the esterification rate was studied at a MA to PEG ratio of 1.2 : 1 and the amount of catalyst of 1.5%. Figure 3 showed that the esterification rate increased rapidly with increasing reaction temperature, reached 56.60% at 105°C, and then increased rather slowly to 56.77% with the further increase of temperature up to 115°C. However,

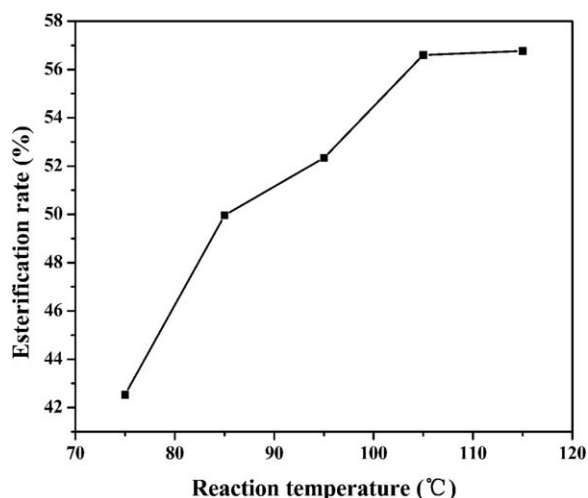


Figure 3. The influence of reaction temperature on esterification rate.

Table II. Effect of Ratio of MA and PEG on the Esterification Rate

$n(\text{MA}) : n(\text{PEG})$	MA (g)	PEG (g)	Esterification rate (%)
1.05 : 1	12.87	50	50.91
1.1 : 1	13.483	50	51.98
1.2 : 1	14.709	50	52.41
1.3 : 1	15.935	50	52.64
1.4 : 1	17.161	50	52.24

it seemed to be unsuitable for the esterification reaction as MA was more likely to evaporate at such a high temperature. Thus, the optimum reaction temperature was determined to be 105°C.

Given that MA can be easily evaporated at high temperature, the molar ratio of MA to PEG is preferably not less than 1 : 1. The effect of different feed ratios of MA to PEG on the esterification rate was studied at a fixed reaction time and temperature. Table II showed that the esterification rate increased slightly at first with increasing ratio of MA to PEG, reached 52.41% at a molar ratio of 1.2 : 1, and then remained essentially unchanged with the further increase of the molar ratio of MA to PEG. Thus, the optimum molar ratio of MA to PEG was determined to be 1.2 : 1.

Figure 4 showed that the peaks at 3436.6 and 2877.0  $\text{cm}^{-1}$  were the stretching vibration absorption of  $-\text{OH}$  and  $\text{C}-\text{H}$  in  $-\text{CH}_2-$ . The characteristic absorption of  $-\text{C}=\text{O}$  of MA at 1855 and 1786  $\text{cm}^{-1}$  disappeared. The peak at 1727.9  $\text{cm}^{-1}$  was the stretching vibration absorption of  $-\text{C}=\text{O}$  of the carboxyl group, the peak at 1640.7  $\text{cm}^{-1}$  was the characteristic absorption of  $\text{CH}=\text{CH}$ , the peaks at 1405.1 and 1249.5  $\text{cm}^{-1}$  were the vibration absorption of  $\text{C}-\text{O}$  bond of the acid and ester group, and the peak at 1105.7  $\text{cm}^{-1}$  was the characteristic absorption of  $\text{C}-\text{O}-\text{C}$ . This product was determined to be MA ester of PEG (MA-PEG).

### Copolymerization

The esterification product and AA were copolymerized at a given ratio of 1 : 1 in water for 4, 5, 6, and 7 h, respectively,

