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# Preparation and Dynamic Mechanic Properties of Surface-Modified Coal Gangue Powder/Styrene-Butadiene-Styrene Composites†

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In this work, native coal gangue powders were modified by γ-aminopropyltriethoxysilane coupling agent (KH550) and coal gangue powders/styrene-butadiene-styrene composites were prepared by mixing process. The structure and surface properties of modified coal gangue powders were characterized by Fourier transform infrared spectroscopy (FTIR), contact angle measuring instrument and thermogravimetric analysis (TGA). The effect of different dosage of coal gangue powders on coal gangue powders/SBS composites was also systematically studied. It is reported that KH550 can effectively improve the hydrophobic property of coal gangue powders. It can also be found that modified coal gangue powders brings well dynamic mechanical properties to styrene-butadiene-styrene, especially when the dosage is 20 phr and the overall best performance of coal gangue powders/styrene-butadiene-styrene composites can be achieved.

**Key Words: Styrene-butadiene-styrene, Coal gangue powder, Silane coupling agent, Surface-modification: dynamic mechanic properties.**

## INTRODUCTION

Thermoplastic elastomer styrene-butadiene-styrene triblock copolymer (SBS) rubber is a commercially important polymer which is of practical use in a wide variety of applications. Moreover, it has often been used as the raw material of reinforced and toughened composites[1,2]. Coal gangue is a complex industrial solid waste discharged when coal is excavated and washed in the production course. Its major chemical composition is $SiO_2$ and $Al_2O_3$ and its major mineralogical composition is quartz and feldspar[3]. The amount of coal gangue accumulated in China has already reached 3.8 billion tons. Moreover, the stockpile of gangue is increasing at a rate of 0.2 billion tons per year[4]. The disposal of such a large quantity of this solid waste requires a lot of land and has caused many serious environmental problems.

Many studies have been carried out to investigate the use of coal gangue in building materials. However, the utilization rate of coal gangue in cement as mixture is always lower than 15 % due to its weak cementitious capability[5]. However, coal gangue has the potential to be used as polymer filler. It is a mixture of inorganic and organic components, on which some unsaturated points and polar functional groups, such as hydroxyl, carboxyl, *etc*., locate. Some coal gangue powder and its product through calcination or with surface treatment have been successfully used as rubber filler, even partially replaced the traditional rubber reinforcement, such as carbon black. However, it has not been practically used in plastics and thermoplastic elastomer rubber filling or modification[6,7]. As a result, the mechanical performance especially the dynamic mechanic properties of coal gangue powder filled composites has rarely been touched, though it is indispensable for enlarging the application of this filler.

In this work, the dynamic mechanic properties of neat styrene-butadiene-styrene (SBS) triblock copolymer (30 wt. % PS) and its coal gangue powder (10-30 wt. %) containing composites have been investigated by rubber processing analyzer (RPA). In order to compare in the compatibility between coal gangue powder and the SBS matrix, an organic silane coupling agent was used to modify the surface of coal gangue particles. Therefore, the fracture surfaces of modified coal gangue powder with a coupling agent and native coal gangue powder filling SBS matrix composites were discussed.

## EXPERIMENTAL

The coal gangue powder (360 mesh) was obtained from WangFengGang Coal Preparation Plant of Huainan City Anhui Province in China, with listed components (wt. %) of $SiO_2$ 56.35, $Al_2O_3$ 21.04, $Fe_2O_3$ 5.85, CaO 3.11, MgO 1.18.

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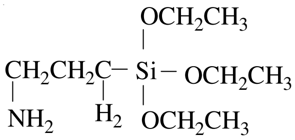
Styrene-butadiene-styrene (4452) was produced by the Beijing Yanshan Branch of Petrochemical Co. Ltd., in China. SBS (4452) is a linear polymer, containing 30 wt. % styrene, the average molecule weight is 110,000 g/mol.

