Purification, Surface Modification of Coal Ash Silica and Its Potential Application in Rubber Composites

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ABSTRACT: This article reports the purification and surface modification of coal ash silica and afterwards its utilization as reinforcing filler in solution-styrene-butadiene rubber/butadiene rubber (S-SBR/BR). The coal ash silica free of unwanted metal ions/mineral oxides was obtained using phosphoric acid. The chemical composition of the purified coal ash silica in comparison to impure coal ash indicates the presence of characteristic hydroxyl functional group at 3440 cm^{-1} and an increase in the oxygen content as determined with the help of Fourier Transform Infrared and x-ray photoelectron spectroscopy, respectively. The contact angle analysis shows that after purification the polar part of the surface energy increased to 17.5 from 12 m Jm^{-2}. While the surface area increased to an order of magnitude, i.e., 11.6 to 110.5 m^2 g^{-1}. The modification of purified silica particles with bis(3-triethoxysilylpropyl) tetrasulfane reveal the functionalization of hydroxyl to -Si-O-R groups as detected at 1560 cm^{-1}. As a consequence, the modified silica based S-SBR/BR composite resulted in improved mechanical properties due to enhanced silica-rubber interaction. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1493–1501, 2010

Key words: modification; silicas; reinforcement; mechanical properties; composites

INTRODUCTION

Naturally occurring coal is one of the cheapest and abundant source of energy generation. A substantial amount of coal is consumed annually in thermal power plants for producing electricity. The byproducts produced by the combustion of coal primarily consist of fly and bottom coal ash. These residual byproducts composed mainly of silicon, aluminum, iron, and oxygen are widely used in plastic products to improve performance and reduce costs. However, the disposal of coal ash has simultaneously posed an increasingly difficult challenge because of the volume involved, the particulate nature of it and the varied chemical composition which limits the number of acceptable disposal areas.

Recently, past efforts have been dedicated to find alternative and economic uses for coal ash such as utilzation as an additive in Portland cement.[1-3] However, the fraction of the coal ash applicabe for use in concrete represents only a minor portion of the total available amount. It has been long desired to find alternative applications for the coal ash e.g., as a mineral oxide filler for industrial items. More specifically, synthetic-precipitated silica has been widely used for reinforcement in rubber material and has proved to be as effective as carbon black.[4] Extensive works in this area is focused on improving the interaction between the filler particles and polymer matrix through compatibility. However, the presence of highly hydrophilic siloxane and silanol groups results more in filler–filler rather than filler–polymer interaction.[5] Because of this fact the dispersion of silica in the polymer matrix (specifically rubber) is much more difficult. Therefore, for enhanced dispersion, coupling agents such as bis(3-triethoxysilylpropyl) tetrasulfane (TESPT), i.e., (Si69) and bis (3-triethoxysilylpropyl) disulfide (TESPD) are widely used. Silica can be found from various sources, such as precipitated silica by precipitation of an aqueous sodium silicate solution, fumed silica by pyrogenic process, and silica from natural resources (e.g., rice husk ash and coal ash). In recent years, silica from natural resources have attracted numerous investigators to incorporate it as an alternative reinforcing filler for natural and synthetic rubber composites because of cost-saving, good mechanical properties, better dimensional stability, and environmental issues.[6-9] Depending upon the source and the makeup of the coal being consumed, the

components of the fly ash vary considerably. However, most of the coal ash contains silicon dioxide (SiO_2), calcium oxide (CaO), aluminium oxide (Al_2O_3), and iron oxide (Fe_2O_3). As a matter of fact, the ash particles generated at thermal power plant need to be disposed outside the plant premises. The disposal of such byproduct needs large areas and also the transportation expenses. The best option to utilize such materials is to exploit it as filler for the polymeric materials. This is very promising approach as the coal ash contains $\sim$ 40–50% silica by weight. The published data and conclusive information on the use of coal ash as potential filler in polymer materials is very limited.[10] Garde et al.[11] have reported that the mechanical properties of polyisoprene rubber filled with unmodified fly ash particles were inferior, however, in the presence of silane coupling agent the mechanical properties improved due to homogeneous dispersion. Sombatsompop et al.[6] have found that the addition of silica from fly ash in the natural rubber/styrene-butadiene rubber composites improve the elastic behavior, including compression set and resilience tests, and its properties were better than as compared to that of the commercial precipitated silica. It was found that by introducing untreated fly ash particles in the natural rubber composites, the mechanical properties were similar to those of commercial silica filled composites at silica contents of 0–30 phr.[8] Alkadesi et al.[10] have investigated the properties of polybutadiene rubber filled with silane (Si69) modified fly ash and have observed improved mechanical properties in comparison to the unmodified fly ash filled rubber.

The presence of Fe_2O_3 in coal ash limits its application as reinforcing filler in rubber matrix. However, the extraction of Fe_2O_3 from the coal ash may extend its useful application in various fields. Therefore, the present work aims to incorporate the coal ash silica in rubber matrix as potential filler. For this reason, the coal ash is first purified by using phosphoric acid to leach out various undesired mineral oxides. Furthermore, to improve compatibility between the coal ash silica and rubber matrix, surface modification using Si69 is carried out. In addition, a variety of mechanical properties in order to validate the reinforcement ability of modified coal ash silica in comparison to non modified in SSBR/BR rubber composite is discussed.

