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Stearic acid coating on circulating fluidized bed combustion fly ashes and its effect on the mechanical performance of polymer composites

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ABSTRACT

The aim of this work was to test circulating fluidized bed combustion fly ashes (CFAs) for its potential to be utilized in polymer composites manufacturing to improve its toughness. CFAs was coated by stearic acid and used in the composite of polypropylene/ethylene vinyl acetate/high density polyethylene (PP/EVA/HDPE) by molding process method. The resulting coated and uncoated CFAs were fully characterized by particle size analyzer, contact angles, powder X-ray diffraction (XRD), thermogravimetric analysis/differential thermal analysis (TGA/DTA), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The stearic acid coated onto the surface of CFAs particles in the physical and chemical ways, and the total clad ratio reached 2.05% by measuring TGA/DTA curve. The percentage of CFAs particles focused to a narrow range 2–4 μm and the median mean size was 3.2 μm more than uncoated CFAs. The properties of hydrophobic and dispersive of CFAs particles improved and original activity was reserved after stearic acid coating. The stearic acid was verified as a coupling agent by how much effect it had on the mechanical properties. It showed the elongation at break of PP/EVA/HDPE reinforced with 15 wt% coated CFAs (c-CFAs) was 80.20% and higher than that of the uncoated. The stearic acid treatment of CFAs is a very promising approach to improve the mechanical strength due to the incorporation of stearic acid on the CFAs surface, and hence, further enhances the potential for recycling CFAs as a suitable filler material in polymer composites.

1. Introduction

Circulating fluidized bed combustion (CFBC) has exhibited quite a few advantages, such as high combustion efficiency, large reduction in SO_2 and NO_X emissions, wide fuel flexibility, low combustion temperature (850–900 °C), and significant desulfurization rate [1]. As one of the main promising solutions for a clean, reliable, and economic combustion technology, CFBC of solid fuels have been used broadly and the amounts of the globally produced CFBC fly ashes (CFAs) steadily increase [2,3].

CFAs generally contains a range of alkali and transition metal elements which are commonly represented as oxides of Si, Al, Fe, S, Ca, Mg, K and Na even though these occur as complex mineral and glassy phases. Several recent studies reported the most unburnt carbon [4], CaO [5] and sulphur compounds such as $CaSO_4$ and CaS [6] were found from the sulphation process in CFBC boilers. Now, the disposing of CFAs is thrown out in industrial premises, ponds or landfills, this method of disposing CFAs has several drawbacks due to high water requirements, generation of dust clouds and formation of high-pH leachate once the CFAs has been landfilled [7]. This type of disposal of the CFAs causes both resource dissipation and environmental pollution. In addition, CFAs could also affect human health through direct inhalation or ingestion of airborne or settled ash. The effect on the ecological equilibrium of these wastes increases and together with the other industrial wastes may reach the levels to the point of threatening natural lives. Therefore, the recycling of the CFAs is not only an attempt to decrease environmental pollution but also an effort to increase economical effectiveness [8]. Therefore, it is necessary to utilize this material for potential use in various systems. In recent majority studies, the CFAs was used to road way fill [9,10] and construction materials such as bricks [11,12], concrete [13] and asphalt [14]. However, there was little report about CFAs as filler in polymer.

Compounding CFAs with polymer offers an attractive alternative in developing new polymeric materials and introducing a desired property is a conventional practice. Based on similar approach noted utilization of mineral fillers such as $CaCO_3$, clays, mica [15], talc, aluminum, iron, and the conventional pulverized

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coal combustion fly ashes [16–20] to fill polymer, CFAs is utilized in the preparation of composites.

In general, polymeric composite materials filled with mineral fillers lead to a loss in the mechanical properties of the polymer due to the incompatibility between the fillers and polymer. Therefore, a variety of coupling agents could be used to bind the surface of the fillers to polymer [21]. There were many beneficial reports on chemically coating fillers that displayed a better adhesion with a polymer matrix than that of uncoated ones [22,23].

The stearic acid as a universal and inexpensive surfactant cannot form covalent bonds, which has been used as coupling agents in filled polymer systems [24,25]. The primary aim of this study is to report the effect of stearic acid on the interface properties of CFAs, and discuss the feasibility of coated CFAs (c-CFAs) by stearic acid as a filler to be used in polymer.

2. Materials and methods

2.1. Materials

The CFAs utilized in this work were derived from Sichuan power's circulating fluidized bed (CFB) boiler firing for sulphur capture. The oxide analysis revealed the following composition: 39.68% SiO_2, 15.19% Al_2O_3, 12.19% Fe_2O_3, 8.58% SO_3, 13.84% CaO, 0.23% Na_2O, 0.72% MgO, 1.16% K_2O, 1.74% TiO_2 and 0.08% P_2O_5. High density polyethylene (HDPE, 5502) was purchased from Sinopec, China. Polypropylene (PP, T300) was purchased from Sinopec Maoming Petrochemical, China. Ethylene vinyl alcohol (EVA, va28%) was purchased from Mitsui, Japan. Stearic acid was procured from Tianjing, and ethanol with the purity of 99% from Chengdu, China.

