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Studies on the Effect of Silane Coupling Agent (2.0%) on the Mechanical Properties of Flyash-filled Polybutadiene Rubber

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Flyash, a waste product of thermal power stations which is generated in huge quantities, poses problems in its disposal. It contains a variety of inorganic oxides and is available in finely powdered form. Attempts have been made for its utilisation as a filler in elastomers and plastics. It is important to note that flyash in untreated form does not contribute in enhancing mechanical properties of composites significantly. In this paper, flyash treated with silane coupling agent (Si-69®) was studied as a filler in polybutadiene rubber. A comparison of properties of composites filled with treated and untreated flyash revealed that the composites with treated flyash exhibited better properties. Flyash treated with silane coupling agent gave greater reinforcement than untreated flyash. The treatment resulted in the enhancement of mechanical properties of composites of the said rubber. In this study, properties of composites filled with treated and untreated flyash were compared. The properties studied were tensile strength, modulus at 100% and 400%, Young's modulus and hardness. Tensile strength was improved by 193%, modulus at 400% improved by 700% and Young's modulus improved by 170%.

Key words: polybutadiene rubber; silane; coupling agent; flyash; composites; mechanical properties; Si-69®

Flyash is an absolutely low cost inorganic waste product of thermal power stations is posing a menace and hence requires to be utilised for curbing environmental pollution. Attempts have been made to utilise flyash meaningfully for various purposes[1–2] *viz*. chemical field, agricultural field, cement and construction industries *etc*., but very few attempts have been made as a filler in elastomers and plastics[3,4] which could be the largest field for its large-scale utilisation. As such, flyash does not contribute to reinforcement in its untreated form. It was reasoned that promotion in adhesion between its surface with matrix material could bring about reinforcement. Coupling agents which work as molecular bridges at the interface between two dissimilar substrates, such as inorganic fillers and an organic polymer matrix[5], were considered in the study.

Typically, silane-treated inorganic fillers are hydrophobic, organophilic and organo-

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functional. When incorporated into polymer systems, they often promote adhesion, catalyze, improve dispersion and rheology. Furthermore, it also improves impact strength, prevent embrittlement, improves mechanical properties *etc*. Reactivity of such coupling agents is possible with diverse substrates[3–11]. A study on the effect of treatment has been carried out earlier using flyash treated with 2% silane coupling agent[14–15]. The results of the study were encouraging and hence this work was undertaken to ascertain the effect treatment of 2.0% coupling agent on the tensile properties of composites.

EXPERIMENTAL PROCEDURE

Materials

The coupling agent [(Si-69®): Bis (3-triethoxy silyl propyl) tetrasulphide] was imported from Degussa-Huls of West Germany. The flyash was procured from the thermal power station of Deepnagar, Bhusawal, Jalgaon (M.S), India. The *cis*-1, 4-polybutadiene rubber was manufactured by Indian Petro-chemical Corporation Limited, Baroda, India. The other chemicals used (such as a stearic acid, zinc oxide, N - (1,3 - dimethyl butyl) - N - phenyl - *p* - phenylene diamine (antioxidant), tetramethyl thiuram disulphide (TMTD), zinc diethyl dithiocarbamate (ZDC) and Sulphur) were manufactured by Bayer India Ltd. The physical parameters of the silane coupling agent, the constituents of the flyash and the characteristics of the polybutadiene are reported in *Tables 1*, *2* and *3*, respectively.

Particle Size Analysis

Surface area is a major parameter in connection with filler-matrix interaction for reinforcing purposes. The finer the particle size, the higher is the surface area and hence the higher the reinforcement. The details regarding particle size distribution of the flyash used in the study are given in *Figure 1*. The data was used to establish the mean particle size, which was found to be 2 µm. The analysis was obtained from a Shimadzu SALD –2001 instrument by a Shimadzu (Asia Pacific) Pvt. Ltd. Singapore.