EXPERIMENTAL

Materials

Solution-styrene–butadiene rubber (S-SBR, CE 3418-01) and polybutadiene rubber (BR, high cis Nd BR, CB25), were obtained from, Lanxess, Germany. Zinc oxide, stearic acid, diphenyl-guanidine (DPG),

n-cyclohexyl-2-benzothiazole-sulfenamide (CBS) and soluble sulfur used in this study were of industrial grades. The silane-coupling agent TESPT [bis (triethoxysilylpropyl) tetrasulfane] and modified silica particles (coupsil 8113) were used from Degussa, Germany. The fly and bottom ash were collected from Lakhara Power Generation LTD, Pakistan. The data regarding chemical composition of coal ash was supplied by the company and is presented in Table I.

Purification and surface modification of coal ash silica

The coal ash particles have been purified using acid leaching method. In the first stage, 250 g of impure particles were soaked in 500 mL of 1% phosphoric acid solution and the fine particles were removed from the mixture by flotation. The separated particles were filtered and dried in an oven at 100°C. A 100 g of the dried fine particles were mixed in 50 mL of 85% phosphoric acid solution with continuous stirring and the resulting mixture was heated at 100°C for 30 min. The mixture was diluted with distilled water and filtered. A successive washing of the residue was carried out to remove the unreacted acid and later filtered. The filtered particles were dried at 100°C in an oven and were used for surface modification. The average amount of the recovered particles was 69.9 g which makes the percentage yield $\sim$ 70%.

Surface modification of silica particles was carried out using Si69 silane coupling agent. An appropriate amount of Si69 (7% of dry particles weight) was stirred in toluene for 10 min. To this, a catalytic amount of a mineral acid was added and the stirring continued for another 10 min at 50°C. A predetermined amount of purified coal ash silica particles was added to this solution. The resulting mixture (Si69 and silica particles in toluene) was stirred for 1 h at 50°C. The mixture was then filtered and washed with distilled water followed by ethanol

TABLE I
The Chemical Constituents of Coal Ash Samples Collected from Lakhara Power Generation Ltd., Pakistan

S. No	Main constituents of coal ash	Relative amount (%)
1	CaO	5.98
2	MgO	1.86
3	SiO_2	49.85
4	Al_2O_3	14.31
5	Fe_2O_3	22.85
6	K_2O	0.60
7	Na_2O	1.34
8	SO_3	4.63

addition to remove the unreacted Si69. The modified particles were dried in an oven for 24 h at 100°C.

Filler characterization

The infrared spectra were recorded on a Vertex 80v (Bruker) FTIR spectrophotometer (4000–400 cm^{-1}, resolution 2 cm^{-1}, 32 scans per measurement) from Bruker Optik GmbH, Ettlingen, Germany. Potassium bromide (KBR) pallets were prepared from the different grades (impure, purified and modified) of coal ash silica particles and the spectra were recorded in transmission mode.

The chemical composition of the coal ash silica particles was determined using a ESCALAB iXL 220 spectrometer from Thermo-VG scientific (Datacomp Scientific, Toronto, Canada) operating at a pressure range of 1×10^{-8} to 1×10^{-10} mbar, equipped with an Al/Mg twin anode. Spectra were recorded at a takeoff angle of 30° and with pass energy of 100 eV for survey scans. For each sample, a detailed scan of the O1s, C1s, N1s, and Si2p lines was performed with a step width of 0.1 eV and pass energy of 20 eV. The calibration of the binding energy (BE) scale was made by setting the C1s BE of the neutral carbon (C-C and C-H bonds) peak at 284.6 eV.

The advancing and receding contact angle of the coal ash silica particles was determined according to Wilhelmy plate method. The measurements were carried out on DataPhysics DCAT 21 Tensiometer (Filderstadt, Germany). The sample container was cleaned by with distilled water and then dried in oven.

To calculate the surface energies from the wetting data, a series of test liquids with different surface tension (and polarity) was used: Water (Millipore Milli-Q-Quality), Formamide (Merck, Darmstadt, Germany), ethyleneglycol (Fisher Scientific, Loughborough, UK), dodecane (Merck Schuchardt, Hohenbrunn, Germany), hexadecane (Merck, Darmstadt, Germany), ethanol (Uvasol, Merck, Darmstadt, Germany) and mixtures of ethyleneglycol (EG) or ethanol respectively, with water (EtOH : H2O, 10 : 90 and EG : H2O, 20 : 80). The test fluid was filled into the container and the temperature was maintained at 20°C before each measurement. The particles were first adhered on an adhesive tape (TESA 55733, Beiersdorf Germany) and the loosely held particles were blown away by a stream of nitrogen.[12,13] The particles adhered on tape surface were used for Wilhelmy contact angle measurements. To carry out the measurements the tape was fixed into the tensiometer holder and immersed into the test liquid and the resulting advancing and receding contact angle values were recorded. The same procedure was repeated for all samples with other test liquids. The dispersive and polar part of the surface energy of the particles was obtained by fitting Fowkes' equation[14,15] given below,

$$\cos \theta = -1 + \frac{2\sqrt{\gamma_s^d \gamma_l^d}}{\gamma_l} + \frac{2\sqrt{\gamma_s^p \gamma_l^p}}{\gamma_l} \qquad (1)$$

where γ_l is the surface tension of the liquid γ_s is the surface energy of the solid; while $\gamma_l^p \gamma_s^p$ correspond to the polar part of surface tensions and surface energies respectively. Whereas $\gamma_l^d \gamma_s^d$ correspond to dispersive part of the surface tensions and surface energies, respectively.

