Asian Journal of Chemistry; Vol. 28, No. 10 (2016), 2217-2222

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19930

Synthesis of New Fly Ash Composite Materials and its Influence on Compressive and Flexural Strength of Concrete

WENPING WANG*, HUAIHUA ZHAO, XIAOHUA CAO and JIANWEI LI

School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, P.R. China

*Corresponding author: Tel./Fax: +98 551 62904027; E-mail: wap@hfut.edu.cn

Received: 26 February 2016; *Accepted*: 30 April 2016; *Published online*: 30 June 2016; AJC-17970

This article reports the fabrication of the new fly ash composite materials using surface-initiated atom transfer radical polymerization (ATRP) technique. The surface of fly ash were densely grafted with 2-(3,4-epoxycyclohexyl)ethyltrimthoxysilanol (KH566) and then opened ring reaction with poly(itaconic acid-co-acrylic acid) *via* two methods. Structural properties of the new fly ash composite materials are investigated by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. The new fly ash composite materials not only increase significantly the compressive strength of the fly ash concrete, but also increase the flexural strength of the fly ash concrete. New fly ash composite materials are integrated with cement-based building materials, the new fly ash composite materials possess some outstanding properties, which leads to vast potential applications in reinforcing the strength of concrete.

Keywords: Radical polymerization, Fly ash, Modified, Composite materials, Concrete, Compressive strength, Flexural strength.

INTRODUCTION

Fly ash, with a predominant composition of alumino-silicate, is a coal combustion byproduct due to the coal burning for power generation [1]. Recently more research has been conducted on the utilization of fly ash, with the purpose of preventing the threat to environment and making full use of it [2-4]. Fly ash is used widely in concrete, which is a most widely mineral admixture [5]. Nevertheless, due to developing the cracks, fly ash concrete has some shortcomings, for example, shrinkage and cracking, low early strength, poor toughness, high brittleness, low shock resistance and so on, that restrict its applications [6,7]. To improve the early strength of fly ash concrete, a fighting strategy has come into use in the recent years, included making the fly ash active by all kinds of methods [8-11]. However, activation of fly ash improving the early strength of fly ash concrete is unsatisfactory.

In this study, fly ash were modified with water-soluble polymers such as poly(itaconic acid-co-acrylic acid) using a three-step synthetic approach. To date, there is no published report on the preparation of new fly ash composite materials and the influence of fly ash on the compressive strength and flexural strength of the concrete. In this paper, the comparison and analysis of concrete added new fly ash composite particles and pristine fly ash particles on workability and the durability is performed through the experiments, included compressive strength, flexural strength of modified fly ash concrete, stability and fluidity of cement paste.

EXPERIMENTAL

Acrylic acid (AA), itaconic acid (IA), sodium hydroxide, sulfuric acid (> 98 %), 2,2-azobisisobutyronitrile (AIBN) and toluene were purchased from Sinopharm Chemical Regent Co. 2-(3,4-Epoxycyclohexyl)ethyltrimthoxysila (KH566, > 98 %), was purchased from Silicone Materials Co. (Wuhan University). Polycarboxylate superplasticizer (SPs) (646) was purchased from Changzhou Architectural Research Institute Co. Ltd. All the chemicals were used as received without further purification except the AIBN and fly ash. The ordinary Portland cement of 42.5 grades was purchased from Anhui Conch Cement Company Limited. Fourier transform infrared spectroscopy (FIIR) (Model Nicolet67, Thermo Nicolet, USA), X-ray photoelectron spectroscopy (XPS) (Model ESCALAB250Xi, Thermo, USA) and thermogravimetric analysis (TGA) (Model STA449F3, NETZSCH, Germany). Chemical compositions of cement and fly ash were given in Table-1.

