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Improvement in mechanical properties of SBR/Fly ash composites by in-situ grafting-neutralization reaction

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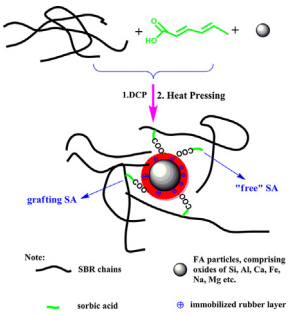
HIGHLIGHTS

- In-situ grafting-neutralization reaction is introduced into SBR/FA/SA composites.
- An immobilized rubber layer is formed on the surface of FA particles.
- Great enhancement is observed in mechanical properties of SBR/FA/SA composites.
- It is the first time to use of FA in rubber composites on a large scale.

GRAPHICAL ABSTRACT



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ABSTRACT

A growing increase in fly ash (FA) becomes a serious problem for environmental protection. In order to alleviate this problem, many people have tried to use FA to prepare polymer composites. However, due to the lack of hydroxyl groups on the surface of FA, the conventional surface treatment method for FA, such as silane or titanate coupling agent modification, is unacceptable and application of FA in the polymer industry is still a huge challenge. In this work, in-situ grafting-neutralization reaction takes place within styrene butadiene rubber/FA/sorbic acid (SBR/FA/SA) composites during the vulcanization process. Experimental data show an immobilized rubber layer is established on the surface of FA, which originates from strong interactions among SBR, FA and SA. As a consequence, the tensile strength of SBR/FA/15SA composite is about 215% higher than that of SBR/FA composite, along with larger elongation at break and modulus, which suggests stronger reinforcing effect of FA/SA for SBR composites and opens a new road to use FA in the polymer industry.

1. Introduction

Fly ash (FA) is the by-product of coal-fired thermal power stations, the number of which increases year by year because of the growing demand for coal-fired electric power. Chemical components of FA are comprised of oxides of Si, Al, Ca, Fe, Na, Mg etc. Due to benefits of low density, low cost, strong filling ability, smooth spherical surface and good processability [1], FA has been successfully utilized [2] in construction [3] industries by mixing FA with cement to achieve high compressive strength concrete [3,4]. However, the consumption rate of FA still cannot catch up with the growth. In some areas of the world, the treatment of FA is mainly the dumping approach, which causes serious environment problem by contaminating the surrounding atmosphere or water and also takes up space for landfill. Thereby, how to explore the field of FA in practical application has attracted people's tremendous attention over the decades [3,5–7].

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Polymer is a kind of organic material that is commonly used in the industry and daily life. The purpose of incorporating inorganic filler into the polymer matrix is not only to achieve special properties of polymer composites [3,6,8–15], but also to reduce the cost. For environmental protection and sustainable development, people have taken a great effort to prepare polymer/FA composites that meet the requirement of practical application [6,8–12]. By chemical and functional surface treatment of FA, Bora et al had successfully prepared polymer/functioned FA composites for microwave absorption [16] and electromagnetic interference shielding [17–19]. Verma [9] examined the mechanical properties of high-density polyethylene (HDPE)/untreated FA composites and found that tensile and flexural moduli were improved with the addition of FA up to 25%, except for the elongation at break, which may be ascribed to the size of FA particles [20] and good stress transformation between the polymer matrix and the FA particles [21]. In the rubber industry, Sombatsompop [22] investigated the properties of natural rubber (NR) or styrene butadiene rubber (SBR)/raw FA composites thoroughly and found that the comprehensive mechanical properties of composites had decreased monotonously by addition of FA, suggesting the non-reinforcing effect of FA for rubber composites without surface modification. To overcome this disadvantage, silane coupling agents were adopted to modify rubber/FA composites [23–26]. Surprisingly, properties of these rubber composites were similar to the unmodified ones, indicating silane coupling agent modification method was unacceptable for rubber/FA composites. It is widely acknowledged that properties of rubber composites are closely associated with bound rubber. In order to uncover the reason of non-reinforcing effect of FA for rubber composites and to change the specific area of raw FA ($< 1 m^2/g$), Garde treated FA with acid-base to get a much larger specific area ($146 m^2/g$), which was comparable to that of precipitated silica [27]. However, by modifying with bis(triethoxysilylpropyl)tetra-sulphane (TESPT, silane coupling agent), little bound rubber formation was found in rubber/FA composites and the tensile strength of vulcanizate with 30phr treated FA was very poor, suggesting limited reinforcement was obtained for the acid-base modified FA. Similar experiment results also could be found anywhere [28]. All these results pointed to the reason of lack of hydroxyl groups on the surface of FA because FA was filtered from flue gases of coal-fired thermal power stations, which cannot offer reacting site to chemically bond with silane coupling agents. As a consequence, utilization of FA to reinforce rubber composites is still a significant challenge in the rubber industry nowadays.