The verification of the chemical coupling of Si69 to the coal ash silica particles was carried out using a thermogravimetric analyzer (Q500, TA Instruments, USA) starting from ambient temperature to 800°C in high resolution mode with heating rate of 10K/min under nitrogen atmosphere. The balance measurement accuracy is 0.1% and for temperature calibration the well known curie temperature of nickel standard sample was measured as a reference. The weight loss as a function of temperature for modified and non modified silica particles was recorded.

The specific surface area of the coal ash silica particles was measured according to Brunauer, Emmett and Teller (BET method) as described in the standard DIN 6613. The surface area of the particles is here calculated from the N$_2$-isotherm which is estimated at the boiling point of liquid nitrogen.

Stress–strain behavior of the SSBR/BR composites was determined according to ISO 527 method at a cross-head speed of 200 mm/min using tensile testing machine from Zwick GmbH, Ulm Germany.

Micro structure morphology and dispersion of filler were determined with the help of LEO 435 scanning electron microscope (SEM—acceleration voltage 20 kV) manufactured by LEO Electron Microscopy Ltd, Cambridge, England. Cryogenically fractured elastomeric composites were used for the dispersion analysis of filler in the rubber matrix.

Sample preparation

The details of the rubber formulation are provided in Table II. A 50:50 mixture of SSBR/BR rubber was first charged to the internal mixer (PolyLab Haake Rheomix, Thermo Electron Corp.) and masticated for 3 min. The silica particles were incorporated to the masticated rubber and blending continued for another 10 min. In the second step, the rubber mixture was taken out from the internal mixer and the curatives were added on a two roll laboratory mill from Polymix 110L, Servitic, Germany, at room temperature. A constant friction ratio of 1:2 was maintained between the milling rolls. Approximately 2

S. No.	Rubber recipe	Amount (phr[a])
1	SSBR/BR, 50/50	100
2	Filler	30
3	ZnO	3
4	Diphenyl-guanidium (DPG)	2
5	N-Cyclohexyl-2-benzothiazolsulfanamid (CBS)	1.7
6	Stearic acid	2
7	Sulfur	1.4
8	Si69	6.5

[a] Parts per hundred of rubber.

mm sheets were drawn out from the mill and cured in hot press (fontune, Holland) under a pressure of 200 MPa at a temperature of 140°C up to their corresponding optimum cure time.

RESULTS AND DISCUSSION

The data provided in Table I shows that the coal ash (fly and bottom) is composed of three major components: SiO_2, Fe_2O_3, and Al_2O_3. According to ASTM standard[16] the coal ash with such a distribution of components is classified as class F, which is either derived from anthracitic or bituminous coals. This type of ash is pozzolanic in nature, and contains less than 10% lime (CaO). Besides these, elements such as carbon, fluorine, sodium, and titanium were also found in the ash sample used in this work.

The cleaning of coal ash is carried out to obtain filler grade particles. A mineral acid treatment of the coal ash was proposed and adopted in the present investigations where the oxides of alkali, alkaline, and transitions metals reacts with the acid and form their soluble respective salts. For example, the oxides of iron (Fe_2O_3) form soluble ferric phosphate on reaction with phosphoric acid (H_3PO_4)[17-19] as given in eq. (2).

$$2H_3PO_4 + Fe_2O_3 \rightarrow 2FePO_4 + 3H_2O \qquad (2)$$

Using this procedure, the metal oxides have been removed from the coal ash by treating with phosphoric acid. The solid residue free of most metal oxides containing mainly silica particles was recovered by filteration. Table III shows the trace elements and the BET surface area of the impure coal ash (prior to purification) and the purified silica particles. It can be observed that both grades of impure coal ash, virgin fly ash (V-FA) and virgin bottom ash (V-BA), contain similar elemental distribution except that no flourine was detected in the V-BA. The mass percentage of the silicon element has increased from 17 to 41% due to purification. This increase in the mass percentage of silicon is the

result of the leaching out of the CaO, Fe_2O_3, and Al_2O_3 etc. from the particles. However, small amount of aluminum and iron elements in purified ash silica was also detected. Because of purifcation the BET surface area of the coal ash also increased. by an order of magnitude. as shown below in Table III. The purification of the coal ash silica particles is due to the leaching out of the above mentioned oxides and as a consequence the surface area of the purifiead coal ash particles (BA-Si and FA-Si) increased. These observations show that the above described method can be successfully applied to obtain high surface area silica particles from coal ash for various applications.