Treatment on Flyash by Silane Coupling Agent

The coupling agent (2 g) was mixed[2–14] with ethylalcohol (100 mL) to make a solution for applying to the filler (100 g). One gram of the coupling agent was used for 100 g of flyash. The filler (flyash) was mixed with the solution of coupling agent in ethanol which was continuously stirred to ensure uniform distribution of the coupling agent, mixing was continued for 30 min. The treated filler (flyash) was then dried at 100ºC in an oven for 5 h to allow complete evaporation of the ethanol.

Preparation of Composites

The compounding of the rubber was carried out on a laboratory scale two-roll mill. The rubber was first masticated for 5 min and then the ingredients were added sequentially as shown in *Table 4*. After the addition of all of the components, the compounding was then continued for further 30 min to ensure a homogeneous mix. The curing characteristics were determined using a multichannel DTA. The curing time was determined by subjecting compounds to DTA at 150ºC for various intervals and observing the thermograms[3-5].

This compounded matter was then vulcanised using sulphur system by press curing method (compression moulding machine) at 150ºC for

TABLE 1. PHYSICAL CHARACTERISATION OF COUPLING AGENTS (SI-69®)

Item	Particulars
Chemical Name	Bis (3 –triethoxy silyl) propyl tetrasulphide
Typical purity	95%
Molecular weight	639.06
Specific gravity	1.07
Refractive index	1.074
Flash point	91ºC
Boiling point	250ºC
Density (g/cm)	1.0850
Viscosity	11–12 cp
pH	7–9

TABLE 2. CONSTITUENTS OF FLYASH

Compounds	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 3. CHARACTERISTICS OF POLYBUTADIENE RUBBER

Item	Particulars
Trade Name	Cisamer 1220®
Manufacturer	IPCL Baroda, India
Appearance	Light amber/bale
Polymerization system	Solution
Microstructure	98% *cis*
Specific gravity	0.91
Mooney viscosity	43 ML_{1+4} 100ºC
Ash content	0.1%

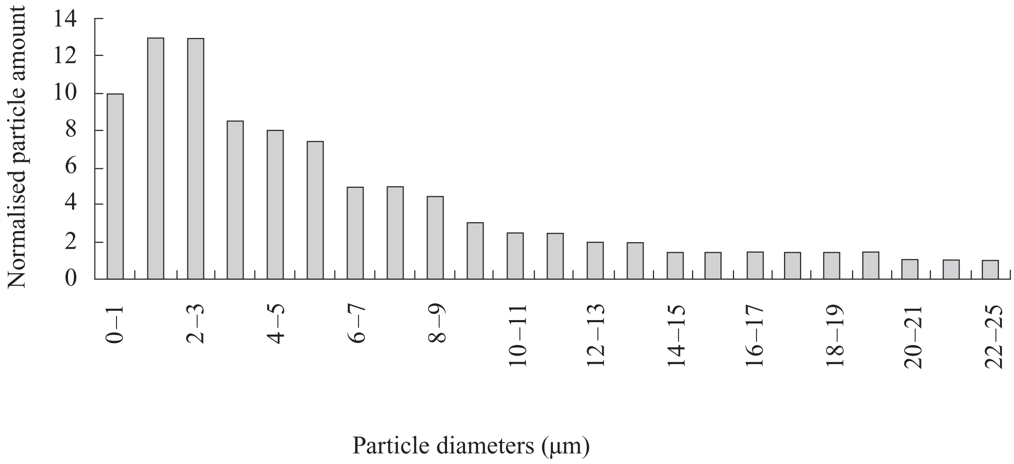


Figure 1. Particle size distribution of flyash.

TABLE 4. COMPOUNDING RECIPE

Component	Proportion
PBR	100
Stearic acid	2.0
Zinc oxide	3.0
Antioxidant[a]	1.0
Accelerator (1)[b]	0.5
Accelerator (II)[c]	0.5
Sulphur	1.5
Filler (Untreated/treated)	Variable (0–100)
Curing time	30 min
Curing temperature	150ºC

[a] N - (1,3 - dimethyl butyl) - N - phenyl - p - phenylene diamine
[b] Tetramethyl thiuram disulphide (TMTD)
[c] Zinc diethyl dithiocarbamate (ZDC).