The reagents in the experiments such as ethyl acetate, stearic acid, *etc*., were analytical pure reagents (AR). γ-aminopropyltriethoxysilane coupling agent (KH550) was purchased from Nanjing Shuguang Chemical Group Co. Ltd., in China, its molecular formulas is listed in **Scheme-I**. They were used without further treatment.



$$\underset{NH_2}{CH_2}CH_2\underset{H_2}{C}-\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Si}}-OCH_2CH_3$$

**Scheme-I:** Molecular formula of silane coupling agent

**Preparation of surface-modified coal gangue powder:** To functionalize the surface of the particles, 10 g of coal gangue powder was dispersed in 500 mL of ethyl acetate with the aid of ultrasonic agitation, followed by reacting with 1.5 g of γ-aminopropyltriethoxysilane coupling agent at 80-85 ºC with stirring for 12 h. The reaction product was then filtered and washed using ethyl acetate and dried at 50 ºC for 12 h under vacuum. Coupling agent-modified and unmodified coal gangue powder were coded respectively as M-gangue and N-gangue to ease the following discussion.

**Preparation of surface-modified coal gangue powder/ SBS composites:** The composites in our experiments were prepared by HAAKE Polylab OS mixer (Polylab OS, Thermo Scientific GmbH, Germany) at a rotor speed of 40 rpm and the beginning temperature of 145 ºC for 10 min (within this time period torque was stabilized). The compounds were then compression molded into 2 mm thickness sheets by 180 ºC for 8 min. To ease the following discussion, the sample codes and chemical compositions of additives are summarized in Table-1.

TABLE-1
SAMPLE CODES AND CHEMICAL COMPOSITIONS OF ADDITIVES

| Sample codes | SBS (wt. g) | M-Gangue (wt. g) | N-Gangue (wt. g) | Stearic acid (wt. g) |
|---|---|---|---|---|
| S-0 | 100 | 0 | 0 | 1 |
| S-1 | 100 | 10 | 0 | 1 |
| S-2 | 100 | 20 | 0 | 1 |
| S-3 | 100 | 30 | 0 | 1 |
| S-4 | 100 | 0 | 10 | 1 |
| S-5 | 100 | 0 | 20 | 1 |
| S-6 | 100 | 0 | 30 | 1 |

**Characterization methods:** In order to represent detailed information of coal gangue powder before and after surface modification with KH550, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and contact angle measuring instrument (CAMI) were performed to characterize the structures and properties of M-gangue and N-gangue. FTIR spectra of M-gangue and N-gangue were carried out on spectrometer (Nicolet Co., Nexus-870, USA) with a resolution of 4 $cm^{-1}$ for which the samples were palletized with KBr powder. TGA studies were performed with a thermogravimetric analyzer (TA instruments, SDT 2960, USA). The samples were scanned from 30-700 ºC at a heating rate of 10 ºC/min under nitrogen atmosphere. Surface hydrophilicity of coal gangue powder was investigated by contact angle measuring instrument (CAMI) (Kino Co., SL200C, USA) at the temperature of 25 ºC, water was dropped on the sample surface and the angle values was taken as its contact angle.

The SBS/coal gangue powder composites were characterized by rubber processing analyzer (RPA) and scannin electron microscopy (SEM) observations. The dynamical mechanical characteristics of the samples were measured through RPA in scanning mode at a frequency of 60 cpm and strain of 0.5 degree from 50-150 ºC temperature scanning, at temperature of 60 ºC and strain of 0.5º from 1.0-1800 cpm frequency scanning, at temperature of 60 ºC and frequency of 60 cpm from 0.1-8.0º strain scanning with an rubber processing analyzer (Gotech Testing Machines INC., RPA8000, Taiwan). The fracture surfaces of composites were observed with the scanning electron microscopy machine (SEM, Hitachi, S-3000N, Japan) at an accelerating voltage of 15 kV.

## RESULTS AND DISCUSSION

**Contact angle measuring of coal gangue powder:** Surface hydrophilicity of coal gangue powder was investigated by contact angle measurements (Fig. 1). After surface modification, the contact angle increases from 25.86º to 97.15º in water, suggesting the increasing surface hydrophobicity and the decreasing surface free energy of coal gangue powder[8]. These changes are likely due to the carbon backbone of coupling agent which is hydrophobic and the surface of coal gangue is modified successfully. It can be inferred coal gangue powder modified with KH550 can be dispersed in polymer materials more easily than native coal gangue powder.