The corresponding FTIR spectra of the same samples of the coal ash particles are shown in Figure 1. As can be observed from the spectra, all of the samples at 1098 and 793 cm^{-1} show significant stretching vibrations, which corresponds to Si=O=Si bond. The peaks at 1432 and 3633 cm^{-1} in the V-BA corresponds to calcium-oxygen stretching vibrations. After purification the peak disappeared, while at the same time new peaks at 1630 and 3430 cm^{-1} corresponding to hydroxyl functional group on silica particles have emerged. However, in the case of the both V-FA and V-BA there is no indication of

TABLE III
Elemental Composition and Surface Area of Impure
(V-FA & V-BA) and Pure (BA-Si) Particles

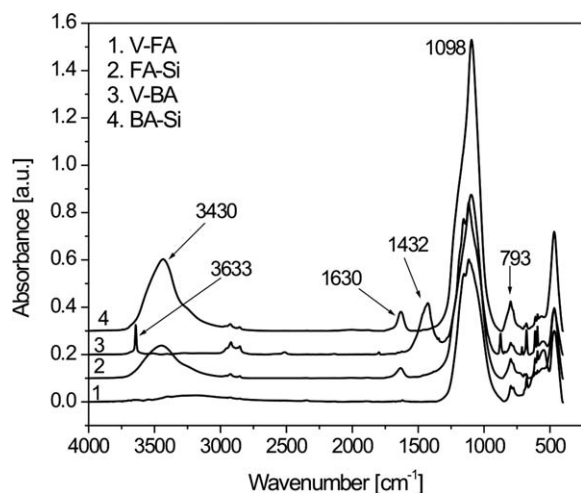| S. No.	Filler type	Atom	Mass conc. (%)	BET Surface area m^2 g^{-1}
1	V-FA	C 1s	10.67	11.6
		O 1s	47.53	
		F 1s	0.41	
		Na 1s	0.81	
		Al 2p	11.17	
		Si 2s	14.36	
		S 2p	5.92	
		Ca 2s	2.19	
		Ti 2p	0.87	
		Fe 2p	6.07	
2	V-BA	C 1s	10.95	11.6
		O 1s	47.47	
		Na 1s	0.33	
		Al 2p	13.15	
		Si 2s	17.80	
		S 2p	2.35	
		Ca 2s	4.53	
		Ti 2p	0.67	
		Fe 2p	2.74	
3	BA-Si	C 1s	3.91	110.5
		O 1s	50.31	
		Al 2p	3.73	
		Si 2s	41.0	
		Fe 2p	1.05	
4	FA-Si	C 1s	4.56	112.0
		O 1s	51.35	
		Al 2p	4.14	
		Si 2s	39.0	
		Fe 2p	0.95	

Figure 1 Comparison of the FITR spectra of FA-Si, BA-Si with V-FA,V-BA.

hydroxyl peaks at 1630 and 3430 cm^{-1}. These results confirm that the silica surface of both V-FA and V-BA particles is mainly covered with mineral oxides. This finding is exactly in correlation with the XPS results, where an increase in the silica mass content has been observed after purifcation. Therefore, in view of the spectroscopic findings, it can be concluded that chemical purification of both the V-FA and V-BA not only eleminates the unwanted mineral oxide from the silica surface but also exposes the active hydroxyl functional groups for further reaction with the base matrix or the coupling agent.

The FTIR and XPS results show the effect of the purification of both the V-FA and V-BA on their chemical compositions. Interestingly, similar observation in the characterization of the surface energy of the impure V-FA, V-BA and purified BA-Si, FA-Si particles have also been observed. The surface energy data obtained for these particles have been systematically analyzed and are presented in Figure 2. The surface energy of the different grades of coal ash silica particles is the contribution of dispersive and polar part. The dispersive part corresponds to the dispersive interaction forces, detemined by bulk properties of the materials and the polar part describes the surface polarity. It is obious from the figure that all grades of coal ash silica particles have the same magnitude of dispersive part. On the contrary a significant variation in the polar part can be observed. This variation is due to the purification of the coal ash particles. Comparing V-BA with V-FA particles, the polar part of V-BA is lower as compared to the V-FA. This is possibly due to the presence of higher amount of iron oxide in V-FA, as clearly supported from the XPS data provided in Table III. In case of the BA-Si & FA-Si particles a higher value of polar part than impure particles has been observed. This is due to the fact that the sur-

face functionality of the particles has significantly changed by treatment with the acid, more specifically the particles are surrounded by hydroxyl groups. This explanation is based on the finding from the FTIR data shown in Figure 1.

For the effective utilization of the purified coal ash particles, i.e., BA-Si and FA-Si in polymer matrix, a prior surafce modification is strongly desired. This is required to achieve compatibility between the silica particle and the polymer matrix. This has been extensively studied in various composites by diferent investigators.[20,21] The main issue associated with such particles is the higher surface energies that intiate the particles agglomeration. The strong Van der Waal's forces lead to agglomeration of the particles. This results in poor dispersion and lack of compatibilty with the polymer matrix.[10,22] In order to prevent the agglomeration, the purified particles have been modified using silane (Si69) coupling agent. The one end of Si69 is chemically bonded onto the particle surface and the other end which is compatible with the polymer matrix extends into it, thereby making the particles compatible with the polymer matrix. The surface modification reaction of the silica particles is explained in reaction Scheme 1.

