Effect of Coupling Agent on the Mechanical Properties of Fly Ash–Filled Polybutadiene Rubber

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ABSTRACT: Fly ash, a waste product of thermal power stations generated in huge quantities, has been posing problems of its disposal. As such it contains a variety of inorganic oxides and is available in finely powdered form. Attempts have been made for its use as a filler in elastomers and plastics. It is important to note that fly ash used in in untreated form does not significantly enhance the mechanical properties of composites. In this work, fly ash treated with silane coupling agent (Si-69) was used as a filler in polybutadiene rubber (PBR). The comparison of properties of composites filled with treated and untreated fly ash revealed that the composites with treated fly ash showed better reinforcing properties. Thus the silane coupling agent used here promoted adhesion between fly ash and the PBR. The improvement in mechanical properties in general and tensile properties (tensile strength, modulus 100% and modulus 200%, hardness) of the composites in particular were observed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1322–1328, 2004

Key words: polybutadiene rubber; silane coupling agent; fly ash; composites; mechanical properties

INTRODUCTION

Expanding industrial activities demand materials that are expected to satisfy increasing requirements of strength, modulus, heat distortion temperature, low coefficient of expansion, and reduction in cost. This demand has provided a wide scope for the use of polymeric composite materials. The strength of the composite can be improved by the use of coupling agents.

Silane coupling agents are considered useful as promoters of adhesion between mineral fillers and organic matrix. They impart improved mechanical strength as well as chemical resistance to composites.[1] The silane coupling agents with the appropriate functionality provide chemically bonded coupling between the mineral filler particles and the rubber network and are responsible for the improved reinforcing action of mineral fillers. The alkoxy group of the silane coupling agent can be easily hydrolyzed to generate the silanol group (–Si—OH) in aqueous solution during silane treatment.

The effect of coupling agent on the mechanical properties of fly ash–filled polybutadiene rubber (PBR) is the focus of this article. Fly ash, an absolutely low cost inorganic waste product of thermal power stations, continues to pose a hazard and must thus be used in applications that help to curb environmental pollution.

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Attempts have been made to use fly ash purposefully for various applications,[2–4] for example, in the chemical field, agricultural field, cement and construction industries, and polymer industries, but very few attempts have been made for its use as a filler in elastomers and plastics,[2,3] which could be the largest field for its large-scale use.

Si-69 was selected because it is used to improve the reinforcing capability of fillers with the silanol group on their surface (e.g., silicas, silicates, clay, etc.), and also as an integral part of curing systems to improve crosslinking network properties. The main constituent of fly ash is silica, and thus Si-69 was selected.

However, silica particles tend to agglomerate because of hydrogen bonding of silanol groups, which are functional groups on the surfaces of the silica particles. For improving the dispersion of silica particles into rubber, the mixing time must be increased. When dispersion of silica particles into rubber is insufficient, a problem of processability may arise.

Moreover, the surfaces of the silica particles are acidic. Therefore, basic substances used as vulcanization accelerators are rendered inefficient. These problems are overcome by using a commercial silane coupling agent like Si-69 developed by Degussa-Huls (Germany).

EXPERIMENTAL

Materials

The coupling agent [(Si-69): bis(3-triethoxy silyl propyl) tetrasulfide] was imported from Degussa-Huls

TABLE I
Physical Characterization of Coupling Agents (Si-69)

Chemical name	Bis(3-triethoxy silyl) propyl tetrasulfide
Typical purity	95%
Molecular weight	639.06
Specific gravity	1.07
Refractive index	1.074
Flash point	91°C
Boiling point	250°C
Density, g/cm	1.0850
Viscosity	11–12 cp
pH	7–9

(Germany), whose physical characteristics are detailed in Table I. Fly ash was procured from the thermal power station at Deepnagar, Bhusawal [Jalgaon (M.S.), India]; its constituents are presented in Table II. PBR, a *cis*-1,4-polybutadiene rubber was manufactured by Indian Petrochemical Corp. (IPCL, Baroda, India) (see Table III), and other chemicals used were manufactured by Bayer India Ltd.