Synthesis of new fly ash composite materials

Synthesis of FA-OH: To a 500 mL beaker, 100 g fly ash particles were dispersed in 150 mL sodium hydroxide solution (30 wt. %) and heated to 80 °C under reflux and rapid stirring for 8 h. Thereafter the slurry was neutralized to pH = 7 by

TABLE-1
CHEMICAL COMPOSITIONS OF CEMENT AND FLY ASH

Materials	Composition (wt. %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss
Cement	20.12	7.45	3.03	62.26	1.65	0.86	0.23	2.04	2.36
Fly ash	57.36	26.74	7.25	2.98	1.84	2.36	1.47	–	–

drop-wise adding sulfuric acid solution (20 wt. %). The activated fly ash-particles were obtained after being washed with water several times and dried in vacuum condition.

Synthesis of FA-KH566: 50 g fly ash particles, 100 mL toluene and 8 mL KH566 were placed in a 250 mL flask equipped with a magnetic stir bar. The mixture was stirred at 80 °C for 4 h. The resulting solution was washed with toluene and filtered. The product, denoted as FA-KH566, was dried in vacuum condition at 60 °C for 24 h.

Synthesis of IA-co-AA: Itaconic acid (IA, 10 mL) and distilled water (20 mL) were added into a three-necked round-bottom flask at room temperature, stirred with vigorous magnetic at 80 °C for 1 h. A mixture of acrylic acid (AA, 50 wt. % in water, 60 mL) and ammonium persulfate (APS, 1 wt. % in wate, 60 mL) was added into the flask at a rate of 2 mL/min. After being stirred for 2 h of the mixture at 80 °C, the solvent was removed using a rotary evaporator. Finally, the product, polymer were dried at 80 °C under vacuum for 24 h.

Synthesis of FA-KH566-IA-AA: In a 500 mL round-bottomed flask, 10 g poly(itaconicacid-co-acrylicacid) and 50 g FA-KH566 were dispersed in 100 mL distilled water and then the mixture was placed in a 60 °C oil bath under reflux and rapid stirring for 4 h. Washed with distilled water for several times and filtered, dried under vacuum at 60 °C for 24 h, finally FA-KH566-IA-AA was obtained.

Fluidity of fly ash/cement paste: 300 g cement, 87 g of water and 1.2 g polycarboxylate superplasticizers (646) were weighed and put into a bowl and mixed for 2 min at high speed. In this study, the cement paste were prepared at a water-to-binder ratio of 0.29, with 10, 20 and 30 % equivalent replacement of cement by fly ash, FA-OH and FH-KH566-IA-AA, respectively. The cement paste specimen was sealed in a container during the testing intervals of 0, 30, 60 and 90 min. The fluidity of the cement paste was measured with a mini-slump cone (a height of 60 mm, upper diameter 36 mm and bottom diameter 60 mm). The mixing and measurement processes were carried out according to the Chinese standard GB/T 8077-2000 test methods.

Concrete test: The concrete for the test specimens was mixed in an air-conditioned laboratory with an ambient temperature of approximately 25 °C and a relative humidity of 80 %. The mixing was carried out using a pan mixer. The fly ash concretes were designed with a water-binder ratio of 0.33 and a cement content of 440 kg/m^3. Polycarboxylate superplasticizers (646), an initial setting retarder, was added to both mixes in order to simulate the production and delivery of ready-mix concrete. The concretes are prepared with three different fly ash, FA-OH and FA-KH566-IA-AA and the equivalent replacement level is 10, 20 and 30 %. Compressive strength and flexural strength tests were performed in accordance with the appropriate standard specifications on the test specimens at different ages after casting. The mix details of the fly ash concrete are shown in Table-2.

RESULTS AND DISCUSSION

Formation mechanism of the new fly ash composite materials: Fly ash was organically modified by grafting with water-soluble polymers of acrylic acid and HPEG *via* a three-step synthetic approach as illustrated in Fig. 1. The first step involved the activation of silanol group (-OH) on the surface of fly ash. The second step consisted of conversions of –OH groups to epoxy groups using KH566 under a specified reaction condition. Finally, poly(itaconic acid-co-acrylic acid) were grafted *via* free radical polymerization.

FIIR analysis: Fig. 2 shows the FT-IR spectra of poly(itaconic acid-co-acrylic acid). A strong peak assigned to the O-H vibration can be seen at 3511 and 3123 cm^{-1}. The absorption bands of C=O stretching at 1725 cm^{-1} and C-O banding at 1401 cm^{-1} appears. However, the peaks at 1630 cm^{-1} assign to the C=C stretching disappears. The results confirm that poly(itaconic acid-co-acrylic acid) was successfully prepared.