The FTIR spectra of the modified (BA-Si-Si69) and unmodifed BA-Si particles are shown in Figure 3. The peaks at 3430 and 1630 cm^{-1} correspond to hydroxyl (-OH) groups in the BA-Si particles. After modification with Si69 the hydroxyl functional has been successfully reacted to form Si-O-R bond, where R is $(C_2H_5O)_2$-Si-S_4-Si-$(OC_2H_5)_3$. The evidence of such chemical bonding can be observed in the appearance of a distinct peak at 1560 cm^{-1} in Figure 3. The new peaks at 2924 and 2850 cm^{-1} in the modified BA-Si particles also indicates the presence of Si69. The FTIR spectra show that Si69 is chemically bonded with silica hydroxl groups that can be
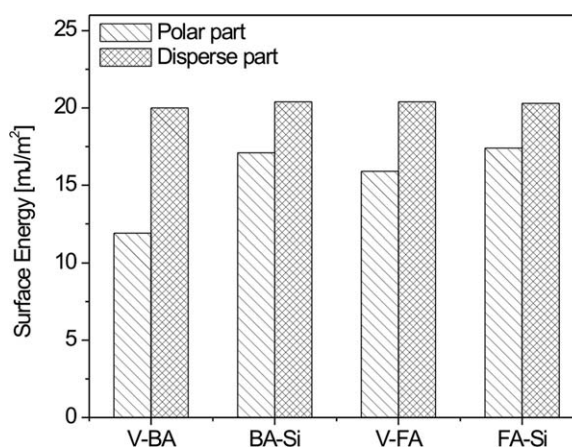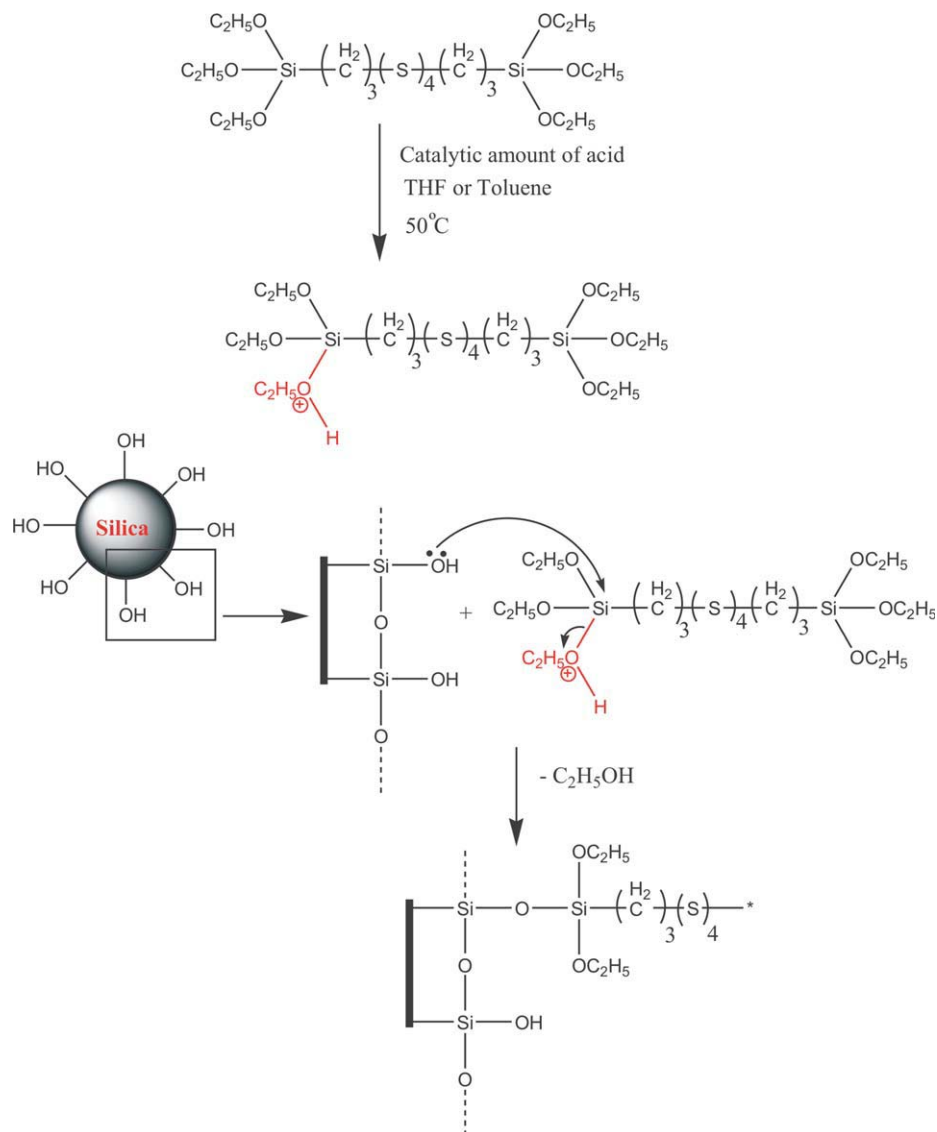

Figure 2 Comparison of the polar and disperisive part of the surface energy of the purified and nonpurified particles.

