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Preparation and Fire-Resistant Properties of Fly Ash Floating Beads/Epoxy Resin Coatings†

QINGPING WANG*, HUI WANG, FANFEI MIN and JINBO ZHU

School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, P.R. China

*Corresponding author: E-mail: wqp.507@163.com

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The surface of fly ash floating beads were modified by using silane coupling agent and the fly ash floating beads/epoxy resin fire-resistant coatings were prepared through mixing method. The surface composition and micro-morphology of modified fly ash floating beads were studied by FT-IR and SEM. The fire-resistant properties of fire-resistant coatings modified by fly ash floating beads were tested through combustion method. The influence of the content of fly ash floating beads was discussed and combining with changes of the opposite surface temperature. The fire-resistant mechanism of fly ash floating beads was also proposed. The results showed that the characteristic functional groups of silane coupling agent appeared on the surface of modified fly ash floating beads, the surface grafting phenomenon was obvious. With the increase of the content of fly ash floating beads, the fire-resistant properties increased firstly and then decreased. When the content of fly ash floating beads was 5 %, it could make the fire-resistant properties of fire-resistant coatings to achieve the best.

Keywords: Fly ash floating beads, Surface modification, Fire-resistant properties.

INTRODUCTION

Fly ash floating beads were aluminosilicate inorganic powder materials, extracted from fly ash, mainly composed of SiO_2 and Al_2O_3, generally grey in colour, transparent hollow glass spheres under the microscope. Fly ash floating beads had a variety of features, such as light mass, wear resistance, reflective, radiation resistance, high temperature resistance, acid and alkali resistance, self-lubricating, *etc*[1-7]. Fly ash floating beads were widely used in rubber, plastics, adhesives, coatings and functional materials and other fields. Due to the physical and chemical characteristics of fly ash floating beads, the dispersion of fly ash floating beads in polymer and the interfacial adhesion between fly ash floating beads and polymer were poor, which might result in two-phase separation[8,9]. Therefore, fly ash floating beads needed to be modified to improve the compatibility with polymer. Because of the broad applicability and the better modified effect, silane coupling agent was widely used in the field of polymer. General principles of selecting silane coupling agent were as follows: vinyl silane for polyolefin, sulfur silane coupling agent for sulfur vulcanized rubber, epoxy or ammonia silane for epoxy resin. This paper studied the fire-resistant properties of ultra-thin fire retardant coatings for steel structure prepared by modified fly ash floating beads as fillers. Based on the research, fly ash floating beads were modified by silane coupling agents KH-550 and KH-570, the surface composition, micro-morphology of modified fly ash floating beads and the compatibility with polymer were also studied. The fire-resistant properties of the coatings were tested and its fire-resistant mechanism was also explored.

EXPERIMENTAL

After removing impurities by using diluted hydrochloric acid, fly ash floating beads were washed by deionized water until the pH value was 7 and then dried. Some solution was prepared, the mass ratio of ethanol and water was 2:1. Silane coupling agent was added with 12 % of fly ash floating beads, then moved into a magnetic stirrer with the time of 0.5 h, the temperature of 80 ºC, the speed of 1500 rpm. After this, fly ash floating beads were added into the prepared solution, stirred for 3 h, then removed into the drying oven for 24 h. At last, modified fly ash floating beads were obtained. The surface composition and micro-morphology of modified fly ash floating beads were studied by NICOLET-380 Fourier transform infrared spectroscopy (FT-IR) and S-3000N scanning electron microscopy (SEM). With stirring, modified fly ash floating beads were added into epoxy matrix coatings, after

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curing, their interface bonding state was observed by SEM. The unmodified and modified fly ash floating beads were coated on the steel surface by different mass percentages after mixing with paint, then the expansion ratio and unexposed surface temperature were measured according with the relevant provisions of GB12441-2005.

RESULTS AND DISCUSSION

Surface modification analysis of fly ash floating beads: Silane coupling agent was a kind of low-molecular organic silicon compound having a special structure. Its chemical formula was $RSiX_3$, where R represented amino group, mercapto group, vinyl group, epoxy group, cyano group and methacryloxy group, *etc*. These groups had a strong ability to respond with the different types of the base resin, where X represented a hydrolyzable group such as halogen, alkoxy, acyloxy, *etc*., these groups produced silanol after hydrolysis. The silanol reacted with the hydroxy group on mineral surface to produce silicon-oxygen bond. Therefore, silane coupling agent could not only react with the hydroxy group of inorganic substance but also the long polymer chain molecular, which could connect two materials with different properties to improve various properties. It was inevitable to be worn and extruded in the production process of fly ash floating beads, the -Si-O-Si- broken bonds were abundant on the surface, which could combine with H_2O from air to form vast -Si-OH or -Si-O-Si-. Owing to the silanol group had the common gender of alcohols, because of its strong reactivity, it was easy to react with external functional groups. Then these surface groups reacted with the coupling agent or absorbed the coupling agent to change the surface properties finally.