TABLE-2
MIX COMPOSITIONS OF CONCRETE

Sample No.	Mix compositions (kg/m^3)							
	Cement	Fly ash	FA-OH	FA-IA-AA	SPs (646)	Sand	Stone	Water
1	440	0	0	0	4.9	688	1122	146
2	396	44	0	0	4.9	688	1122	146
3	352	88	0	0	4.9	688	1122	146
4	308	132	0	0	4.9	688	1122	146
5	441	0	44	0	4.9	688	1122	146
6	392	0	88	0	4.9	688	1122	146
7	343	0	132	0	4.9	688	1122	146
8	441	0	0	44	4.9	688	1122	146
9	392	0	0	88	4.9	688	1122	146
10	343	0	0	132	4.9	688	1122	146

SPs = Polycarboxylate superplasticizers

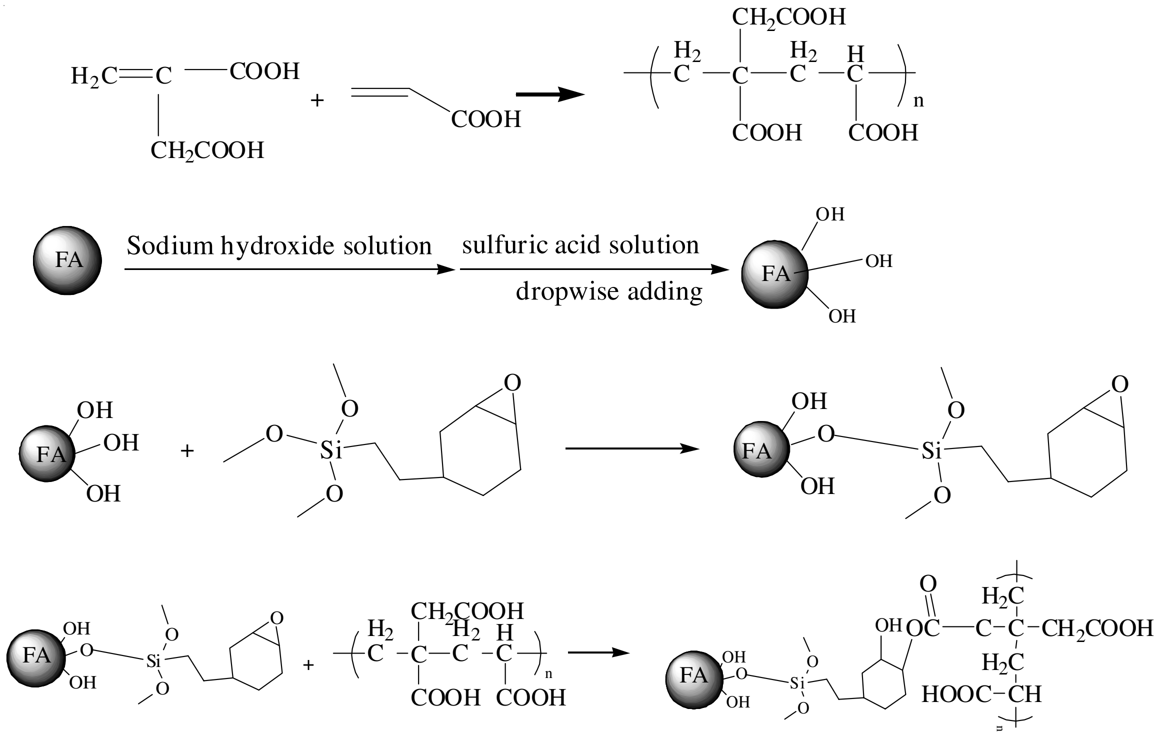

Fig. 1. Grafting polymerization from fly ash *via* free radical polymerization

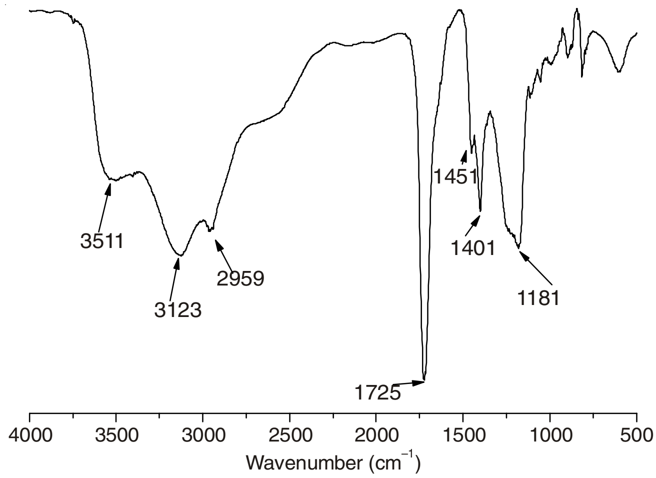

Fig. 2. FT-IR spectra of poly(itaconic acid-co-acrylic acid)

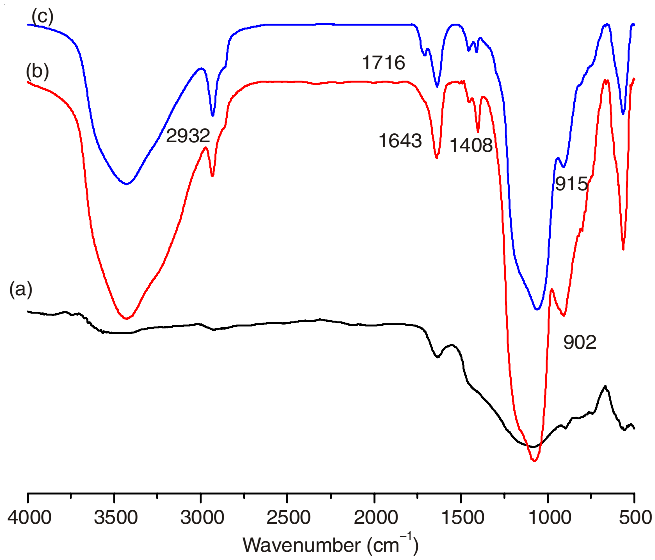

Fig. 3. FT-IR spectra of (a) FA-OH, (b) FA-KH566 and (c) FA-KH566-IA-AA

Fig. 3 shows the FT-IR spectra of (a) FA-OH, (b) FA-KH566 and (c) FA-KH566-IA-AA. A strong peak assigned to the Si-O-Si vibration can be seen at 1020 cm^{-1} for all the samples. Upon the activation of particles to produce FA-OH, the absorption bands of –OH stretching at 3442 cm^{-1} and H-O-H banding at 1640 cm^{-1} appears. The new peaks at 2932 cm^{-1} and 1408 cm^{-1} assign to the C-H stretching and C-O, respectively of (b) FA-KH566. The new peaks at 1716 cm^{-1} assign to the C=O stretching of (c) FA-KH566-IA-AA. Based on the above date, it confirmed that fly ash modified with organic compounds on the surface was successfully prepared.

XPS study: The C1s spectrum of the FA-KH566-IA-AA shown in Fig. 4(a) can be fitted into three peak components with band energies at about 284.4, 284.9 and 286.4 eV, attributable to the C-Si, C-H/C-C and C-O species, respectively. The appearance of C-Si, C-H/C-C and C-O components confirmed that KH566 had been successfully grafted on the surface of fly ash. Compared with Fig. 3(a), the new peak components with band energies at 288.9 eV (attributable to O-C=O species) appears, which confirm that poly(itaconic acid-co-acrylic acid) had been successfully grafted on the surface of fly ash.