2.2. Preparation of c-CFAs

The as-received CFAs were subjected to surface treatment with stearic acid. 3 g stearic acid was dissolved in the 62 mL ethanol at 60 °C. The CFAs (100 g) were dispersed in distilled water (200 mL) with sonication for 20 min, and then the pH value was adjusted to around 8 with 1 M H_2SO_4 solution. The slurry of CFAs was added dropwise into the stearic acid solution under vigorous stirring at 30 °C for 30 min. The CFAs treated by stearic acid was washed repeatedly by hot ethanol (~60 °C) until no crystal precipitation came from the washing solution at room temperature. It was guaranteed that the stearic acid was successfully coated on the surface of CFAs. The treated CFAs were dried at 110 °C for 12 h, then ground to form powder.

2.3. Fabrication of composite

Prior to mixing with materials, the PP, EVA and HDPE were dried in an oven for 10 h at 50 °C (T_m of EVA is 60 °C) and the uncoated CFAs was dried in an oven for 4 h at 110 °C, respectively.

The composites were fabricated by molding method. The ratio of PP/EVA/HDPE by mass was 10/2/1, and the content of c-CFAs or CFAs was fixed to 15 wt%. PP and HDPE were fed into the double-roll open mill (KT-202-A, Shanghai Greate Instrument Co. Ltd., China) melt blending at 190 °C, then EVA and CFAs (or c-CFAs) were added to blend. The compounds molded were fed into plate vulcanization machine (BL-6170-B, Bolon precision testing machines Co. Ltd., China) at 180 °C and 10 MPa for 8 min.

2.4. Analytical instruments for characterization

In order to find the optimal experimental conditions, the zeta potential of CFAs was tested before the surface modification process by Zeta Pals (Brookhaven Instruments Corporation) and the pH value was changed from 1 to 12. Brookhaven Instruments Corporation 90 Plus Laser Particle Size Analyzer was used to determine the particle size distribution. The powders were suspended into the sample cell with absolute ethyl alcohol after agitating in an ultrasonic bath to obtain maximum dispersion of particles. The contact angles of the powders were measured by the sessile drop method (performed with a DSA30 surface tension measuring system of KRUSS) by deposing a small drop (five drops per sample) of 10 μL of pure water on tablets formed from powder. The tablets were made by a compression under a load of 7 MPa using an FW-4A power press, and the diameter was 12.65 mm and thickness ranged from 0.27 mm to 0.3 mm. The shape of the drops was observed and used to determine the contact angles. Wide angle X-ray diffraction (WAXRD) spectra of samples were obtained using X'Pert Powder (PANalytical). The spectra were collected ranging from 3° to 80° with a step size 0.02 and 0.5 s at each step by diffracted beam graphite monochromators with Ni filtered Cu Kα radiation source generated at 40 kV and 20 mA. Thermogravimetric analysis/differential thermal analysis (TGA/DTA) of the samples were undertaken using a simultaneous thermal analyzer (STA), Netzsch STA 449C, Germany. The measurements were carried out using approximately 10 mg samples in an oxygen atmosphere with a heating rate of 20 °C/min over the temperature range from room temperature (25 °C) up to 1000 °C. The thermal analysis data was recorded using alumina as an inert reference material. The specific surface area was calculated at 77 K via the Brunauer–Emmett–Teller (BET) method with a Quanta chrome Autosorb-1MP instrument using nitrogen gas. Transmission electron microscopy (TEM, JEOL JEM-100CX) was used with a field emission gun, which provided high resolution. The ash particles were dispersed in ethanol followed by sonication. A drop of diluted suspension was poured on copper grid, which was directly injected in the sample injection holder after air drying. Infrared spectra of the powders were obtained using a FT/IR-BM PerkinElmer FTIR spectrometer. The samples were prepared using KBr pellets containing powders of approximately 0.75 wt% (2 mg of CFAs in approximately 200 mg of KBr powder). X-ray photoelectron spectroscopy (XPS) was undertaken for determination of powders surfaces for providing the information of elemental composition as well as electronic states in the surface region of materials [26] by PHI5300 (PerkinElmer Physics Electronics, USA) with resolution of 0.1 eV at 250 W (Al Kα, 12.5 kV). The tensile properties of the composites were determined using an Instron 1185 with crosshead movement 50 mm/min. The tensile specimens (150 mm × 10 mm × 4 mm), which were prepared following ISO 527-1:1993 standard procedures. Five samples were tested in each category and the average value was reported in this article.

3. Results and discussion

3.1. Zeta potential of CFAs water-solutions with the different pH values

The most important parameter defining surface properties of electrostatically stabilized solids in aqueous solutions is the zeta potential value [27]. The relation between the zeta potential and pH for the CFAs are shown in Fig. 1. In this plot, it showed that the isoelectric point (IEP) of CFAs was around pH 2. The surface of CFAs was electronegative when the pH was above 2. Thus, the stearic acid was easily absorbed on the CFAs surface. The zeta potential value decreased with the increase of pH value till the pH value reached 7–9, and appeared the maximal absolute value at 20 mV. Therefore, it could be presumed that there were more hydroxyl groups on the surface of the CFAs when the absolute value of the zeta potential was high. In other words, the surface modification of CFAs should

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