



# Novel magnetic crosslinked composites with fly ash as filler via facile “one-pot” in-situ radical bulk polymerization



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## ARTICLE INFO

### Article history:

Received 4 August 2013

Received in revised form 24 September 2013

Accepted 29 September 2013

Available online 31 October 2013

### Keywords:

Fly ash

Magnetic composite

In-situ polymerization

Crosslinking reaction

Mechanism

## ABSTRACT

Fly ash (FA), generated during the combustion of coal for energy production, is an industrial by-product which results in environmental risk. To make the waste profitable, novel crosslinked fly ash/polystyrene (FA/PS) composites were prepared via the facile in-situ “one-pot” radical bulk polymerization of styrene in the presence of the FA particles with  $\gamma$ -methacryloxypropyl trimethoxy-silane (KH-570) as the coupling agent in the present work. It makes FA profitable by using the waste as the filler for composites. The effect of the amount of FA and coupling agent on the properties of the FA/PS composites were investigated by thermal analysis, scanning electron microscopy (SEM) and swelling technique. Their structural model was proposed on the basis of the thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and swelling analysis. The magnetic properties of the FA/PS composites were also investigated.

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## 1. Introduction

Fly ash (FA), generated during the combustion of coal for energy production, is an industrial by-product. Since large-scale coal firing for power generation began in the 1920s, many millions of tons of ash and related by-products have been generated. The current annual world production of coal ash is estimated around 600 million tones, with FA constituting about 500 million tones at 75–80% of the total coal ash produced [1]. Thus, the amount of coal waste, released by factories and thermal power plants, has increased throughout the world, and the disposal of the large amount of FA has become a serious environmental problem and so considerable research for its utilizations has been undertaken [2] such as building materials [3], adsorbents [4] and fertilizers [5].

Fillers have been usually used as addition to various polymeric matrices in order to reduce the production cost and/or to improve certain characteristics. FA containing 90% globular particles with a reasonable size distribution, low density, good shape with good dispersibility and fluidity, is suitable as low-cost filler for polymer-based composites. However, the use of FA as a filler is still not widespread due to the weak interfacial interaction between the untreated FA particles and the polymeric matrices, due to the low friction of the FA surface, and the low whiteness value resulting in

an undesirable appearance to the final product [6], although FA could provide composites with magnetic properties [7].

FA had been investigated as the filler for epoxy resin [8], polyethylene (PE) [9], polypropylene (PP) [10], poly(vinyl chloride) (PVC) [11], poly(vinyl alcohol) (PVA) [12] and polystyrene (PS) [13], polyester resin [14], natural rubber [15], polyurea [16], poly(ether-ether-ketone) (PEEK) [17], via the physical blending technique. The in-situ polymerization technique was only reported for the FA-based composites with the conductive polymer [7] and MC Nylon-6 [18] as matrices. By now, there is no work on the FA/vinyl-based polymer composite prepared via the in-situ polymerization technique due to the poor dispersibility of FA in the organic systems, although the functional silane had been revealed to improve the interfacial properties of FA and polymeric matrices.

The in-situ radical bulk polymerization is known as the promising mass production technique for polymer-based composites due to the facile procedure and the excellent dispersibility of fillers in polymer matrices, after the fillers had been surface-modified to improve their dispersibility in organic monomers. In our previous work, we developed the in-situ “one-pot” radical solution polymerization to graft polystyrene from the surfaces of the  $\text{SiO}_x$  nanoparticles by facile heating the toluene dispersion containing styrene,  $\text{SiO}_x$  nanoparticles, functional silane and initiator [19]. In the approach, the two reactions, the surface-modification of the  $\text{SiO}_x$  nanoparticles and the copolymerization of the functional silane and styrene, occurred simultaneously. So the polystyrene grafted  $\text{SiO}_x$  nanoparticles were produced. Most

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recently, the similar approach had been reported to prepare the polyacrylic/titania nanoparticle (NP) hybrid thin films through the microwave-assisted polymerization [20].

By now, there are only little work reporting the crosslinking inorganic/polymer composites with the inorganic nanomaterials such as functionalized multiwalled carbon nanotubes (MWCNT) [21] or silica quantum dots [22] as the crosslinkers, in which there were two steps in the preparation procedures. In the present work, the novel crosslinked fly ash/polystyrene (FA/PS) composites were synthesized via the facile in-situ “one-pot” radical bulk polymerization in the presence of FA particles with  $\gamma$ -methacryloxypropyl trimethoxy-silane (KH-570) as the coupling agent. Their crosslinking mechanism was proposed and the effect of the amount of FA and coupling agent on the properties of the FA/PS composites were investigated via the thermal analysis and swelling technique.

## 2. Experimental

### 2.1. Materials and reagents

Fresh fly ash (FA) with diameter of 0.5–10  $\mu\text{m}$  was obtained from Datang Gansu Power Generation Co., Ltd. in China (main constituents: silica ( $\text{SiO}_2$  58.64%), alumina ( $\text{Al}_2\text{O}_3$  21.32%), calcium oxide ( $\text{CaO}$  5.02%), iron oxide ( $\text{Fe}_2\text{O}_3$  7.20%), magnesium oxide ( $\text{MgO}$  1.58%) and manganous oxide ( $\text{MnO}$  2.23%)). Polystyrene with a number, average relative molecular weight of  $1.58 \times 10^4$  was purchased from Lanzhou Petrochemical Company.