30 min in a chrome-plated mould having cavity dimensions (15 cm × 15 cm × 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 (50 µm thick) in an automatic sputter coater (Polaron Equipment Ltd., Scanning electron microscope coating unit E 5000, UK). Acceleration potential was 20 kV. Photographs of representative areas of the sample were taken at the same magnifications.

Measurement of Mechanical Properties

Mechanical properties such as tensile strength, modulus at 100% and 400% were determined on dumbbell shaped specimens (in confirmation with *ASTMD–412*) in a universal testing machine (R & D Equipment, Mumbai, India). The sheets from which specimen were cut had been conditioned for 24 h prior to subjecting to the universal testing machine (100 kg load cell), at a crosshead speed of 50 cm/min. Hardness was measured on Durometer (Blue-steel, India) on Shore–A scale.

RESULTS AND DISCUSSION

Comparison between treated and untreated flyash-filled PBR composites was made by testing the composites for mechanical properties *viz*. tensile strength, moduli at 100% and 400%, and hardness. Treated flyash composites showed improved mechanical properties and a mechanism of adhe-sion due to the coupling agent is proposed for flyash as the filler. *Figures 2* and *3* show scanning electron micrographs of the PBR composites with untreated and treated flyash. It was clear from the figures that the distribution of treated flyash in rubber matrix was quite homogeneous.

Tensile Strength

The dependence of tensile strength on volume fraction of flyash is shown in *Figure 4*. It was observed that on increasing the volume fraction of (both treated and untreated) flyash, the tensile strength increased because the filler had reinforcing ability. Both the untreated and treated showed this ability. The treatment substantially improved the extent of reinforcement. After attaining the maximum (corresponding to 0.50 volume fraction), a decline started. This decline was because of a de-wetting effect, which resulted from inadequate matrix material to hold the filler particles. The peak values of tensile strength of the composites corresponded to 2.77 MPa and 1.20 MPa, for treated and untreated flyash, respectively. It is noteworthy that the tensile strength of flyash-treated PBR composites was much higher than that of the untreated flyash-PBR composites.

Modulus at 100% and 400% Elongation

The dependence of modulus at 100% and 400% elongation with volume fraction of treated and untreated flyash-PBR composites is shown in *Figures 5* and *6*, respectively. In both the cases, moduli increased initially, attained a maximum value for a particular value of concentration of fillers and it decreased. The peak values of moduli of both the composites lied between 0.5 and 0.52 volume fractions of flyash treated and untreated. The modulus of treated flyash was about 10 times higher than that of untreated flyash. The initial rate

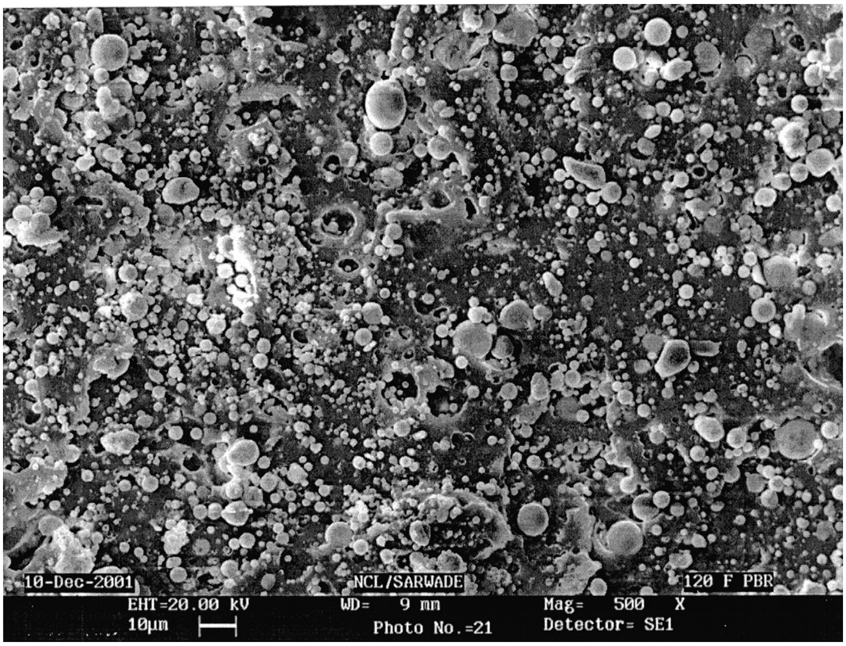


Figure 2. SEM of untreated flyash filled-PBR at volume fraction (0.56).