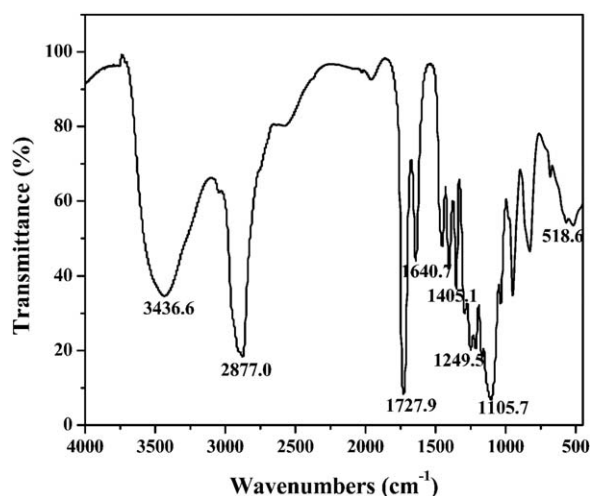
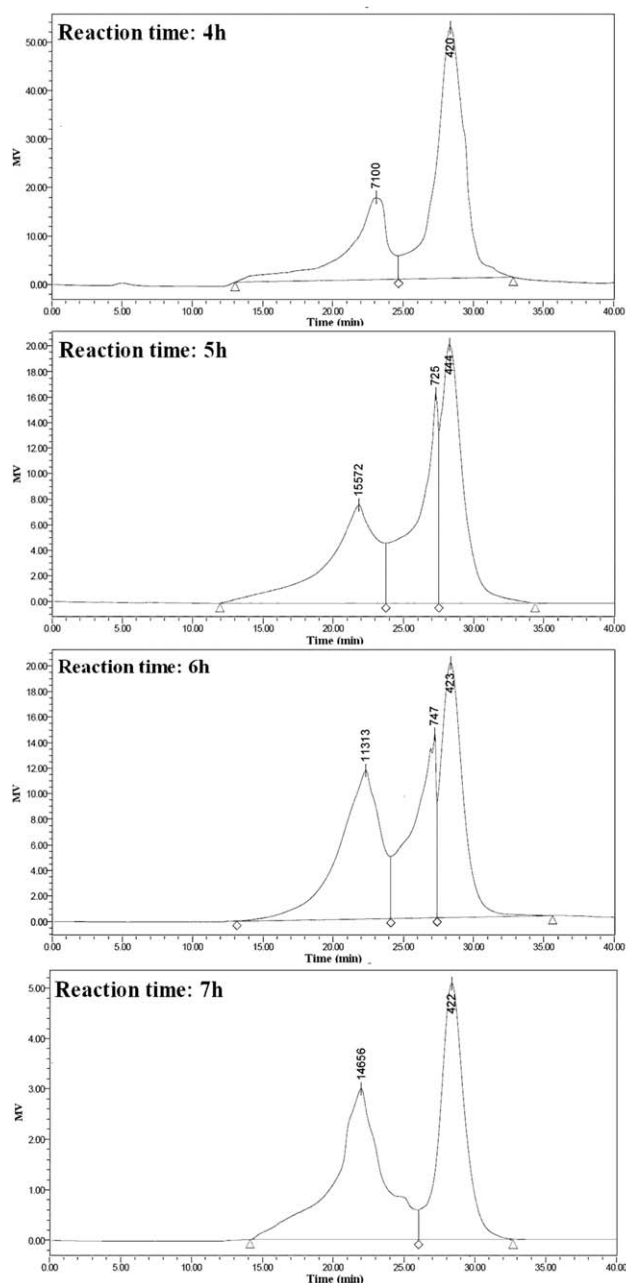


Figure 4. The FT-IR spectra of MA-PEG.



**Figure 5.** The result of GPC on copolymer product in different reaction time.

and the molecular weight and distribution were measured. Figure 5 and Table III showed that the number-average molecular weights ( $M_n$ ) were 7479, 11,737, 12,964, and 16,448, the

**Table III.** The Effect of Reaction Time on Molecular Weight and Distribution of Copolymer

Reaction time (h)	$M_n$	$M_w$	MP
4	7479	10,256	7100
5	11,737	16,032	15,572
6	12,964	18,156	11,313
7	16,448	25,384	14,656

weight-average molecular weights ( $M_w$ ) were 10,256, 16,032, 18,156, and 25,384; and the polydispersity indexes ( $M_w/M_n$ ) were 1.37, 1.37, 1.40, and 1.54 for the copolymerization products obtained at a reaction time of 4, 5, 6, and 7 h, respectively.

The MA-PEG and AA were copolymerized at a feed ratio of 0.6, 0.8, 1, 1.2, and 1.4 for 6 h, and the molecular weight and distribution were measured. Figure 6 and Table IV showed that  $M_n$  was 9214, 9485, 12,964, 10,433, and 7406,  $M_w$  was 11,457, 9852, 18,156, 16,568, and 9085, and  $M_w/M_n$  was 1.24, 1.04, 1.40, 1.59, and 1.23 for the products obtained at a feed ratio of 0.6, 0.8, 1, 1.2, and 1.4, respectively.