Fig. 1a and b were FT-IR spectra of fly ash floating beads modified by silane coupling agent KH-550 and KH-570. Fig. 1a showed that the hydroxy absorption peak of fly ash floating beads at 3550 cm^{-1} decreased after modification, which indicated that the surface hydroxyl groups of fly ash floating beads underwent a chemical reaction. The absorption peak of the characteristic functional group^2 -NH of KH-550 appeared at 1750 cm^{-1}. The shape of -Si-O-Si- absorption peak of modified fly ash floating beads changed at 800 cm^{-1}, which indicated -Si-O-Si- formation. Fig. 1b showed that the absorption peak of fly ash floating beads at 1652 cm^{-1} was vibrational absorption peak of C=O in Si-(C=O)-R (R represented H or hydrocarbyl), this was because that there was a reaction between C=O in KH-570 and the hydroxy group on the surface of fly ash floating beads, which caused that the peak position shifted to 1652 cm^{-1}. The hydroxy absorption peak of fly ash floating beads at 3550 cm^{-1} decreased and the shape of -Si-O-Si- absorption peak of modified fly ash floating beads shifted at 800 cm^{-1}. These suggested silane coupling agent reacted with the surface functional groups of fly ash floating beads to produce -Si-O-Si-. From above analysis, it could be inferred that silane coupling agent and fly ash floating beads had gone through a chemical reaction and had produced new chemical bond.

Surface SEM analysis of modified fly ash floating beads: Fig. 2 showed SEM pictures of original fly ash floating beads, fly ash floating beads modified by KH-550 and KH-570. From Fig. 2a, the surface of fly ash floating beads was smooth, like convex spherical balls. From Fig. 2b and c, a layer of something attached to the surface of fly ash floating beads modified by KH-550 and KH-570. Compared SEM images of fly ash floating beads before and after modification, KH-550 and KH-570 both had a bonding action with fly ash floating beads and under the same conditions, the modification effect of KH-570 was better than that of KH-550.