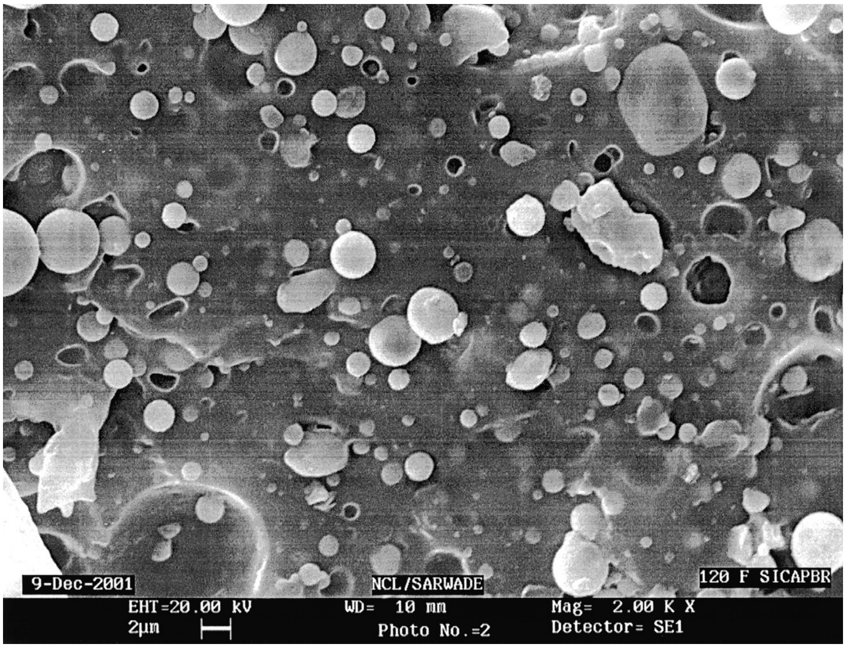


Figure 3. SEM of treated flyash filled-PBR at volume fraction (0.56).

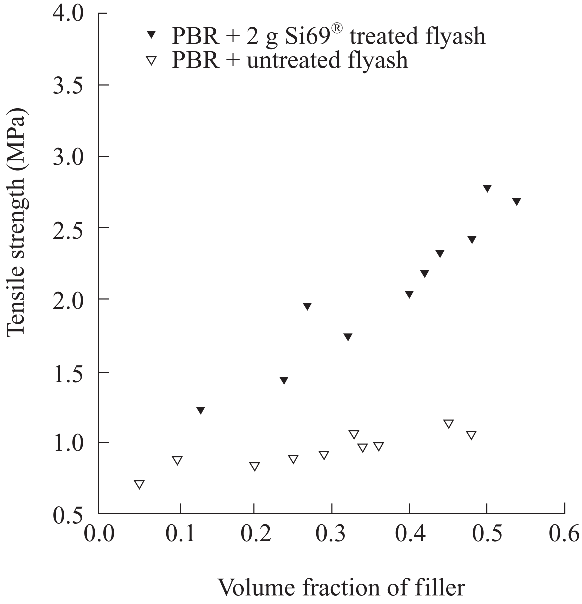


Figure 4. Tensile strength as a function of Volume fraction of treated and untreated flyash-PBR composites.