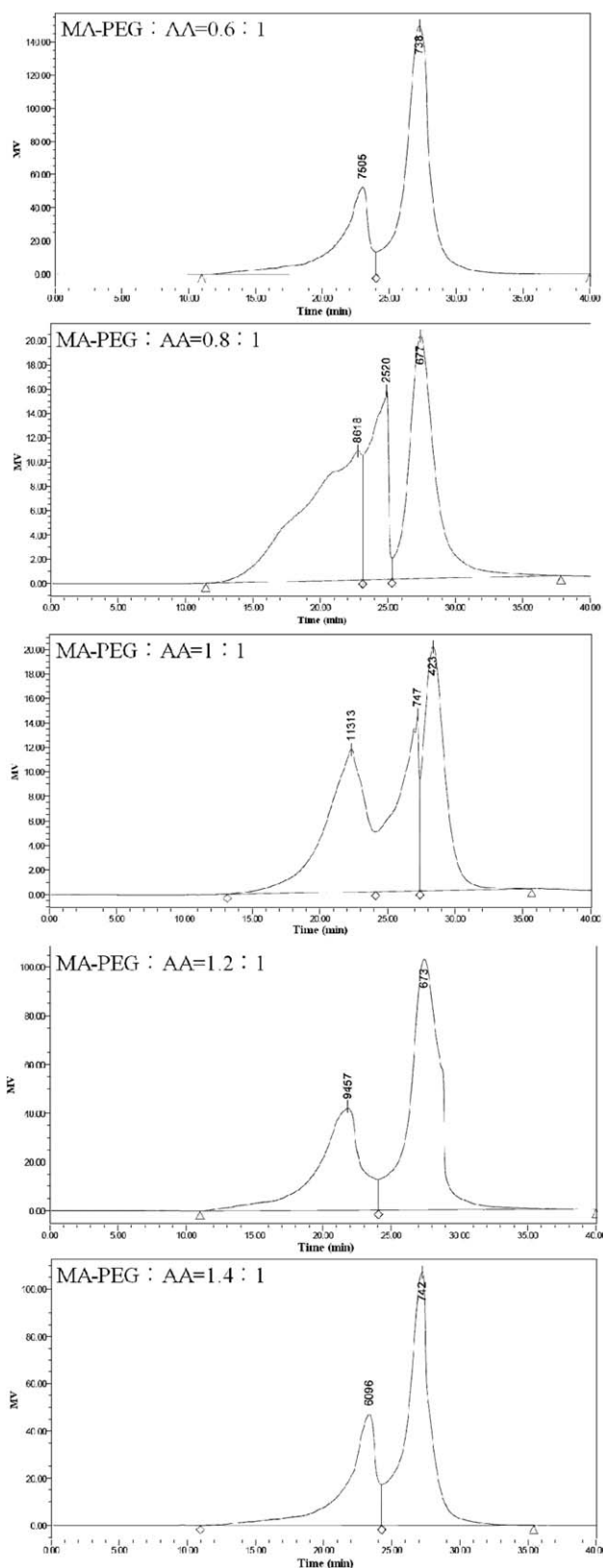
Figure 7 showed that the stretching vibration absorption of  $-\text{OH}$  at  $3424.6\text{ cm}^{-1}$  was stronger than the esterification products due to the considerable amount of  $-\text{OH}$  in AA. The peaks at  $2917.5$  and  $1726.3\text{ cm}^{-1}$  were attributed to the stretching vibration absorption of  $\text{C}-\text{H}$  in  $-\text{CH}_2-$  and  $-\text{C}=\text{O}$  of the carboxyl group. The characteristic absorption of  $\text{CH}=\text{CH}$  at  $1640.7\text{ cm}^{-1}$  was weaker than the esterification products due to that the double bonds were oxidized to form a chain. The peak at  $1248.9\text{ cm}^{-1}$  was the vibration absorption of  $\text{C}-\text{O}$  of the ester group, and the peak at  $1100.8\text{ cm}^{-1}$  was the characteristic absorption of  $\text{C}-\text{O}-\text{C}$ . The product was then determined to be AA copolymer.

#### Effect of Polymer GAs to the Property of Cement

A variety of polymer GAs with different molecular weights were obtained by varying the copolymerization time (4, 5, 6, and 7 h) and feed ratio of MA-PEG to AA (0.6, 0.8, 1, 1.2, and 1.4), and the particle size distribution and specific surface areas of cement with and without GAs were compared.