Particle size analysis

Surface area is a major parameter in connection with filler–matrix interaction for reinforcing purposes. The finer the particle size, the greater the surface area and the greater the reinforcement. Details regarding particle size distribution of the fly ash used in this study are given in Figure 1. The data were used to determine the mean particle size, which was found to be 2 μm. The analysis was done on a Shimadzu SALD-2001 instrument (Shimadzu Asia Pacific, Singapore).

Treatment of fly ash by coupling agent

The coupling agent (1 g) was mixed[12,13] with ethyl alcohol (100 mL) to make a solution for applying to the filler (100 g). One gram of the coupling agent was used per 100 g of fly ash. The filler (fly ash) was mixed with the solution of coupling agent in ethanol with stirring to ensure uniform distribution of the coupling agent; mixing was continued for 30 min. The treated filler (fly ash) was then dried at 100°C in an oven for about 5 h to allow complete evaporation of the ethanol.

TABLE II
Constituents of Fly Ash

Compound	Percentage
Silica (SiO_2)	63.00
Alumina (Al_2O_3)	29.00
Magnesium oxide (MgO)	03.50
Potassium oxide (K_2O)	00.30
Calcium oxide (CaO)	00.15
Sodium oxide (Na_2O)	00.15

TABLE III
Characteristics of Polybutadiene Rubber

Trade name	Cisamer 1220
Manufacturer	IPCL Baroda, India
Description	*cis*-1,4-Polybutadiene
Polymerization system	Solution
Microstructure	98% *cis*
Dispersity	5.2
Mooney viscosity	43

Preparation of composites

Compounding of the rubber was carried out on a laboratory-scale two-roll mill. The rubber was first masticated for 5 min. Additives were added sequentially as given in Table IV. After addition of all of the additives, the compounding was continued for 30 min to ensure homogeneous mixing of the additives. This compounded matter was then vulcanized using a sulfur system by the press-curing method (compression-molding machine) at 150°C for 30 min in a chrome-plated mold having cavity dimensions of 15 $\times$ 15 $\times$ 0.3 cm.

Scanning electron microscopy (SEM)

SEM was carried out by Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, UK). Polymer specimens were coated with gold (to thickness of 50 μm) in an automatic sputter coater (scanning electron microscope coating unit E 5000; Polaron Equipment, UK), at an acceleration potential of 20 kV. Microphotographs of representative areas of the sample were taken at different magnifications (Figs. 2 and 3).

Measurement of mechanical properties

Mechanical properties such as tensile strength and moduli at 100 and 200% were determined by subjecting dumbbell-shape specimens (in conformation with ASTM D-412) to a universal testing machine (R&D Equipment, Mumbai, India). The sheets from which specimens were cut had been conditioned for 24 h before subjecting to universal testing machine (100 kg load cell), at a crosshead speed of 50 cm/min. Hardness was measured on a durometer (Blue-Steel, India) on the Shore A scale.

RESULTS AND DISCUSSION

Comparison between treated and untreated fly ash–filled PBR composites was made by testing the composites for mechanical properties: tensile strength, moduli at 100 and 200%, and hardness.

