



Preparation of carboxylated nitrile butadiene rubber/fly ash composites by in-situ carboxylate reaction

Shuyan Yang*, Ping Liang, Kaihui Hua, Xiaokang Peng, Yanxue Zhou, Zhuodi Cai

Dongguan Cleaner Production Center, Dongguan University of Technology, Dongguan City, 523808, PR China

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ABSTRACT

Fly ash (FA) is a byproduct of thermal power stations, which causes increasing environment pollution in the last decade. The incorporation of FA would deteriorate the performance of polymer composites even modified by silane coupling agents. Thereby, the bulk utilization of FA in polymer industry is still a challenge in the world. In this work, by in-situ carboxylate reaction between carboxyl groups of carboxylated nitrile butadiene rubber (XNBR) and FA particles, an immobilized rubber layer is formed on the surface of FA particles, resulting in a better interface adhesion. As a consequence, the tensile strength of XNBR/20FA composite reaches 23.19 MPa, about 44.0% larger than pure XNBR. Even if the incorporation of FA is up to 40phr, the tensile strength is still about 20.60 MPa, about 28.0% larger than pure XNBR, which opens a new approach to lower polymer product cost and solve the environment pollution.

1. Introduction

Fly ash (FA), a byproduct in large quantities from combustion of coal in thermal power stations, is carried out by flue gases of the boiler and causes severe atmosphere pollution without any treatment [1,2]. Thereby, it must be extracted from flue gases by electrostatic precipitators or filter bags or combination of both. But the stack of FA in the open space would generate raise dust pollution by the aid of wind. One of disposal methods is dumping FA in the landfill, which becomes more expensive due to large tracts of land required for its disposal and also is profuse in natural resource. The best way is to make productive use of FA [3–7]. There are some attempts to utilize FA [2] in construction [6] or materials industries [7,8], such as mixing FA with cement to achieve high compressive strength concrete [9] and making use of FA into polymers to get high performance polymer composites [1,10–12], due to its benefits of low density, low cost, strong filling ability, smooth spherical surface and good processability [13].

FA is basically a concoction of a high portion of silicon and aluminum glass with some minerals, such as calcium oxide, Ferric oxide etc. [2,12,14]. The particle sizes of FA vary from several μm to hundreds μm [1,15], which makes it a potential candidate of a natural particle provider to improve the mechanical properties and overcome the general shortcomings associated with high shrinkage and low stiffness of rubber composites [3,13,16–18]. By incorporation of untreated FA into rubber matrix [3,12,17,18], a relatively low cure time,

low viscosity and bad mechanical properties of rubber composites were achieved, as compared to precipitated silica (PSiO_2), which was ascribed to the much lower structure and surface reactivity of FA particles [13] that resulted in weak filler-filler interactions and rubber-filler interfacial bonding [17,19]. In previous works [20–22], the improvement in interfacial interactions between rubber and inorganic fillers not only facilitates dispersion stabilization of fillers in rubber matrix, but also enhances comprehensive properties of rubber/filler composites, such as mechanical properties, conductivity properties, wet skid resistance and rolling resistance properties etc. Hence, surface modification of FA with acid-base treatments [23,24] or with silane coupling agents [11,12,14,18] became one of the principal methods for converting FA into reinforcing filler bearing covalently functional groups, which should be used to enhance mechanical properties of polymer/FA composites [4,5]. Garde [24] contrastively studied the effect of NaOH, HCl and NaOH/HCl surface treatments of FA on properties of polyisoprene composites. Although modified surfaces of FA by NaOH/HCl treatment became rough and the specific surface area of FA ($146 \text{ m}^2/\text{g}$) was comparable with that of PSiO_2 ($179 \text{ m}^2/\text{g}$), only little bound rubber formation can be found on the surface of FA, which was quite lower than that of PSiO_2 . As a result, the tensile strength of polyisoprene/untreated- or treated- FA composite was very poor. In order to improve interactions between polyisoprene and FA, Grade further modified the surface of FA with bis-(3-triethoxysilylpropyl) tetrasulfane (Si69), a kind of bifunctional silane coupling agent containing both of alkoxy

* Corresponding author.

E-mail address: yangsy@dgut.edu.cn (S. Yang).

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and tetrasulfane functional groups [18]. Unfortunately, the tensile strength of polyisoprene/FA composites was still inferior to those of the compounds with PSiO_2 . Consequently [13], the filling of FA is unable to enhance mechanical properties of rubber composites [1,3,12,17,25,26], which may be attributed to the low structure and low reactivity feature of FA particles. First, the particle size of FA, varied from several μm to hundreds μm , are quite large, as compared to that of PSiO_2 in the range within hundreds nm [27], leading to lower specific surface area of FA. Second, as FA is collected from the flue gases of thermal power stations, the hydroxyl groups on the surface of FA particles would suffer from dehydration reaction under high temperature [28]. As a consequence, the active hydroxyl groups on the surface of FA particles almost disappear. FA particles become round-shaped and have relatively smooth surfaces [1,13]. Therefore, when concerning how to improve mechanical properties of rubber composites, FA can hardly be considered as reinforcing filler in the present modification methods. However, one advantage of FA particles is that they are not easy to aggregate and ready to disperse one by one in the polymer matrix, due to the low structure and surface reactivity. Meanwhile, in terms of environmental protection, how to modify FA as reinforcing filler for polymer composites becomes a practical and urgent requirement.