The particle size distribution of cement was measured by Laser particle size analyzer. Tables V and VI showed that the use of polymer GAs significantly improved the particle size distribution of cement, and the maximum effect was observed at a reaction time of 6 h and the MA-PEG : AA ratio of 1 : 1. The weight percent of the particles of  $0-3\text{ }\mu\text{m}$  increased from 9.53 to 15.23%, and that of the particles of  $3-32\text{ }\mu\text{m}$  increased from 57.78 to 66.63%. However, the weight percent of the particles larger than  $80\text{ }\mu\text{m}$  decreased from 3.18 to 0.91%.

The improved particle size distribution of cement could be attributed to the mitigation of caking and agglomeration during the grinding process. The final polymer GAs obtained in this study are a block copolymer of AA and the esterification product of MA and PEG. These polymers are comb-like consisting of hydrophobic main chains and hydrophilic side chains. The mechanisms responsible for the grinding effect of polymer GAs are that: (1) polymer GAs contain a variety of polar groups. During the grinding of clinker, the cleavage of  $\text{Ca}-\text{O}$  bonds leads to the formation of a large number of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ , thus accelerating the agglomeration of cement particles. However, the negatively charged polar groups in the side chains of polymer GAs could neutralize  $\text{Ca}^{2+}$  to prevent agglomeration and thus improve the grinding efficiency; and (2) The hydrophobic main chains of polymer GAs can be adsorbed on cement particle surface, while the hydrophilic side chains are exposed to



**Figure 6.** The result of GPC on copolymer product in different ratio of MA-PEG and AA.

**Table IV.** The Effect of Ratio of MA-PEG and AA on Molecular Weight and Distribution of Copolymer

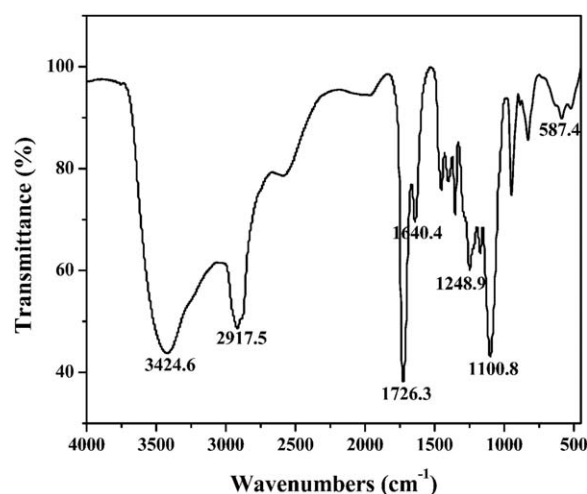
$n$ (MA-PEG) : $n$ (AA)	$M_n$	$M_w$	MP
0.6 : 1	9214	11,457	7505
0.8 : 1	9485	9852	8618
1 : 1	12,964	18,156	11,313
1.2 : 1	10,433	16,568	9457
1.4 : 1	7406	9085	6096

the gas phase, thus forming a steric hindrance between the adsorption layer and cement particles and decreasing the agglomeration of cement particles. For these reasons, it can be concluded that the grinding efficiency of polymer GAs is closely associated with their molecular structures.

Figure 8 showed that the specific surface areas increased from  $375.56 \text{ m}^2 \text{ Kg}^{-1}$  for control sample to 453.74, 468.12, 500.34, and  $482.44 \text{ m}^2 \text{ Kg}^{-1}$  for samples with polymer GAs obtained at a reaction time of 4, 5, 6, and 7 h, with an increase of 20.5, 24.32, 32.87, and 28.12%, respectively.

Copolymerization time determines the molecular weight of the final products. In polymer GAs with low molecular weight, the longer the main chain, the greater the number of active groups, and consequently the better the grinding efficiency. However, as the molecular weight increases, the viscosity of polymer GAs increases, and the solubility decreases. It should also be noted that the number of active groups in a single molecular chain will increase as the main chain length increases, but the number of active groups per unit length of main chain remains largely unchanged. In addition, random-coil polymer GAs with too large molecular weight will embed the active groups and thus decrease the grinding efficiency.