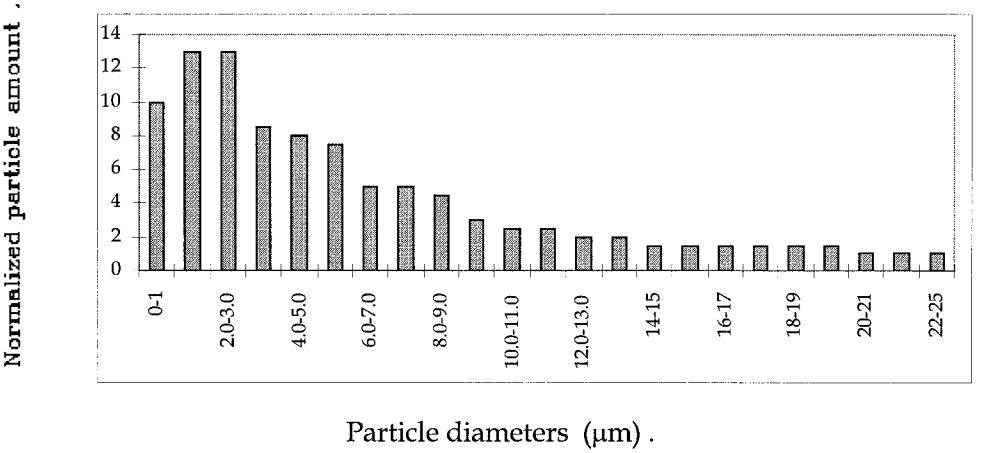


Figure 1 Graph of particle size distribution of fly ash.

Treated fly ash composites showed improvement in mechanical properties and the mechanism of adhesion attributed to the coupling agent was proposed for fly ash as a filler.

Figures 4 and 5 depict SEM microphotographs of PBR composites of untreated and treated fly ash. It is clear from the micrographs that the distribution of treated fly ash in the rubber matrix is quite homogeneous.

Tensile strength

The dependency of the tensile strength on volume fraction of fly ash is represented in Figure 6. It is seen that on increasing the volume fraction of (both treated and untreated) fly ash, the tensile strength increases to a certain value because the filler has reinforcing ability. Both the treated as well as untreated showed this ability. The treatment proved to improve substantially the extent of reinforcement. After attaining a maximum value (corresponding to 0.52 volume fraction), the decline in tensile strength began, which was attributed to the dewetting effect resulting from inadequate matrix material to hold filler particles. The peak values of tensile strength of the composites correspond to 2.0 and 1.7 MPa, for treated and untreated fly ash, respectively. It is noteworthy that the tensile strength of fly ash–treated PBR composites is higher than that of untreated fly ash–PBR composites.

TABLE IV
Compounding Recipe

Component	Proportion
PBR	100
Stearic acid	2.0
Zinc oxide	3.0
Antioxidant[a]	1.0
Accelerator (I)[b]	0.5
Accelerator (II)[c]	0.5
Sulfur	1.5
Treated filler	Variable
Curing time	30 min
Curing temperature	150°C

[a] Antioxidant: *N*-(1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene diamine.
[b] Accelerator (I): tetramethyl thiuram disulfide (TMTD)
[c] Accelerator (II): zinc diethyl dithiocarbanate (ZDC)

Moduli at 100 and 200% elongations

The dependency of moduli at 100 and 200% elongation with volume fraction of treated and untreated fly ash–PBR composites is depicted in Figures 7 and 8, respectively. It is seen that in both cases the moduli initially increase, attaining a maximum value for a particular value of filler concentration, after which values decrease. The peak values of moduli of both composites lie between 0.5 and 0.6 volume fractions of both treated and untreated fly ash. The modulus of treated fly ash is about 2.13 times higher than that of untreated fly ash. The initial rate of increment in the property with increasing volume fraction of the filler was similar in both cases; however, after volume fraction 0.4 the rate of increment for composites filled with treated fly ash was substantially higher.

PBR–fly ash interaction

A mechanism[4–8] of PBR–fly ash interaction resulting from the incorporation of Si-69 into fly ash–filled PBR can be proposed in the following three steps. The unsaturated backbone of PBR, the interaction between PBR and fly ash through condensation of silane coupling agents (Si-69), and surface hydroxyl groups of filler with silanol groups of coupling agent (Si-69) are represented below.