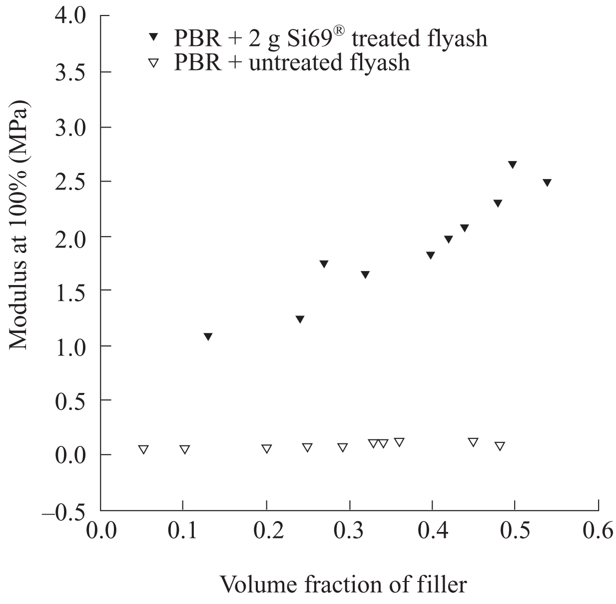


Figure 5. Modulus at 100% as a function of volume fraction of treated and untreated flyash-PBR composites.

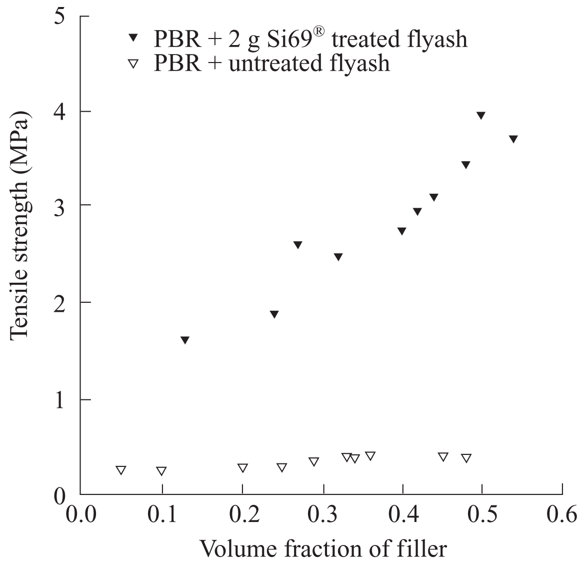


Figure 6. Modulus at 400% as a function of volume fraction of treated and untreated flyash-PBR composites.

of increment in the property with increasing volume fraction of the filler was similar in both the cases.

PBR-flyash Interaction

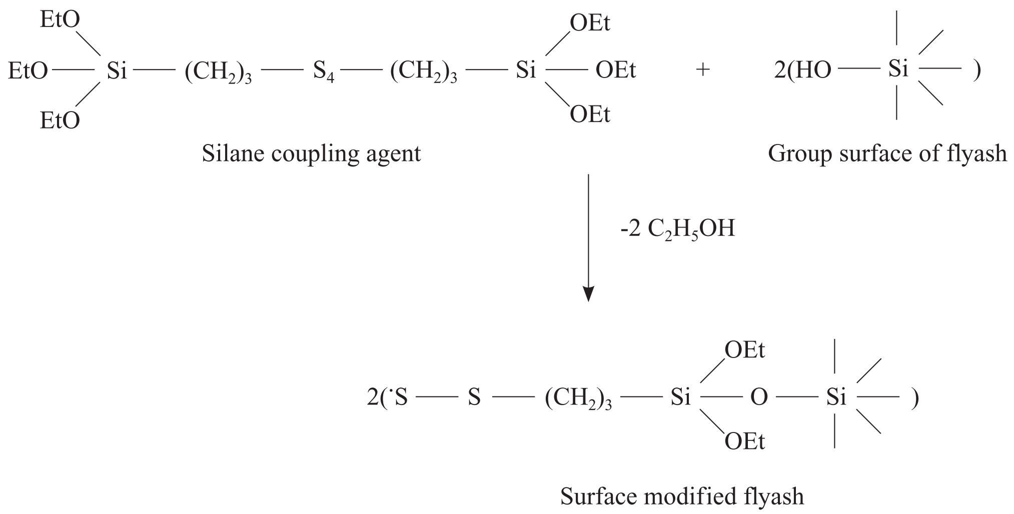
A mechanism[1–12] of PBR-flyash interaction due to the incorporation of Si-69® into flyash-filled PBR has the following two steps. The condensation of the silane coupling agent (Si-69®) with the surface hydroxyl groups of the filler followed by the reaction of the unsaturation backbone of PBR, with the modified flyash, is represented below in *Scheme 1* and *Scheme 2*.