TGA study: Thermal properties of (a) FA-OH (b) FA-KH566 and(C) FA-KH566-IA-AA were investigated using TGA, as presented in Fig. 5(a) does not present any remarkable weight loss up to 800 °C, except for small loss of 1 % due to the loss of the hydroxyl on the surface of fly ash. For the Fig. 5(b), a weight loss of approximate 10 % is associated with the decomposition of most of KH566 domains. In comparison with the Fig. 5(b), the grafted content of polymer

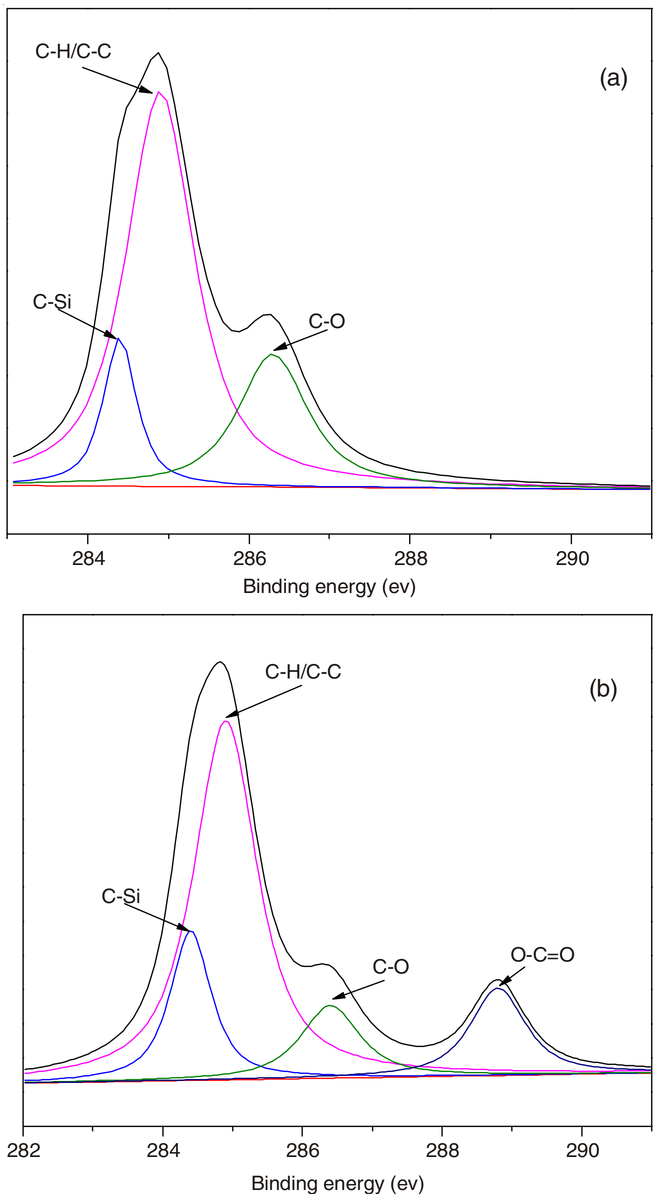

Fig. 4. XPS survey spectra of C 1s spectrum (a) of the FA-KH566 and C 1s spectrum (b) of the FA-KH566-IA-AA.

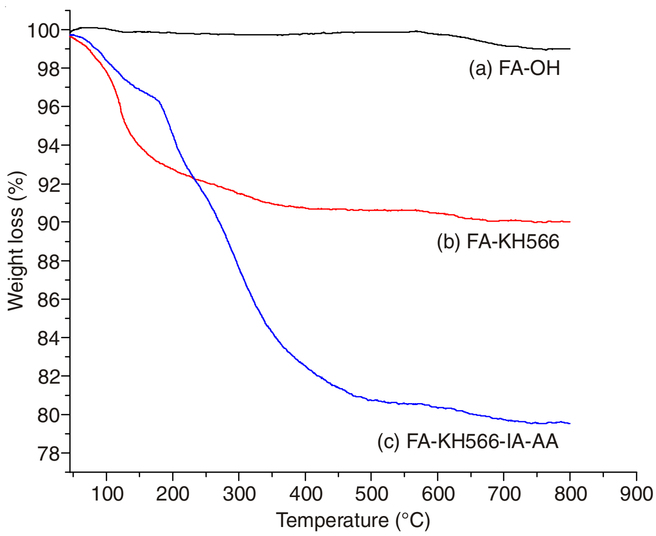

Fig. 5. TGA data of (a) FA-OH (b)FA-KH566 and(C) FA-KH566-IA-AA

on the fly ash surface estimated by the weight loss is nearly 20.5 % of the total amount of composite, indicating that the amount of the grafted polymer is fairly high. In addition, the temperature at which the weight drastically decreases shifted to a high temperature by grafting polymer chains, suggesting that the thermal stability of polymer was enhanced by the formation of covalent bonds to the reactive fly ash.