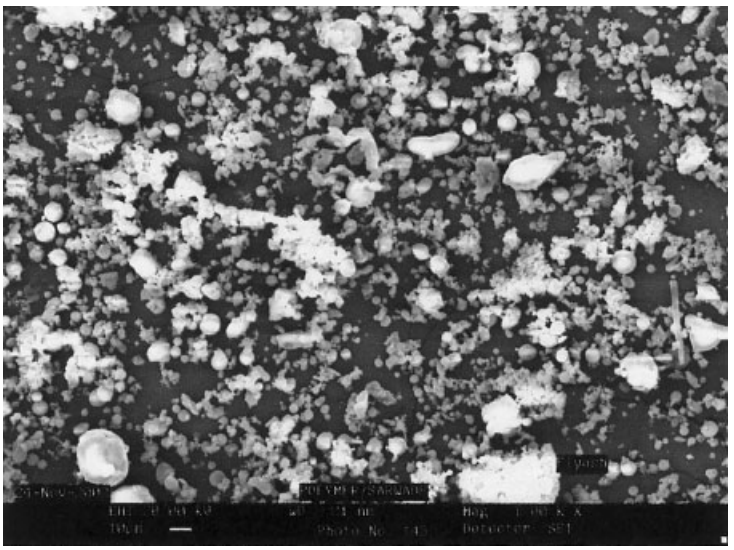


Figure 2 SEM microphotograph of untreated fly ash (microsize: 75 μm).

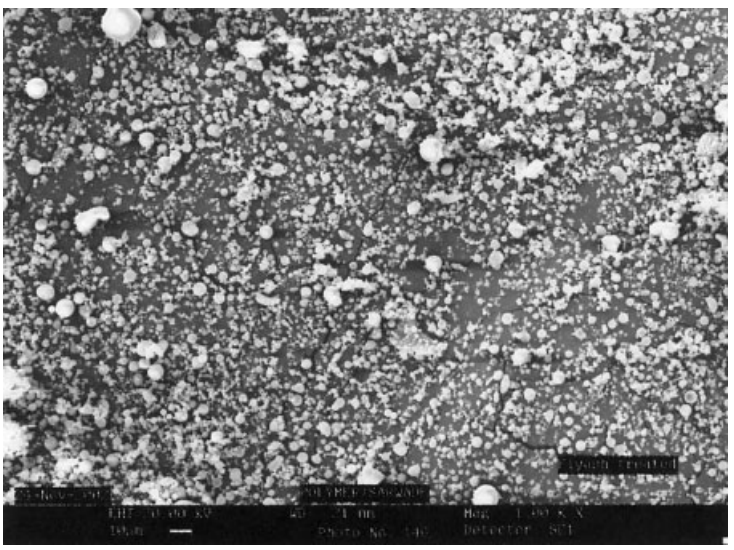


Figure 3 SEM microphotograph of treated (Si-69) fly ash (microsize: 75 μm).

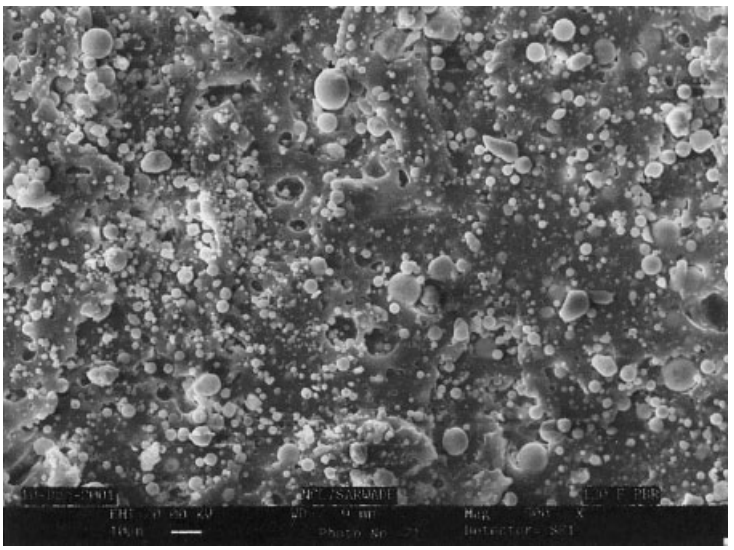


Figure 4 SEM microphotograph of untreated fly ash–filled PBR (volume fraction: 0.558).