Scheme 1 A schematic representation of the coupling reaction between silica hydroxyl groups and Si69 in the presence of catalytic amount of a mineral acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed by the disappearance of peak at 3430 and 1630 cm^{-1}. The total disappearance of these peaks also indicates that the particles surface is completely covered with the adsorbed Si69.

The chemical modification of the BA-Si particles can also be supported from the thermogravimetric analysis. Strictly speaking the TGA provides information related to the thermal stability and the chemical composition of the composites. Figure 4 shows the plots of derivative (DTG) of wieght loss (%Δm/min) as a function of temperature for pure Si69, BA-Si-Si69, and BA-Si particles. The peaks of the DTG curves correspond to the maximum Δm. A significant difference in the temperatures at the maximum Δm can be observed of all the samples. This variation is due to the different

chemical composition of the samples. On comparison, for pure Si69 the maximum Δm occurs at 268°C, while for the BA-Si-Si69 it shifts to 300°C (inset plot in Fig. 4).

The TGA results shows that coupling agent is chemically bonded to the hyrdoxly groups of the silica, rather than a mere physical adsorption. In case of the BA-Si particles, no major changes in Δm are observed except a peak at 641°C (inset plot in Fig. 4). The exact explanation is not known, however the influence of a nitrogen enviornment as well as the pan effect cannot be ignored.

The surface energy of the BA-Si-Si69 and BA-Si particles is depicted in Figure 5. The BA-Si particles show both the polar and dispersive part of the surface engery, whereas the BA-Si-Si69 particles show
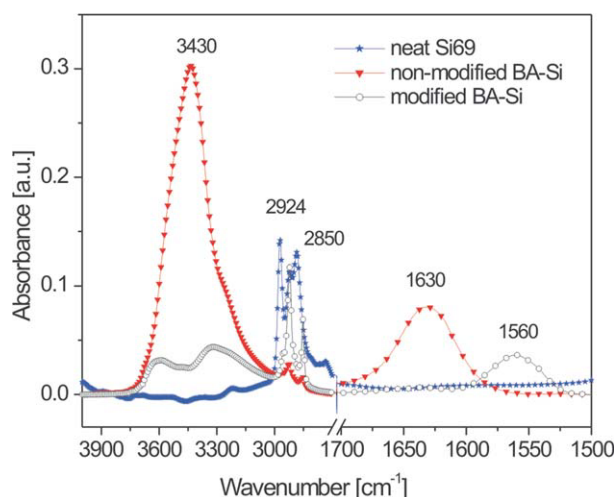
Figure 3 FTIR spectra of the neat Si69, nonmodified, and modified BA-Si particles in the range from 1500 to 4000 cm^{-1}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

only the dispersive part. After modification with Si69 the the polar part of surface energy diminishes due to the formation of Si-O-R.

The purification and surface modication effect can be observed in the scanning electron micrographs shown in Figure 6(a–c). The micrographs show that the silica particles are in the form of agglomerates because of the strong filler–filler interaction. The acid treatment of the impure coal ash particles helps in leaching out of the undesired mineral oxide etc. as shown in Figure 6(a) (prior to acid treatment) and Figure 6(b) (postacid treatment). Because of the leaching out of such particles, the agglomerates are physically modified and results in the development of porous structure as is evidenced in Figure 6(b). The surface area also increased due to the formation
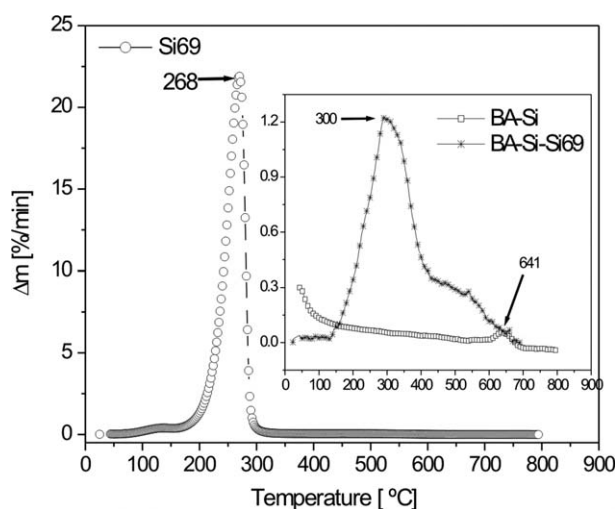