The monomer, styrene (St, analytical reagent, Tianjin, Chemical Co. Ltd., China), was dried over  $\text{CaH}_2$  and distilled under reduced pressure. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN) (Tianjin Chemicals Co. Ltd., Tianjin, China), was re-crystallized from methanol before use.  $\gamma$ -Methacryloxypropyl trimethoxy-silane (KH-570, Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was chemical pure grade and used as received. Tetrahydrofuran (THF), hydrofluoric acid (HF) and other reagents were all of analytical grade reagents and used as received.

### 2.2. Pretreatment of FA

Typically, FA powder (30.0 g) was added onto 60 mL pH 3.0 aqueous HCl solution and stirred for 5 h. After the activated FA particles were filtered and washed thoroughly with water to neutral, the product was dried at 110  $^\circ\text{C}$  for 72 h.

### 2.3. Preparation of fly ash/polystyrene (FA/PS) composites

The FA/PS composites were prepared by the “one-pot” in-situ radical bulk polymerization method. Some polystyrene was added to increase the viscosity of the reacting mixture, so that the deposition rate of the FA particles was slowed down in order to maintain their dispersibility. In a typical procedure, certain amount of the activated FA particles and KH-570 (1.0 mL) were added into a glass polymerizing pipe, and then 17.0 g styrene, 3.0 g polystyrene and 0.085 g AIBN were added into the mixture. Afterwards, the mixture in the sealed polymerizing pipe was treated ultrasonically for 30 min, subsequently heated at 80  $^\circ\text{C}$  for 8 h and rocked wildly after each 30 min. Finally it was heated at 90  $^\circ\text{C}$  for 5 days to make the monomer polymerize completely. After cooling to room temperature, the FA/PS composites were obtained. To investigate the effect of the coupling reagent (KH-570), a composite FA/PS S-4 and a copolymer of styrene and KH-570 (PS-Si) were also prepared without KH-570 or FA, respectively. The polymerizing conditions are summarized in Table 1.

**Table 1**

Composition of the FA/PS composites investigated.

Samples	Styrene (g)	Polystyrene (g)	AIBN (g)	FA (g)	KH-570 (mL)
FA/PS S-1	17.0	3.0	0.085	1.0	1.0
FA/PS S-2	17.0	3.0	0.085	2.0	1.0
FA/PS S-3	17.0	3.0	0.085	3.0	1.0
FA/PS S-4	17.0	3.0	0.085	2.0	0
PS-Si	17.0	3.0	0.085	0	1.0

### 2.4. Analysis and measurements

Bruker IFS 66 v/s infrared spectrometer (Bruker, Karlsruhe, Germany) was used for the Fourier transform infrared (FT-IR) spectroscopy analysis in the range of 400–4000  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ . The KBr pellet technique was adopted to prepare the sample for recording the IR spectra.

The average relative molecular weights of polystyrene in the composites were determined by Gel Permeation Chromatography (GPC) with a HP1100 instrument using binary liquid chromatography pump and ultra-violet detector. THF was used as the eluent at a flow rate of 1 mL/min. The polymers were separated from the FA particles by being treated with mixing solvent of THF and HF with the volume ratio of 9:1.

Thermogravimetric analysis results were obtained with a TA Instrument 2050 thermogravimetric analyzer at a heating rate of 10  $^\circ\text{C}/\text{min}$  from 20 to 800  $^\circ\text{C}$  under nitrogen atmosphere.

Differential scanning calorimetry (DSC, Mettler Toledo DSC) was used to determine the glass transition temperature ( $T_g$ ) of the samples with heating rate of 10  $^\circ\text{C}/\text{min}$ .

The magnetic measurements were performed using a Lake-shore 7400 Series vibrating sample magnetometer (VSM) system at room temperature.

The fractured surfaces of the FA/PS composites were observed with a scanning electron microscopy (SEM) instrument (Hitachi TM-1000, Tokyo, Japan) after being sputter coated with gold.

## 3. Results and discussion

The FA particles were activated by being treated with hydrochloric acid to release its surface hydroxyl groups [7]. The activated FA particles could not be dispersed in styrene due to its hydrophilic surface and big particle size (0.5–10  $\mu\text{m}$ ). After the polymerizing mixture of FA, KH-570 and monomer were treated ultrasonically for 30 min, KH-570 would be assembled onto the surface of the FA particles to decrease their surface polarity. Furthermore, some polystyrene was added to increase the viscosity of the reacting mixture, so that the deposition rate of the FA particles was slowed down in order to maintain their dispersibility. After the in-situ radical bulk polymerization, the apparently homogeneous gray composites were obtained.

The three FA/PS composites (FA/PS S-1, FA/PS S-2, and FA/PS S-3) could not be dissolved in toluene although they were prepared with different amount of FA added. They swelled obviously after being immersed in toluene for 24 h, in which, the un-grafted polystyrene molecules might be washed off (Fig. 1). It indicated that all the three FA/PS composites synthesized with different amount of FA were crosslinked. It was resulted from the crosslinking function of the multi-functional fillers containing more than one polymerizable group [23,24]. The swollen FA/PS composites also seemed homogeneous except for some aggregates of the FA particles visible to the naked eye (Fig. 1). Furthermore, their swelling ratios (weight ratio of toluene adsorbed and composite) were found to be 391%, 574% and 885%, respectively. The swelling ratios increased with increasing the feeding amount of FA in the bulk polymerization. It indicated that the crosslinking

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