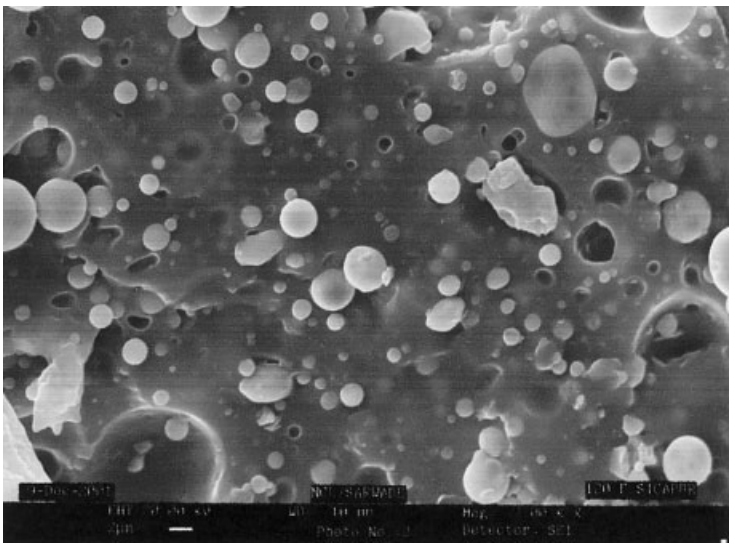


Figure 5 SEM microphotograph of treated fly ash–filled PBR (volume fraction: 0.566).

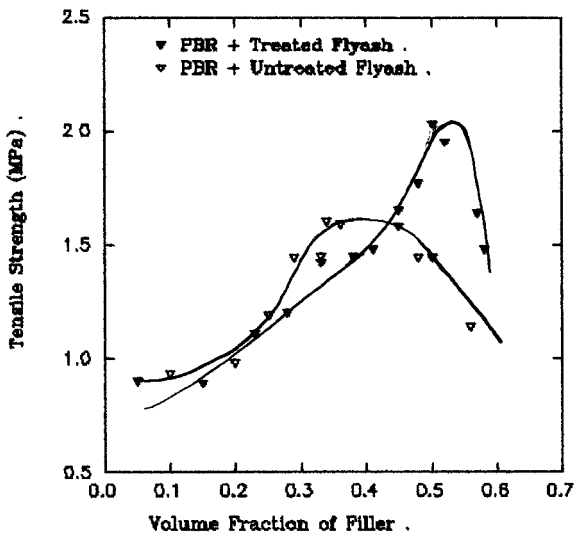


Figure 6 Tensile strength as a function of volume fraction of treated and untreated fly ash–PBR composites.

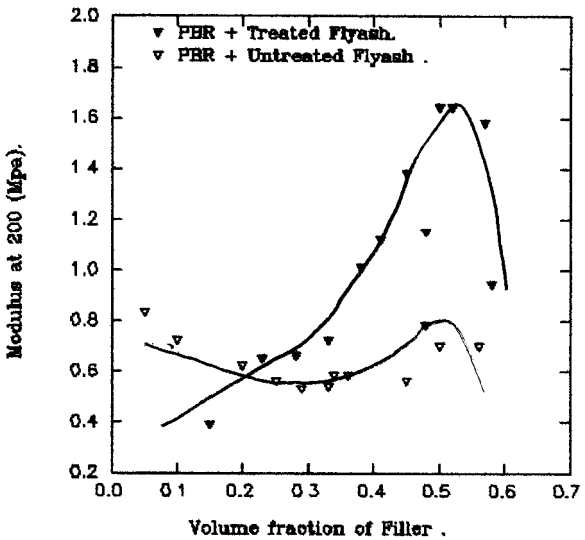


Figure 8 Modulus at 200% as a function of volume fraction of treated and untreated fly ash–PBR composites.