**FTIR analysis:** FTIR was used to characterize the coal gangue powder before and after surface modification with KH550 (Fig. 2). The coal gangue powder is strongly reactive and its surface region of laboratory artifactitious coal gangue powder has a large amount of Si-$NH_2$ and Si-OH groups[1,9]. From curve 'a', ν(O-H) and ν(N-H) combination band can be seen at 3426 $cm^{-1}$. The detection of absorption at 1029 $cm^{-1}$ as well as of a broad and weak band at 910 $cm^{-1}$ in our sample, is probably indicative of the presence of $SiO_2$ and is assigned to the backbone vibrations of Si-O-Si . In the spectrum of modified coal gangue powder (curve b), the strong absorption peak of 1555 and 1480 $cm^{-1}$ belong to -$NH_2$ and -C-N- stretching vibration mode respectively. The Si-O-Si absorption bands are observed at 1050-1000 $cm^{-1}$, but it can be found that the peak of surface modified silicon by KH550 is broader and stronger than that of the native coal gangue powder at 1100-1000 $cm^{-1}$. This indicates that the surface group of coal gangue powder has changed from Si-OH to Si-O-Si. From these, the silane coupling agent is tightly absorbed at the surface of coal gangue by chemisorption[10]. All the results further illustrate that silane coupling agent plays an important role in the coal gangue powder.

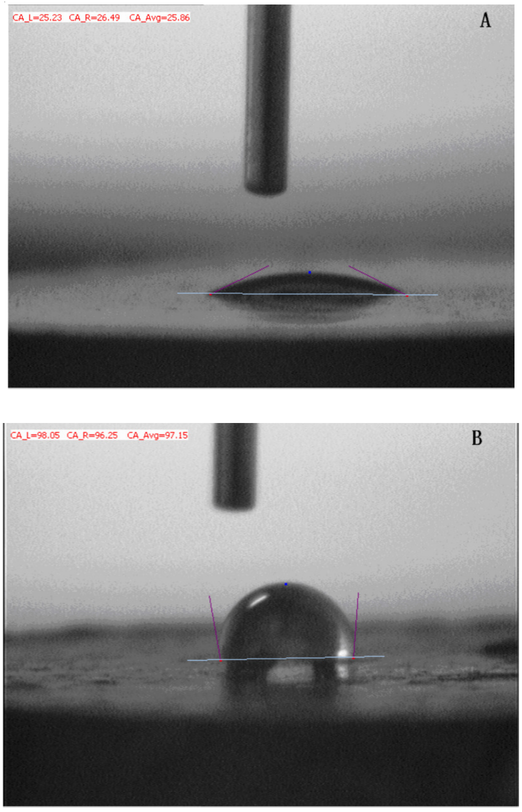


Fig. 1. Contact angle images of coal gangue. (A, native coal gangue powder; B, modified coal gangue powder)

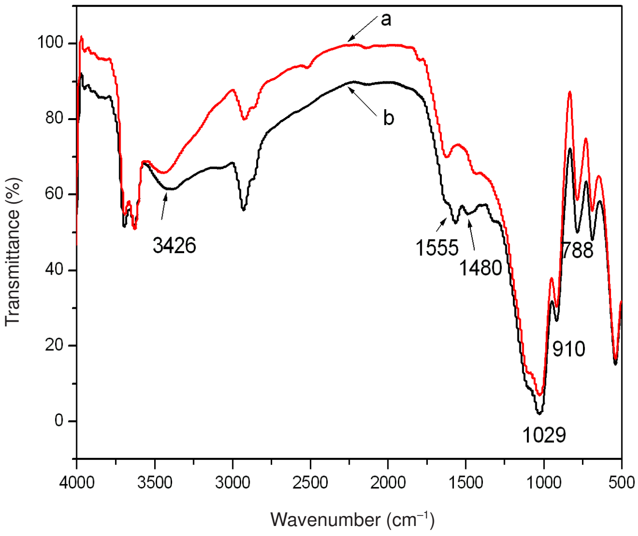


Fig. 2. FTIR spectra of coal gangue powder. (a, native coal gangue powder; b, modified coal gangue powder)