According to the above reaction scheme (*Scheme 1* and *2*), a single molecule of Si-69® could couple by a free radical mechanism with one olefinic unit of the elastomer molecule and also two — OH groups of flyash, resulting in an increased elastomer - filler interaction.

Hardness

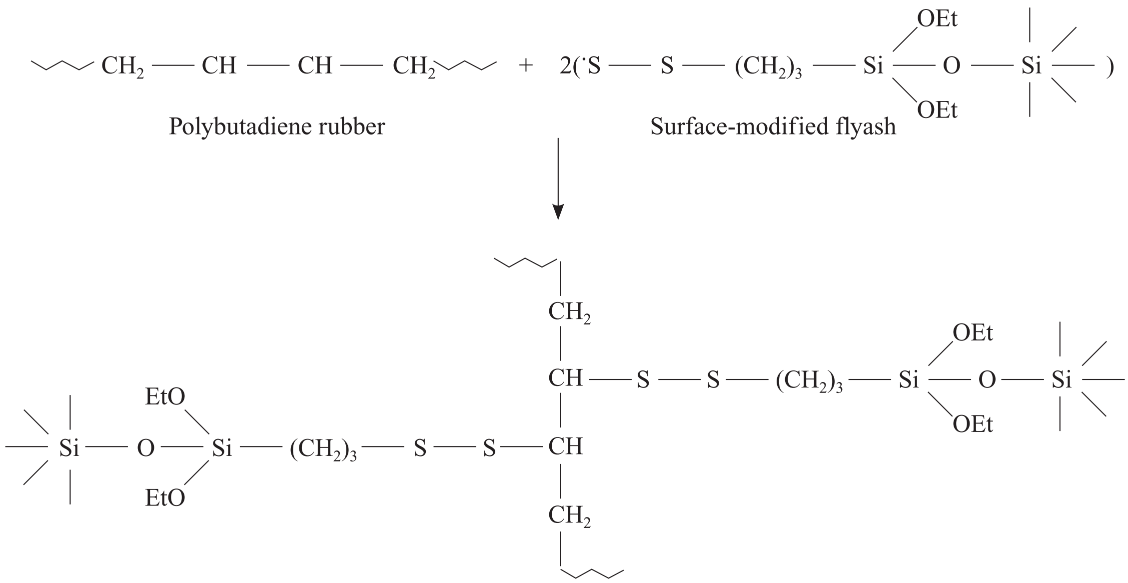
Figure 7 shows the dependence of hardness on concentration of treated and untreated filler in PBR. Hardness of the treated and untreated flyash-PBR composites increased almost linearly with the increase in the concentration of filler. However, hardness did not increase so abruptly on increasing the concentration of untreated flyash. Thus it was clear from *Figure 7* that the treated flyash rubber composites did not show a substantially significant change in hardness compared to untreated flyash rubber composites.

Step I. Reaction between coupling agent and flyash (Surface)