Figure 4 DTG plot of the neat Si69, BA-Si, and BA-Si-Si69 modified silica particles.
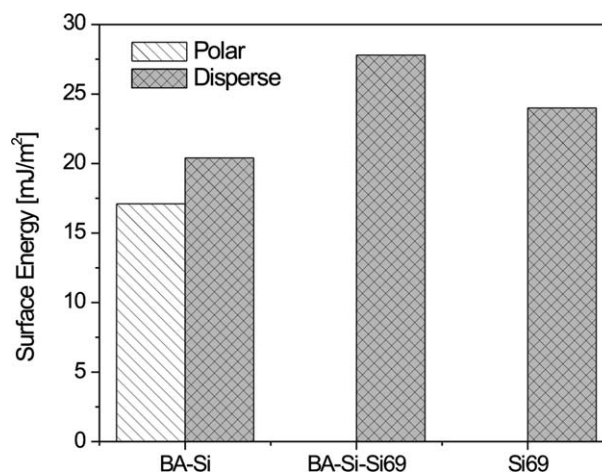

Figure 5 Surface energy plot of the neat Si69, modifed (BA-Si-Si69), and nonmodified (BA-Si) particles.

of such unique porous like structure. As discussed earlier the increase in the BET surface area is due to the formation of porous structure which is due to the leaching out of the metal ions. From the SEM micrographs it seems that the increase in the BET surface area is predominently by the increase in the porsity of the purified particles. The physically modified particles were further chemically modified using Si69 and the resulting micrograph is shown in Figure 6(c). The particles appears not only chemically but also physically modified. This can be evidenced that the fine porous stucture has changed to fine particles of ~10 nm size. However, these particles combine together to form bigger agglomerates.

Figure 7 shows the stress strain curves of the unfilled and filled SSBR/BR composites. The addition of silica, either modified or unmodified clearly demonstrate an improvement in the mechanical properties in comparison to the pure SSBR/BR gum. However, in case of the silica based-composites, the reinforcement effect is much higher for the modified silica particles (coupsil 8113) as compared to the coal ash silica (BA-Si-Si69 and BA-Si particles). Furthermore, the BA-Si-Si69 based-compoistes shows better stress-strain behaviour than the BA-Si. Beside other factors, such variation in the stress strain behavior is primarily associated with the interaction between silica particles and the rubber matrix. To enhance the filler polymer interaction, modifcation of the silica particles is required and this is evidenced in the mechanical properties of the BA-Si-Si69 based-composite. This is because of the reinforcing effect arising due to the silica modification as can be observed from the SEM micrographs shown in Figure 8(a–c). In the case of coupsil 8113 based-composite the particles are uniformally dispersed in comparison with the others. This indicates better dispersion and compatibility of the silica particle with the rubber matrix. The modification of the BA-Si-Si69 particles also demonstrates
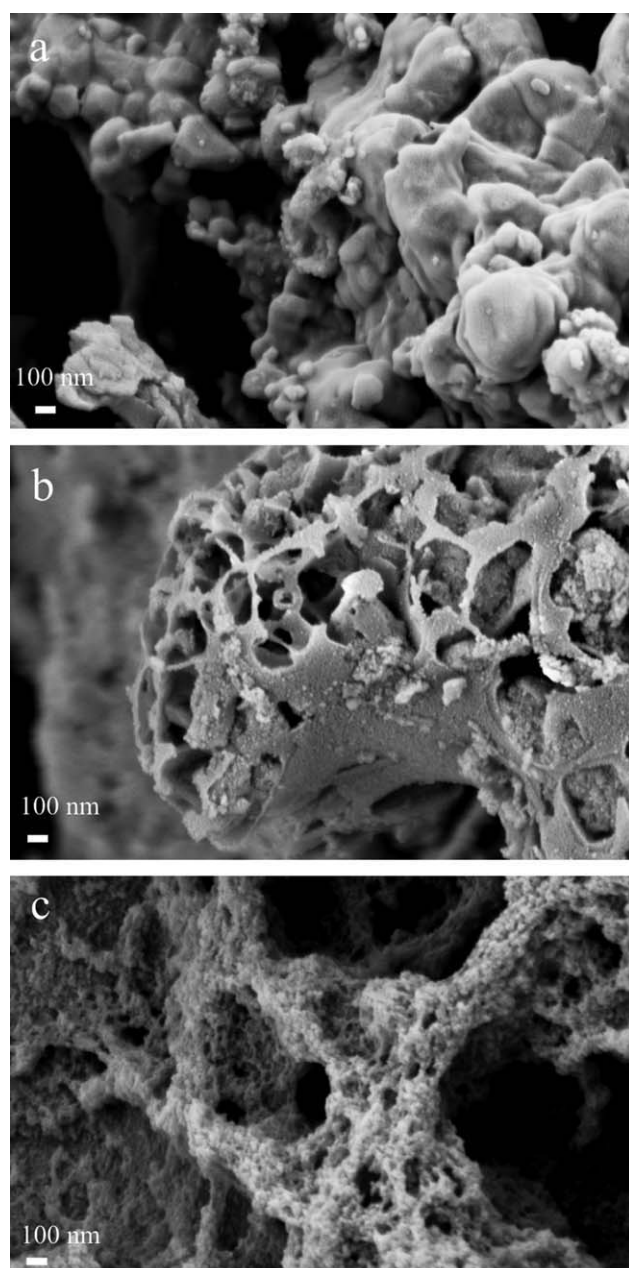
Figure 7 Comparison plot of tensile strength vs elongation of the unfilled and filled SSBR/BR composites.