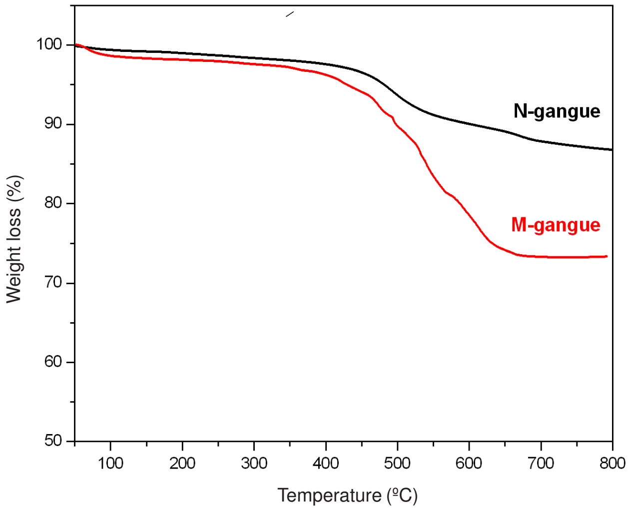


Fig. 3. TGA curves of N-gangue and M-gangue

**TG analysis:** Fig. 3 depicts the TG curves of N-gangue and M-gangue. N-Gangue exhibited two distinct mass loss regions. The mass loss of N-gangue below 300 ºC (about 1.5 %) is due to the release of the physically absorbed water and chemically bonded water in N-gangue. The weight loss between 400-750 ºC (about 12 %) is due to the dehydration of N-gangue into $SiO_2$, $Al_2O_3$, CaO, *etc*. and decomposition of small portion organic matter. The total weight loss of N-gangue is about 13.5 %. However, the TGA curve for M-gangue is largely different from that for N-gangue. At the temperature lower than 300 ºC, little water is released due to the hydrophobicity of aminopropyl surface of M-gangue. M-Gangue begins to lose weight at around 350 ºC and shows a sharp weight decrease from 400 ºC to 680 ºC[11], which is primarily attributed to elimination of the organic moieties on the surface of BM sheets. This suggests that the weight loss is due to mainly the loss of organic and partially the release of little water by dehydration into $SiO_2$, $Al_2O_3$, CaO *etc*. and decomposition of small portion organic matter. The total weight loss of M-gangue is about 26.5 %[12].

### Rubber processing analysis (RPA)

**Effect of temperature:** The rheological behaviour of neat SBS and SBS composites was analyzed through the dynamic temperature sweep experiments at a strain of 0.5° and frequency of 60 cpm in order to establish the temperature dependence of the viscoelastic properties in the solid and the melt state. Fig. 4 shows that the values of G' for SBS initially rapid decrease with increase of temperature from 50 ºC to 80 ºC and then a decrease at a slow as the temperature was increased from 80 ºC to 150 ºC. The temperature dependence of G' for the SBS/coal gangue powder before and after surface modification composites was quite different from that of pure SBS. The composites of 20 doses of M-gangue added to 100 doses of SBS exhibit higher values of G' at temperatures below 80 ºC compared to that of neat SBS and SBS/unmodified coal gangue powder composites. But the temperature above 80 ºC, G' of 30 doses of M-gangue added to 100 doses of SBS composites is more superior. This may be due to the strong attractive interactions existing *via* hydrogen bonding or chain entanglement between the coupling agent and SBS chains. These changes are likely due to more anchoraging points are supplied by 30 doses of modified coal gangue powder[13-15].

**Effect of frequence:** Dynamic frequency sweep tests were conducted for further study on network formation and microstructural changes of the composites in detail. The dynamic frequency scan measurements at 60 ºC temperature and strain of 0.5° of SBS composites with various coal gangue powder loading is shown in Fig. 5. The G' value significantly increases with frequency increase at low frequency region as compared to the high frequency region. Moreover, a noticeable qualitative change in G' *versus* is observed at low frequency region

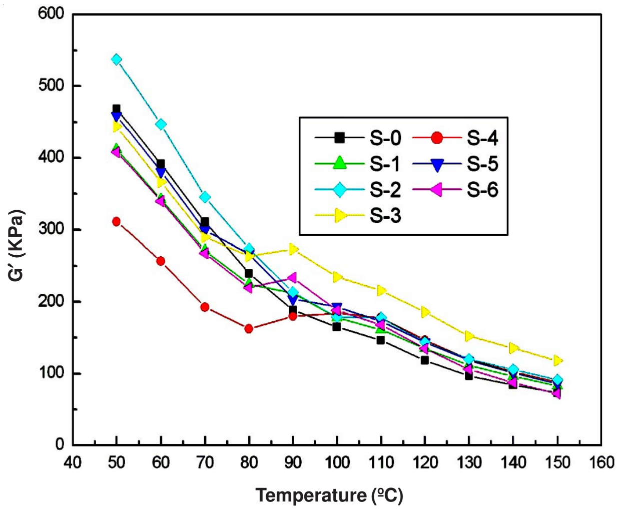


Fig. 4. Evolution of storage modulus *versus* temperature (60 °C/min, 0.5°)