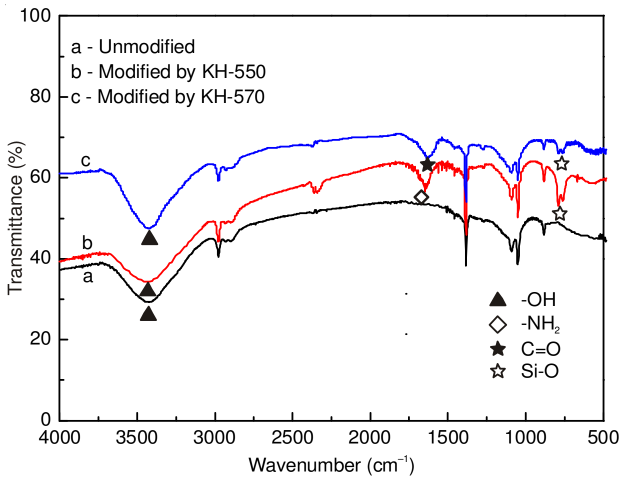


Fig. 1. FT-IR spectrum of fly ash floating beads

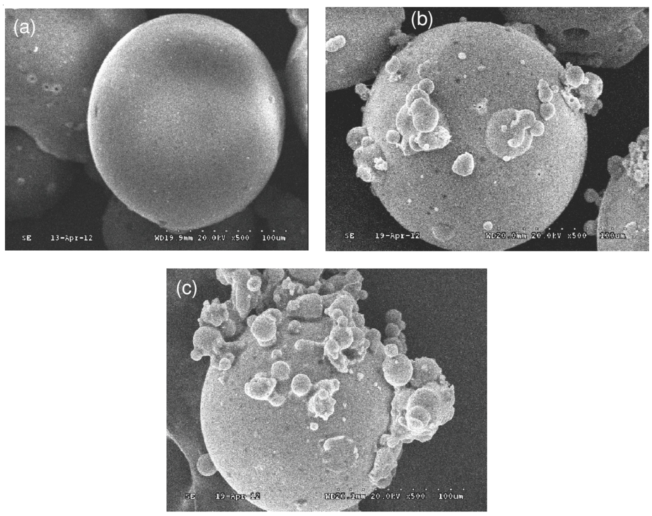
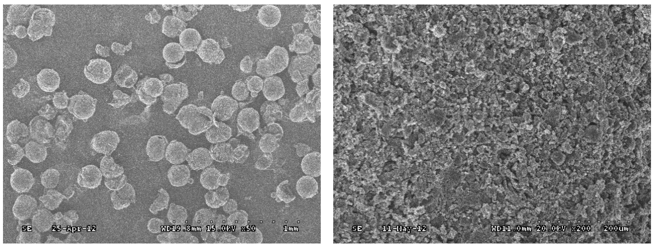


Fig. 2. SEM images of fly ash floating beads (a) unmodified (b) modified by KH-550 (c) modified KH-570

Compatibility analysis: With stirring, unmodified and modified fly ash floating beads were added into epoxy matrix coatings, after curing, their interface bonding state was observed by SEM. From Fig. 3, when unmodified fly ash floating beads were added into the epoxy matrix, there were some fly ash floating beads floating on the surface of the substrate, the compatibility between fly ash floating beads and matrix was poor. But contrary to the above phenomenon, the compatibility between modified fly ash floating beads and matrix was good. Hydrolysable groups of silane coupling agent could react with H_2O in matrix to produce silanol after hydrolysis, then the silanol reacted with the hydroxy group of fly ash floating beads to produce silicon-oxygen bond. The other characteristic functional groups could react with some groups of epoxy, so that it



(a) (b)

Fig. 3. SEM images of fly ash in epoxy resin composite (a) unmodified (b) modified

could form stable chemical bonds between fly ash floating beads with epoxy resin matrix.

Fire-resistant properties test: Fig. 4 showed the relationship between test time and temperature. The opposite surface temperature of blank sample without fly ash floating beads continued to rise in 300 s, the opposite surface temperature reached 400 ºC at 1800 s. The fire-resistant properties of sample with unmodified fly ash floating beads had been improved, the opposite surface temperature only reached 325 ºC at 1800 s. With the additional content of modified fly ash floating beads arranging from 1-5 %, the opposite surface temperature declined gradually at 1800 s and the fire-resistant properties had also improved with the increase of fly ash floating beads. With the additional content of modified fly ash floating beads arranging from 5-9 %, the opposite surface temperature increased gradually at 1800 s and the fire-resistant properties had also dropped with the increase of fly ash floating beads. The fire-resistant properties of coatings had been greatly improved with the addition of modified fly ash floating beads, but the addition of fly ash floating beads had a suitable range. When the additional content of fly ash fly ash floating beads was 5 %, the opposite surface temperature reached minimum 280 ºC, so the optimum addition content of modified fly ash floating beads was 5 %.

Conclusion

Silane coupling agent KH-550 and KH-570 could modify fly ash floating beads. The surface modification effect of silane coupling agent KH-570 was better than that of KH-550. The fire-resistant properties of coatings with modified fly ash floating beads had been improved markedly. When the adding content was 5 %, the test result was the best.

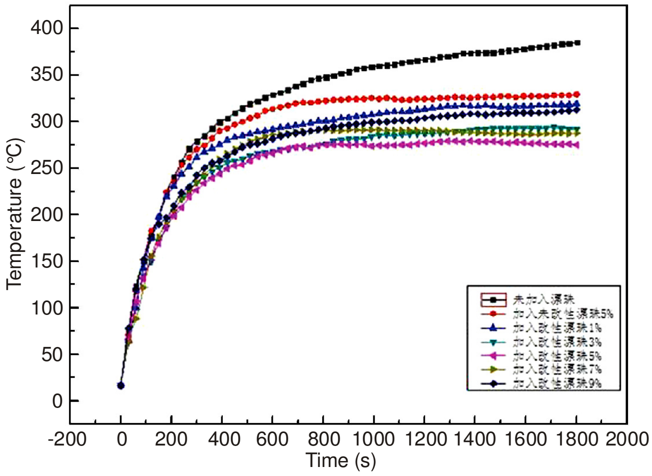


Fig. 4. Effect of fly ash amount added on fire-resistant property

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