Figure 6 (a–c) SEM micrographs of V-BA (a), BA-Si (b), and BA-Si-Si69 (c) particles.

better dispersion and compatibility as compared with the BA-Si. It has been observed that some traces of Fe_2O_3 which could not be completely removed during the purification process. This fact is also supported from the XPS analysis discussed earlier where iron element were detected in purified coal ash. This could also be one of the reasons that the reinforcement potential of Si-Si69 particles is comparatively lower than the coupsil 8113.

CONCLUSION

It has been shown that the modified coal ash silica has the potential to be used as a reinforcing filler in rub-
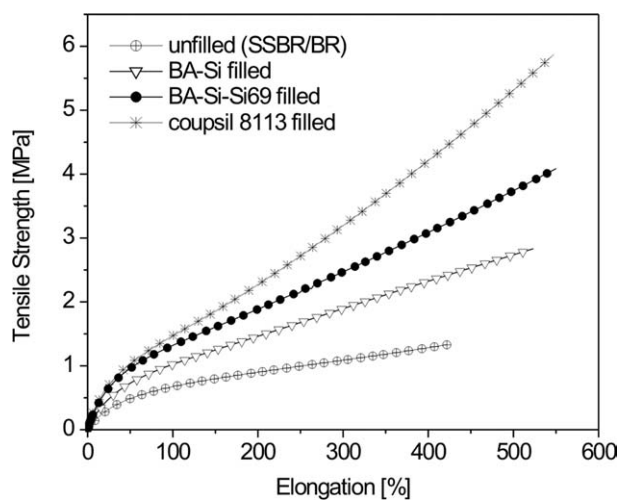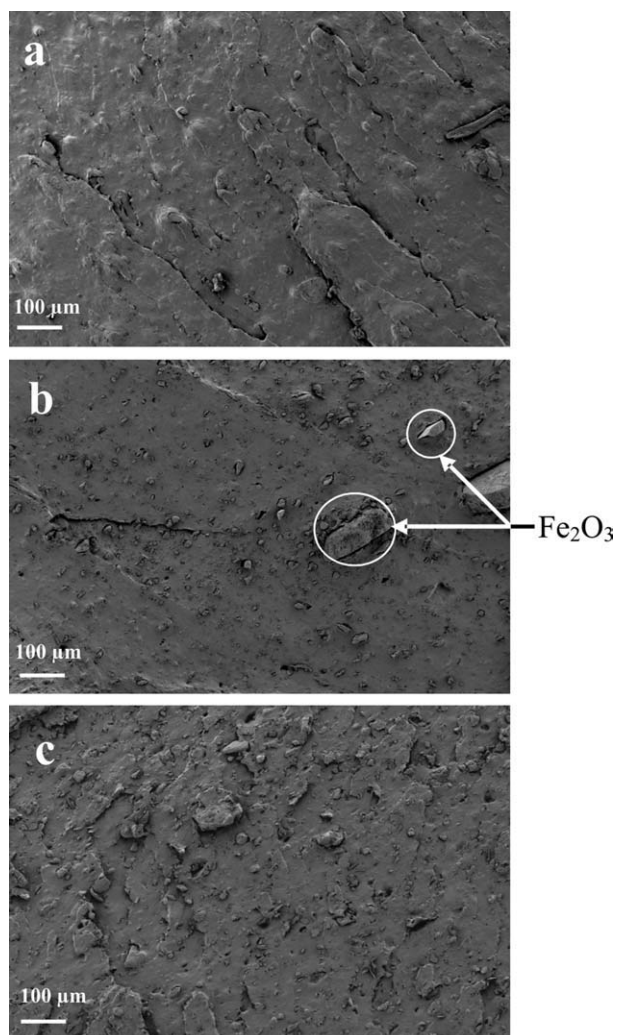
Figure 8 (a–c) SEM micrographs of coupsil 8113 (a), BA-Si (b), and BA-Si-Si69 (c) filled SSBR/BR composites.

ber matrix. The coal ash was first chemically purified and afterwards successfully modified with Si69. The SEM micrographs show that most of the unwanted mineral oxides were leached out from the silica surface during chemical treatment. On the other hand, the spectroscopic analysis reveals the presence of hydroxl functional groups (-OH), an indication of successful functionalization of the purified silica particles. Amongst the filled rubber composites, the Si69 modified particles (BA-Si-Si69 & coupsil 8113) have shown improved mechanical properties. This is due to the enhanced dispersion and interaction of the modified silica particles with the rubber matrix. The rubber composites filled with unmodified coal ash silica exhibited inferior mechanical properties. This is due to the lack of reinforcement capability of the particles. On the contrary, the coupsil 8113 demonstrated enhanced reinforcement than both grades of coal ash silica (BA-Si-Si69 & BA-Si). However, partial extraction of various inert components such as Fe_2O_3 particles and the presence of various other impurities may compromise the reinforcing ability of BA-Si-Si69 particles. It can be concluded that coal ash silica has the potential to further improve the mechanical properties, provided the level of purification as well as the surface modification are upgraded.

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