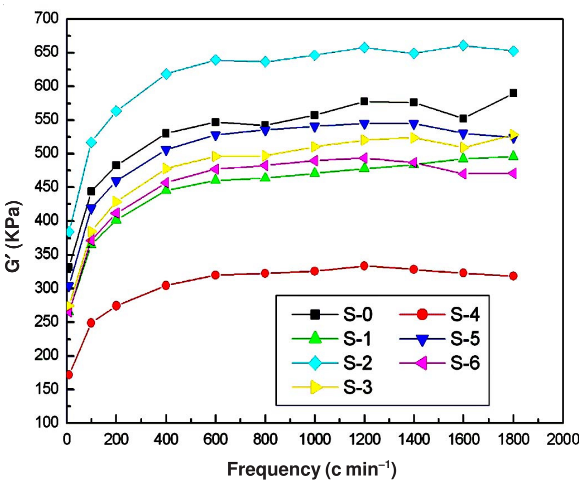


Fig. 5. Evolution of storage moduli *versus* frequency (60 °C, 0.5°)

for 20 doses of M-gangur filled 100 doses of SBS composites. Due to the anchoraging points content correspond with activity of molecular chains of SBS at 60 °C temperature, although the anchoraging points content of 30 doses of M-gangur filled 100 doses of SBS composites are more, but the activity of molecular chains of SBS is limited at 60 °C temperature. It can be inferred 30 doses of M-gangur filled 100 doses of SBS has formed interlocking network[1,14,16].

**Effect of strain:** Fig. 6 shows the dependence of storage modulus (G') of SBS and its composites with different coal gangue powder before and after surface modification loadings on the strain amplitude by the dynamic strain sweep to determine the limits of linear viscoelastic properties and information on the dispersion of filler particles in the polymer matrix at 60 °C temperature and an frequency of 60 cpm. The magnitudes of G' of all the samples exhibit rapid decrease with strain increase at low strains (below 4°) and then a decrease at a slow as the strain was increased. It was observed that the G' value of 30 doses of M-gangue filled 100 doses of SBS composite significantly is higher than that of neat SBS and SBS/others coal gangue powder composites[17,18]. The results of temperature and frequency scanning are illustrated by strain scanning simulation.

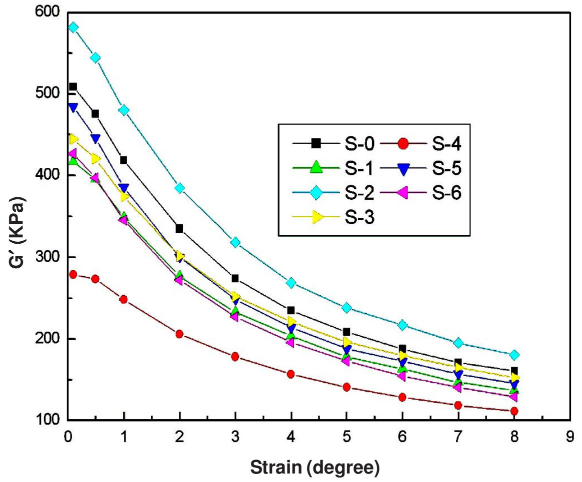
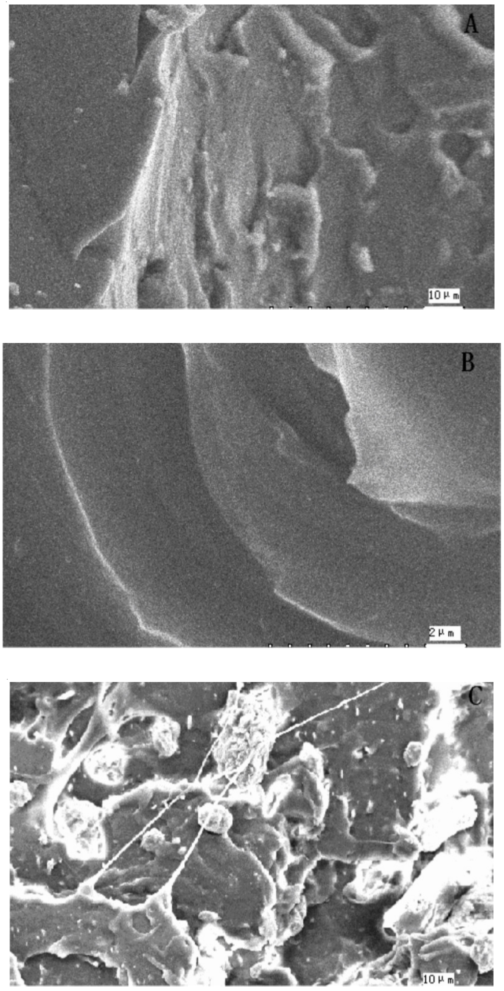