Fluidity of fly ash/cement paste: The minislump spread retention of a, b, c, d, e, f and g is up to 256, 253, 270, 278, 282, 287 and 294 mm, respectively after 0 min, and decrease to 225, 234, 238, 243, 252, 258 and 265 mm at 90 min, respectively. As can be seen from Fig. 6(a), (b), (d) and (f), the fluidity of cement paste with the percentage of blended fly ash increasing. The fly ash actually function as a kind of mineral water reducers. Compared with (b), (d) and (f), the fluidity of cement paste of (c), (e) and (g) increase, respectively. In addition, the more FA-KH566-IA-AA particles the content have, the higher stability paste is. It can be concluded that the hydrophilic polymeric chains grafted on the surface of fly ash have a greater effect on the dispersion retention ability.

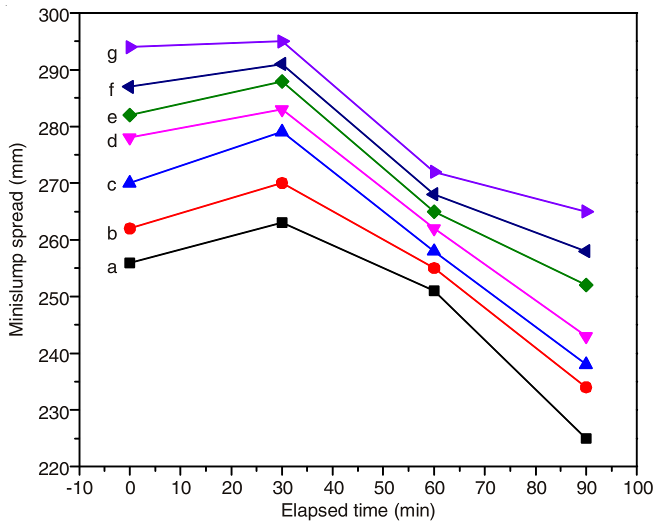

Fig. 6. Fluidity of cement paste of (a) 0 % FA, (b) 10 % FA, (c) 10 % FA-KH566-IA-AA, (d) 20 % FA, (e) 20 % FA-KH566-IA-AA, (f) 30 % FA, (g) 30 % FA-KH566-IA-AA

Strength test: Compressive strength of fly ash (FA, FA-OH, FA-KH566-IA-AA) concrete at 7 days and 28 days are given in Figs. 7 and 8, respectively. It was observed that on addition of fly ash, 7 days strength was decreased at all replacement level. However, at 7 days curing, the compressive strength of FA-KH566-IA-AA concrete was more than that of fly ash and FA-OH concrete at the same replacement level, which was slightly equal to that of ordinary Portland cement concrete. Increase in compressive strength at 7 days curing was 5.2, 10.5 and 15.7 % at replacement level of 10, 20 and 30 % fly ash, respectively. It is also evident that beyond 28 days, the compressive strength increased with the addition of fly ash. Compared with fly ash and FA-OH concrete, 28 days compressive strength of FA-IA-AA concrete is higher. Increase in compressive strength at 28 days curing was 6.6, 9.5 and 8.7 % at replacement level of 10, 20 and 30 % fly ash, respectively.