Figure 9 showed that the specific surface areas increased from  $375.56 \text{ m}^2 \text{ Kg}^{-1}$  for control sample to 410.11, 415.83, 500.34, 448.06, and  $418.66 \text{ m}^2 \text{ Kg}^{-1}$  for samples with polymer GAs obtained at a MA-PEG to AA ratio of 0.6, 0.8, 1, 1.2, and 1.4,



**Figure 7.** The FTIR spectra of copolymer product.

**Table V.** The Effect of Reaction Time on the Particle Size Distribution of Cement

Reaction time (h)	Particle size distribution of cement (W%)				
	0-3 ( $\mu\text{m}$ )	3-32 ( $\mu\text{m}$ )	32-64 ( $\mu\text{m}$ )	64-80 ( $\mu\text{m}$ )	>80 ( $\mu\text{m}$ )
Blank	9.53	57.78	24.63	4.88	3.18
4	11.79	60.56	20.71	3.88	3.06
5	12.25	62.73	19.46	3.24	2.32
6	15.23	66.63	14.76	2.47	0.91
7	14.52	62.66	18.35	2.61	1.86

**Table VI.** The Effect of MA-PEG : AA on the Particle Size Distribution of the Cement

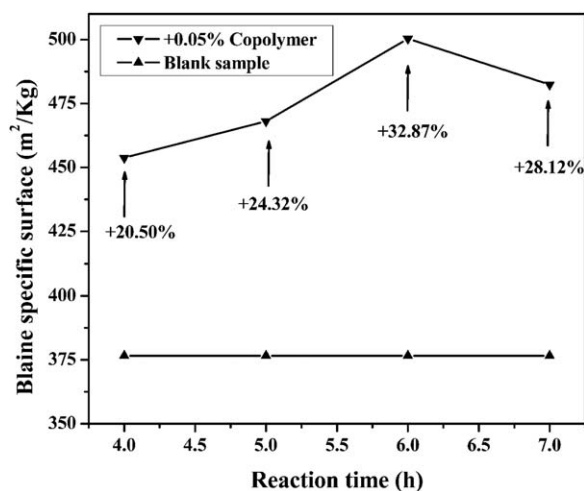
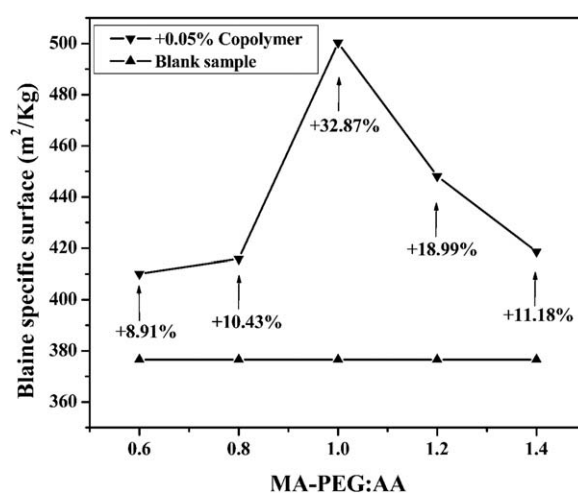
MA-PEG : AA	Particle size distribution of cement (W%)				
	0-3 ( $\mu\text{m}$ )	3-32 ( $\mu\text{m}$ )	32-64 ( $\mu\text{m}$ )	64-80 ( $\mu\text{m}$ )	>80 ( $\mu\text{m}$ )
Blank	9.53	57.78	24.63	4.88	3.18
0.6	9.78	58.63	23.47	4.35	3.77
0.8	10.22	57.77	24.71	3.67	3.63
1	15.23	66.63	14.76	2.47	0.91
1.2	11.35	59.44	23.39	3.57	2.25
1.4	10.68	58.75	23.87	3.28	3.42

with an increase of 8.91, 10.43, 32.87, 18.99, and 11.18%, respectively.

Because MA-PEG and AA contain different active groups, the ratio of MA-PEG to AA determines the proportion of different active groups in the side chains of the final polymer GAs. The results of this study clearly showed that the optimal ratio of MA-PEG to AA was 1 : 1. After the copolymerization reaction, PEG can be grafted onto the main chains of polymer GAs, which may form effective steric hindrance and decrease the agglomeration of cement particles during the grinding process. However, the steric hindrance can also reduce the main chain length and molecular weight, thus inhibiting the grinding efficiency of polymer GAs.