Fig. 6. Evolution of storage moduli *versus* strain (60 °, 60c/min)

**SEM images analysis:** SEM micrographs shown in Fig. 7, reveals that the fracture surfaces of 20 doses of M-gangue filled 100 doses of SBS composite has obvious network structures. It is like due to interaction between the active chain and group of coupling agent and macromolecular chain of SBS form network structures[19]. But the composites of unmodified coal gangue powder filling SBS have not formed network structures because active chain and group of powder surface do not exist. The results of SEM analysis agree with the test results of rubber processing analysis.



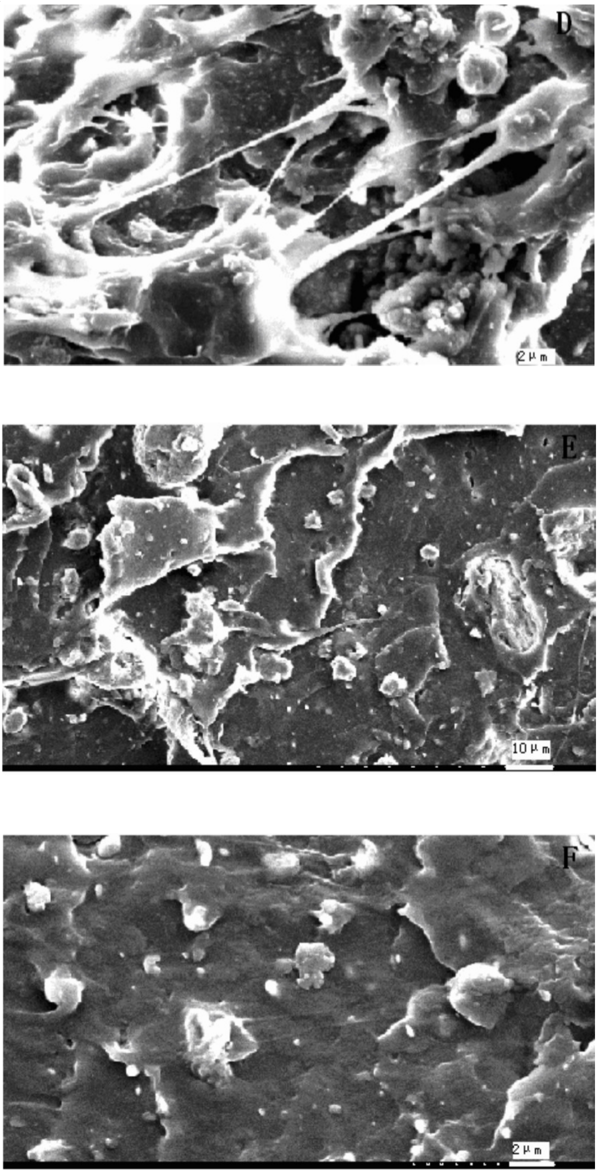


Fig. 7. SEM images of fracture surfaces of composites. (A and B, neat SBS; C and D, 20 doses of M-gangue filled 100 doses of SBS; E and F, 20 doses of N-gangue filled 100 doses of SBS)

## Conclusion

The functional coal gangue particles modified with γ-aminopropyltriethoxysilane coupling agent (KH550) were an effective filler to prepare coal gangue powder/SBS composites with high performance. The modified coal gangue particles can decrease surface free energy of powder, disperse in SBS matrix, make up the defects and enhance the crosslinking network. Almost all the properties of SBS have been improved distinctly just by 20 phr dosage.

## ACKNOWLEDGEMENTS

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