In this work, FA was recorded as completely reinforcing filler for rubber composites. In our previous works [27,29,30], carboxyl-metal ions may reactive with the surface of inorganic particles, resulting in substantial enhancement in mechanical properties of rubber composites. Thus, by constructing in-situ carboxylate reaction under heating, the carboxyl groups of XNBR can react with metal oxides of FA and then anchor on the surface of FA particles through certain chemical bonds, which would enhance interactions between rubber chains and FA particles and improve mechanical properties of XNBR/FA composites by a long chalk. Finally, the reinforcing mechanism of XNBR/FA composites was discussed thoroughly in the work.

2. Experimental section

2.1. Materials and samples preparation

XNBR used in this study was purchased from NANTEX Industry Co., Ltd., with acrylonitrile content of 27.0 wt% and carboxyl group content of 7.0 wt% (NANCAR[®] 1072CG). Fly ash (BET surface area of $1.394 \text{ m}^2/\text{g}$), the chemical components of which were mainly oxides of Si, Al, Ca, Fe, Na, K, Ti, Mg, was supplied by Shajiao thermal power station (Dongguan City, China) and used as-received. Precipitated silica (SiO_2), with the particle diameter of about 900 nm and BET surface area of $134.8 \text{ m}^2/\text{g}$, was supplied by Wanzai County Huiming Chemical Industry Co. Ltd, China. Other ingredients, such as zinc oxide (ZnO), stearic acid (SA), N-cyclohexylbenzothiazole-2-sulphenamide (CBS), 2,2'-dibenzothiazole disulfide (DM), sulfur (S) et al., were commercial grades. For comparison, a control 20phr SiO_2 filled XNBR composite (XNBR/20 SiO_2) was also prepared.

Formulation of XNBR/FA composites was as follows: XNBR, 100; ZnO, 2; SA, 0.5; CBS, 2; DM, 0.5; S, 2; FA, variation. All the unit of ingredients was phr (parts per hundreds of rubber). XNBR/FA composites with different phr FA were marked as XNBR/ χ FA.

First, XNBR was masticated on the roller of an open two-roll mill equipped with cooling water at room temperature five times. Then other ingredients, such as FA (or SiO_2), ZnO, SA, CBS, DM and sulfur, were added to the glue stock one by one within fifteen minutes. After that, resultant compounds were stored for eight hours before the rheometer testing. The rheometer testing was operated on a MDR (M-3000A, Gotech Testing Machines INC., China) at 160°C to get the optimum cure time (t_{c90}) of XNBR/FA compounds. Finally, compounds were cured at a press vulcanizer under 160°C according to their optimum cure times, respectively.

2.2. Characterization

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis was conducted by a Bruker Tensor 27 spectrometer. Spectra were taken from 4000 cm^{-1} to 600 cm^{-1} with the resolving power of 4 cm^{-1} .

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

Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 200F3 instrument with a cooling rate of $-10^\circ\text{C}/\text{min}$ from room temperature to -70°C , under a nitrogen atmosphere. The samples were held at -70°C for 3min, following by a heating course from -70 to 100°C with a heating rate of $10^\circ\text{C}/\text{min}$. Glass transition temperatures of XNBR/FA composites were determined by means of heating stage curves.

The swelling equilibrium test was carried out by immersing about 0.5 g samples into toluene for five days at 25°C . After that, the swelling samples were picked up one by one and the surface toluene was blotted off quickly with filter paper. The specimens were immediately weighed on an analytical balance, and then dried in a vacuum oven until the weight became constant.

Finally, mechanical properties, such as tensile modulus at 300% elongation, tensile strength and elongation at break, of XNBR/FA composites were measured according to ISO/DIS37-1994 specifications by employing Instron3367 electron tensile testing machine with the crosshead speed of $500 \text{ mm}/\text{min}$.

3. Results and discussion

3.1. Interactions between XNBR and FA

Based on the acid-base neutralization theory, the interactions between XNBR and FA may arise from carboxyl groups of XNBR and metal oxides in FA, which can be easily detected by FTIR because of the high sensitivity of FTIR to the dipole moment change of certain group [31–33]. Fig. 1 shows the entire spectra of XNBR, FA and XNBR/20FA in the range from 4000 cm^{-1} to 600 cm^{-1} . In the curve of FA, not any vibration absorption band can be found around 3500 cm^{-1} , indicating that there is rare hydroxyl group in FA due to the dehydration reaction of hydroxyl groups under high temperature. That is the reason why silane coupling agents modified FA cannot improve mechanical properties of rubber/FA composites [3,14,17,24]. Three distinct absorption regions, around 2900 cm^{-1} , 1600 cm^{-1} and 1000 cm^{-1} , respectively,

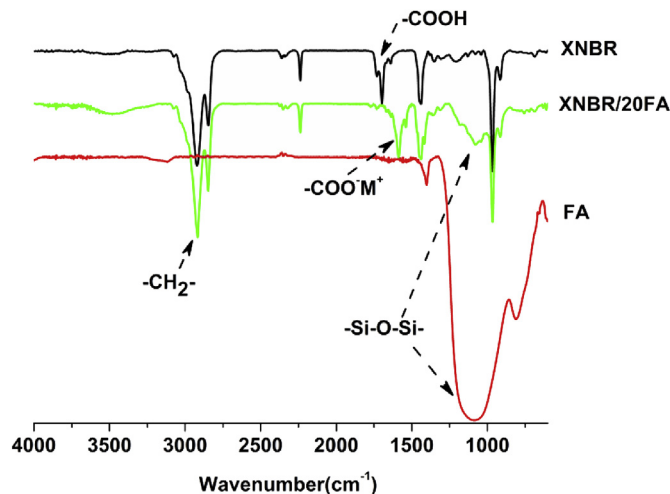


Fig. 1. FTIR traces of XNBR, FA and XNBR/20FA.

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