The results of Blaine specific surface of cement, which indicated the changes in particle size, agreed with the results of particle size distribution of cement clinker. Both clearly showed that the reaction time of 6 h and the MA-PEG to AA ratio of 1 : 1 were most effective in increasing the specific surface area of cement.

Cement mortar strength could be used to indicate the effect of polymer GAs with different molecular weights on the strength development of cement. Particles of 3–32  $\mu\text{m}$  are active ingredients of cement clinker and can improve cement strength.<sup>19</sup> In contrast, particles >32  $\mu\text{m}$  act as filling material and have no effect on the strength development of cement mortar; whereas particles <3  $\mu\text{m}$  are able to obtain a high hydration degree and mechanical strength in one day, and barely increased later

**Figure 8.** The influence of reaction time on the Blaine specific surface of cement.**Figure 9.** The influence of MA-PEG : AA on the Blaine specific surface of cement.

**Table VII.** Effect of Reaction Time on Strength Development of Cement Mortar

Reaction time (h)	Flexural strength (MPa)		Compressive strength (MPa)	
	3 (d)	28 (d)	3 (d)	28 (d)
Blank	5.6	6.6	23.3	39.2
4	5.9	7.0	27.7	42.9
5	6.1	7.4	30.3	44.7
6	6.3	7.7	33.1	47.9
7	6.1	7.5	30.9	46.1

strength. Therefore, clinker particles of 3–32  $\mu\text{m}$  are particularly beneficial for the sustained growth of strength throughout the whole process.

Table VII showed that the use of polymer GAs resulted in a significant improvement in the strength of cement, and the polymer GA obtained at a reaction time of 6 h was most effective. The flexural strength increased from 5.6 MPa at 3 d and 6.6 MPa at 28 d for control sample to 6.3 MPa at 3 d and 7.7 MPa at 28 d, with an increase of 12.5 and 16.67%, respectively; and the comprehensive strength increased from 23.3 MPa at 3 d and 39.2 MPa at 28 d for control sample to 33.1 MPa at 3 d and 47.9 MPa at 28 d, with an increase of 42.06 and 22.19%, respectively.

Table VIII showed that the strength increased to different degrees with the increase of MA-PEG to AA ratio. When the MA-PEG : AA ratio  $< 1$ , it increased with increasing ratio of MA-PEG to AA. The optimum effect was obtained at a MA-PEG : AA ratio of 1 : 1, where the flexural strength increased by 12.5% at 3 d and 16.67% at 28 d, and the comprehensive strength increased by 42.06% at 3 d and 22.19% at 28 d, respectively. However, when the MA-PEG : AA ratio  $> 1$  : 1, it decreased with the further increase of the MA-PEG : AA ratio. Thus, the MA-PEG : AA ratio of 1 : 1 was most effective in increasing the strength of cement.

## CONCLUSIONS

The aim of this study is to synthesize polymer GAs and to investigate their effects on the grindability and strength enhancement of cement. The optimum process conditions were as follows: esterification was conducted at a MA : PEG ratio of 1.2 : 1 at 105°C for 3 h with 1.5% catalyst; and copolymerization was conducted at a MA-PEG : AA ratio of 1 : 1 at 85°C for 6 h. The polymer GA obtained under this condition had a number-average molecular weight of 12,964, weight-average molecular weight of 18,156, and polydispersity index of 1.40. The specific surface areas increased from 375.56  $\text{m}^2 \text{Kg}^{-1}$  for control sample to 500.34  $\text{m}^2 \text{Kg}^{-1}$ , with an increase of 32.87%. The specific surface area of samples obtained under the optimum condition increased by 32.87%, the flexural strength

**Table VIII.** Effect of Ratio of MA-PEG and AA on Strength Development of Cement Mortar

MA-PEG : AA	Flexural strength (MPa)		Compressive strength (MPa)	
	3 (d)	28 (d)	3 (d)	28 (d)
Blank	5.6	6.6	23.3	39.2
0.6	5.7	6.9	25.6	41.3
0.8	5.8	7.0	26.0	40.9
1	6.3	7.7	33.1	47.9
1.2	6.1	7.3	27.1	43.9
1.4	5.8	6.9	26.5	40.8

increased by 12.5% at 3 d and 16.67% at 28 d, and the comprehensive strength increased by 42.06% at 3 d and 22.19% at 28 d as compared with the control sample.

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