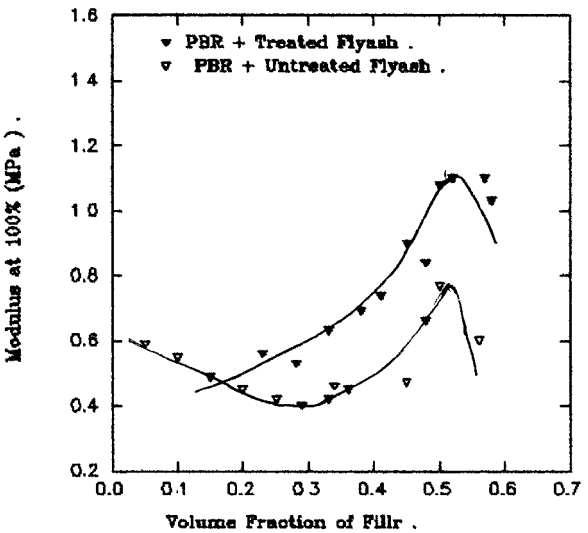


Figure 7 Modulus at 100% as a function of volume fraction of treated and untreated fly ash–PBR composites.

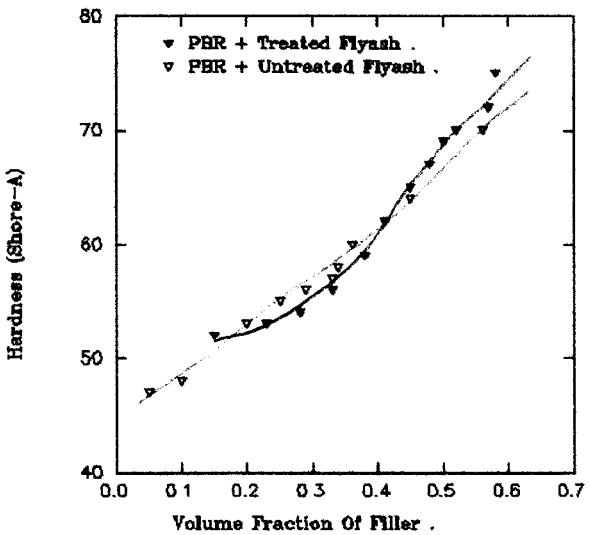
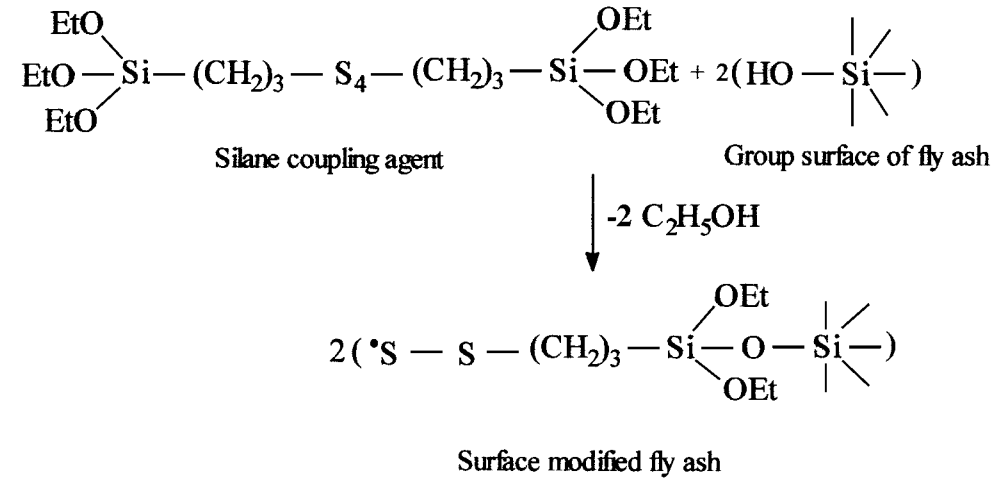
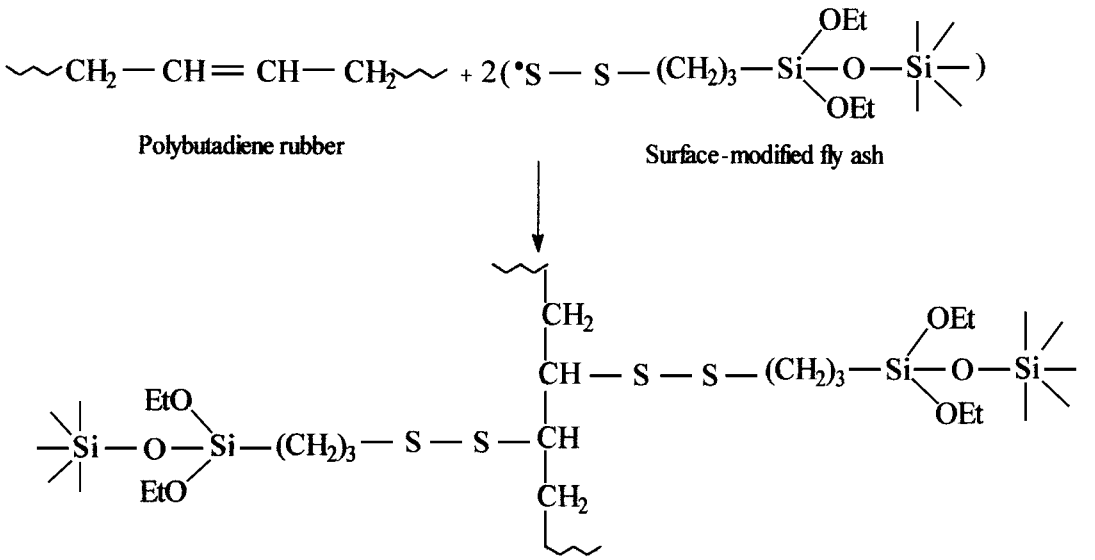


Figure 9 Hardness as a function of the volume fraction of treated and untreated fly ash–PBR composites.

I. Reaction between coupling agent and fly ash (surface)



II. Reaction between surface-modified fly ash and unsaturation in PBR



According to the above reaction scheme, a single molecule of Si-69 can couple free radically with one olefinic unit of the elastomer molecule and also two –OH groups of fly ash, resulting in an increased elastomer–filler interaction.

Hardness

Figure 9 shows the dependency of the hardness on concentration of treated and untreated filler in PBR. It is seen that hardness of the treated and untreated fly ash–PBR composite linearly increases on increasing the concentrations of fillers; however, hardness does not increase abruptly on increasing the concentration of untreated fly ash. Thus it is clear from Figure 9 that the treated fly ash–rubber composites did not show a change in hardness that was more significant than that of the untreated fly ash–rubber composites.

Because the coupling agent is liquid in nature and a lesser quantity was used, it was not expected that the treatment would increase the hardness as occurs in the case of addition of inorganic fillers.

CONCLUSIONS

1. The treated fly ash–PBR composites show superior values of tensile strength compared to those of untreated composites, showing the effect of coupling agent.

2. A similar trend was observed, as in the case of tensile strength, in the behavior of modulus as a function of volume fraction of filler. Higher values of modulus were obtained in the case of treated fly ash composites, indicating the involvement of coupling agent in the composites.
3. The hardness of treated fly ash–filled composite was not significantly changed.

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