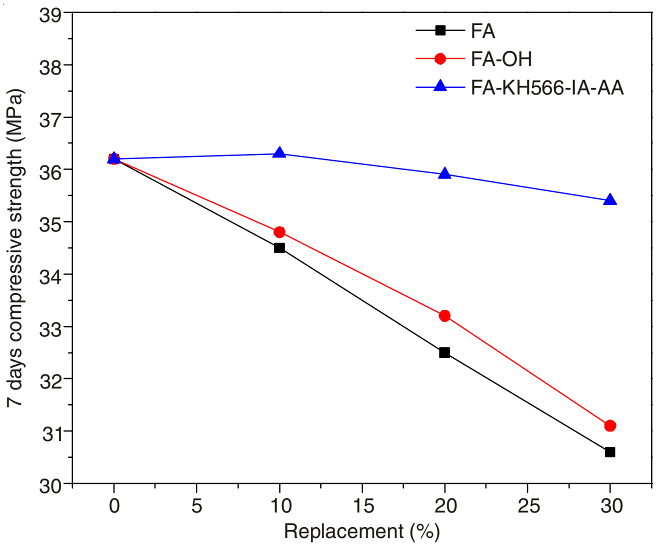

Fig. 7. 7 days Compressive strength of fly ash concrete

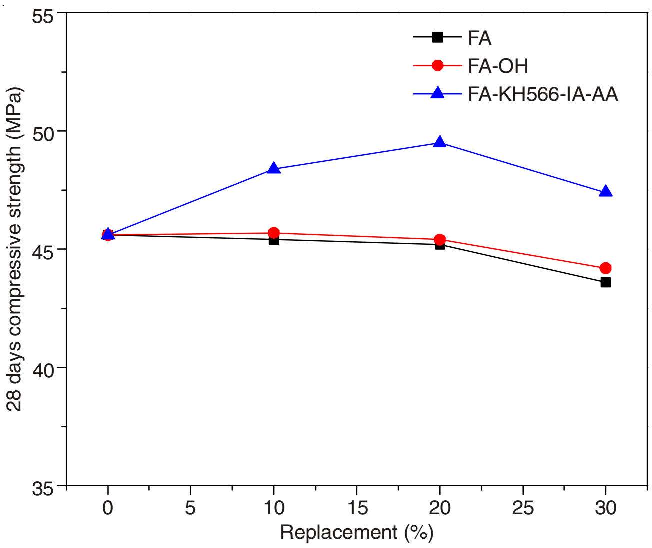

Fig. 8. 28 days Compressive strength of fly ash concrete

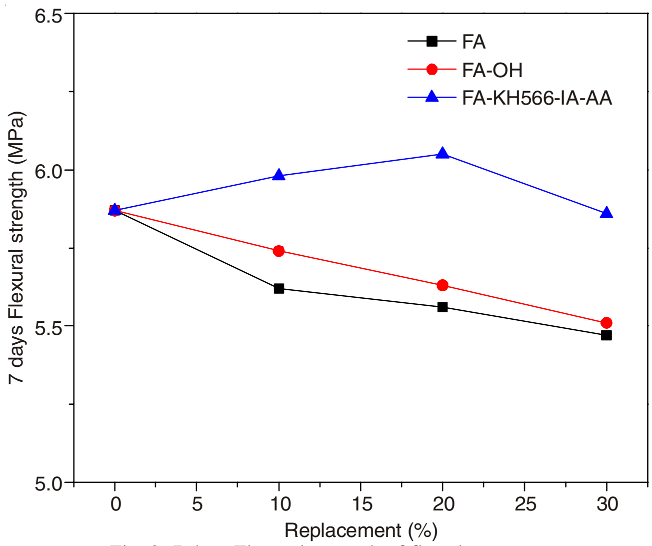

Fig. 9. 7 days Flexural strength of fly ash concrete

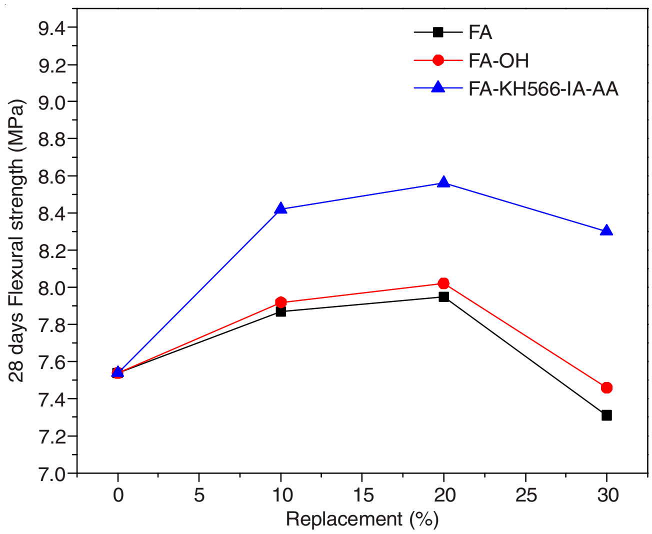

Fig. 10. 28 days Flexural strength of fly ash concrete

Flexural strength of fly ash (FA, FA-OH, FA-KH566-IA-AA) concrete at 7 days and 28 days are given in Figs. 9 and 10, respectively. It was observed that on addition of fly ash, 7 days flexural strength was decreased at all replacement level. At 7 days curing, the flexural strength of FA-KH566-IA-AA concrete was more than that of fly ash and FA-OH concrete at the same replacement level, which was higher than that of ordinary Portland cement concrete. Increase in strength at 7 days curing was 6.4, 8.8 and 7.1 % at replacement level of 10, 20 and 30 % fly ash, respectively. It is also evident that beyond 28 days, the flexural strength increased with the addition of fly ash. Compared with fly ash and FA-OH concrete, 28 days flexural strength of FA-KH566-IA-AA concrete is higher. Increase in strength at 28 days curing was 7.0, 7.7 and 13.5 % at replacement level of 10, 20 and 30 % fly ash, respectively.

Conclusion

Hydrophilic water-soluble polymers were successfully grafted onto the surface of the fly ash *via* coupling reaction and the free radical polymerization, as confirmed by FTIR spectra, TGA and XPS analysis. Three different fly ash (FA, FA-OH and FA-KH566-IA-AA) were employed to investigate the influence on fly ash concrete, including compressive strength as well as flexural strength. It was clearly demonstrated that the new fly ash composite materials could remarkably improve compressive strength as well as flexural strength of