In this work, by introducing the concept of in-situ grafting-neutralization reaction, raw FA as-received was blended with SBR/sorbic acid(SA) to prepare SBR/FA/SA composites, details of which were characterized by X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectrometer (FTIR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) measurements. Properties of SBR/FA composites were greatly improved with SA, providing a new and feasible approach for applying FA in the rubber industry.

2. Experimental

2.1. Materials and sample preparation

SBR-1502 was purchased from Jilin Chemical Industrial Limited Company of China, with 25 ± 1.5 wt% styrene. Fly ash was supplied by Shajiao thermal power station (Dongguan City, China) and used as-received. Sorbic acid (SA) and dicumyl peroxide (DCP) were chemically pure grades. Other ingredients, such as zinc oxide (ZnO), stearic acid, N-cyclohexylbenzothiazole-2-sulphenamide (CBS), 2,2′-dibenzothiazoledisulfde (DM), sulfur (S) et al., were commercial grades.

Formulation of SBR/FA/SA composites were as follows: SBR, 100; ZnO, 5; stearic acid, 1; CBS, 2; DM, 0.5; S, 0.5; DCP, 1, FA, 30; SA, variation. All the unit of ingredients was phr (parts per hundreds of rubber). SBR/FA/SA composites with different phr SA were marked as SBR/FA/χSA. First, SBR was masticated on an open two-roll mill equipped with cooling water at room temperature. Then other ingredients, such as FA, SA, ZnO, stearic acid, CBS, DM, S and DCP were added to the glue stock one by one within fifteen minutes. After that, resultant compounds were stored for eight hours before determining the optimum cure time (t_{c90}) at 170 °C. Finally, vulcanizates were obtained at a press vulcanizer according to their t_{c90} under 170 °C.

2.2. Characterization

XPS spectra of SA and FA/SA were performed on an X-ray photoelectron spectrometer (LVAC-PHI 1800, Ulvac-Phi Company) with an aluminum (mono) K_α source (1486.6 eV) under15 kV and 10 mA. All core level spectra were referenced to the C_{1s} neutral carbon peak at 284.6 eV.

The FTIR analysis of SA and FA/SA was conducted by a Bruker Tensor 27 spectrometer. Spectra were taken from 4000 cm^{-1} to 400 cm^{-1} with the resolving power of 2 cm^{-1}.

To understand the morphology of SBR/FA composites, scanning electron microscopy (SEM, FEI Quanta FEG 250, USA) tests were performed with an accelerating voltage of 8.0 kV. Pictures were taken from tensile fracture surfaces of SBR/FA composites.

DSC measurements were carried out on a Netzsch DSC 200F3 instrument under a nitrogen atmosphere. First, composites were cooled from room temperature to −70 °C with a cooling rate of −10 °C/min, then were held at −70 °C for 3 min, following by a heating course from −70 to 100 °C with a heating rate of 10 °C/min. Glass transition behaviors of SBR/FA composites were determined from the heating process.

Crosslink density was determined by swelling equilibrium test. First, about 0.5 g samples were immersed into toluene for five days at 25 °C. After that, the swelling samples were removed from the solvent one by one and the surface solvent was blotted off quickly with tissue. The specimens were immediately weighed on an analytical balance, and then dried until the weight kept constant. The crosslink density calculation formula can be found anywhere [15,29–31].

Finally, mechanical properties, such as modulus at 300% elongation, tensile strength and elongation at break, of SBR/FA composites were measured by employing Instron3367 electron tensile testing machine according to ISO/DIS37-1994 specifications. The crosshead speed was set at 500 mm/min.

3. Results and discussion

3.1. Evidence of interactions between SA and FA

Binding energy is closely relative to the electron cloud of an atom, which is the reflection of change in the surrounding chemical environment of certain atom [13,15,32]. XPS is a powerful surface analysis technology and capable of detecting the evolution in the binding energy of a given atom. The survey curves of FA, SA and FA/SA are presented in Fig. S1. Details of C1s and binding energy of other atoms are displayed in Figs. 1, S1 and Table1. From Fig. 1(a), 284.6 eV, 285.9 eV and 288.7 eV are ascribed to the binding energy of C—C, C—O and O═C—O groups. When SA is blended with FA and heated, except for C—C in the backbone of SA, the binding energies of C—O (285.8 eV) and O═C—O (288.4 eV) in FA/SA are about 0.1 eV and 0.3 eV lower than that of SA, respectively, suggesting the chemical environment of these groups has changed. In Table1, the variation tendency of different metal atoms in FA/SA is opposite to that of C1s in FA/SA, that is, the binding energies of metal atoms in FA/SA are larger than that of pure FA. It is widely accepted that the binding energy of a given atom depends on the core-level electron density severely. Generally, the core-level binding energy of a given atom increases as the electron density around the atom decreases [13,32]. As the electronegativity of