concrete by polymer of the surface of new fly ash composite materials. One specific feature for new fly ash composite materials is that it has a mass of polymer, which spread around uniformly in concrete and fill the cracks of concrete to increase in effect the cracking resistance performance of concrete and accelerate the hydration of clinker mineral, especially C3S and carboaluminates are formed through reaction between limestone fines. The C3A, resulting in an improvement in early strength. On the other hand, the hydrophilic polymeric chains grafted on new fly ash particles as the polycarboxylate superplasticizers have a greater effect on the dispersion ability to the cement. Much more work should be done to demonstrate the enhancement mechanism of new fly ash composite materials on concrete.

ACKNOWLEDGEMENTS

The authors acknowledge to The National Science Foundation of China (Grant No. 51372059) for financial support.

REFERENCES

1. H.L. Chang and W.H. Shih, *Ind. Eng. Chem. Res.*, **37**, 71 (1998).
2. A. Rubel, R. Andrews, R. Gonzalez, J. Groppo and T. Robl, *Fuel*, **84**, 911 (2005).
3. M. Visa, L. Isac and A. Duta, *Appl. Surf. Sci.*, **258**, 6345 (2012).
4. M. Chareonpanich, T. Namto, P. Kongkachuichay and J. Limtrakul, *Fuel Process. Technol.*, **85**, 1623 (2004).
5. V. Aggarwal, S.M. Gupta and D.S.N. Sachde, *Int. J. Eng. Sci.*, **2**, 4473 (2010).
6. P. Nath and P.K. Sarker, *Cement Concr. Compos.*, **55**, 205 (2015).
7. Y.H. Fang, R. Wang, E.R. Pang and Y. Zhou, *J. Chin. Ceram. Soc.*, **37**, 621 (2010).
8. A.Q. Wang, C.Z. Zhang and W. Sun, *Cement Concr. Res.*, **34**, 2057 (2004).
9. Y.C. Choi, J.H. Kim and S. Choi, *Asian J. Chem.*, **26**, 5514 (2014).
10. S. Kumar and R. Kumar, *Ceram. Int.*, **37**, 533 (2011).
11. N.K. Lee, J.G. Jang and H.K. Lee, *Cement Concr. Compos.*, **53**, 239 (2014).