Scheme 1

Step II. Reaction between surface-modified flyash and unsaturation in PBR



Scheme 2

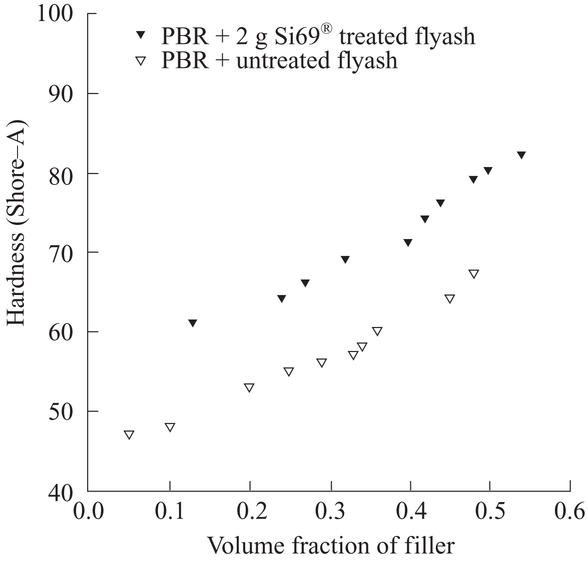


Figure 7. Hardness as a function of Volume fraction of treated and untreated flyash-PBR composites.

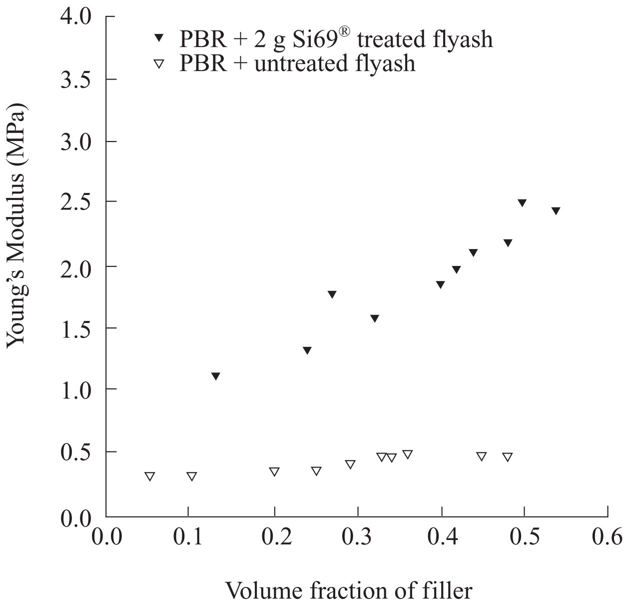


Figure 8. Young's modulus as a function of volume fraction of treated and untreated flyash-PBR composites.

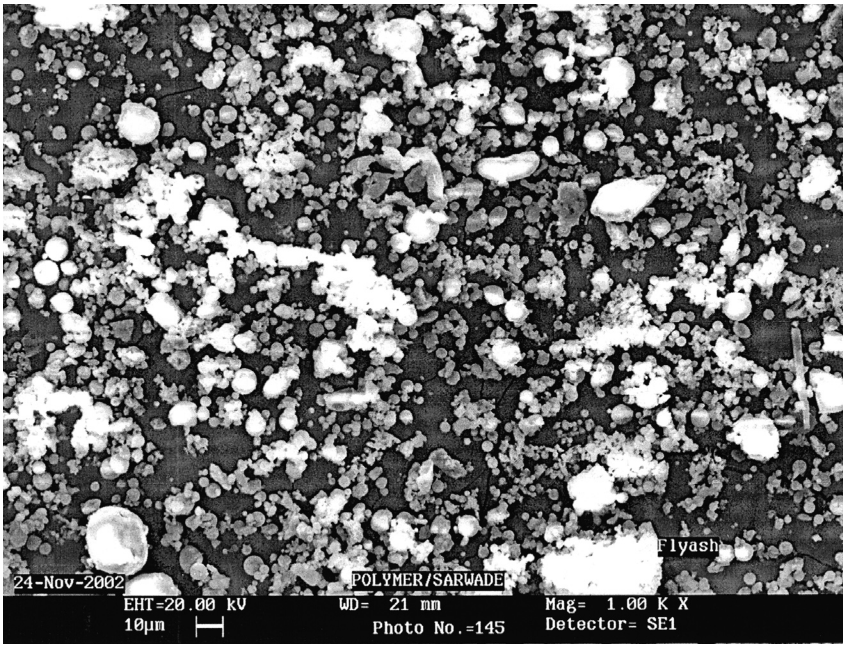


Figure 9. SEM of untreated flyash (75 µ).

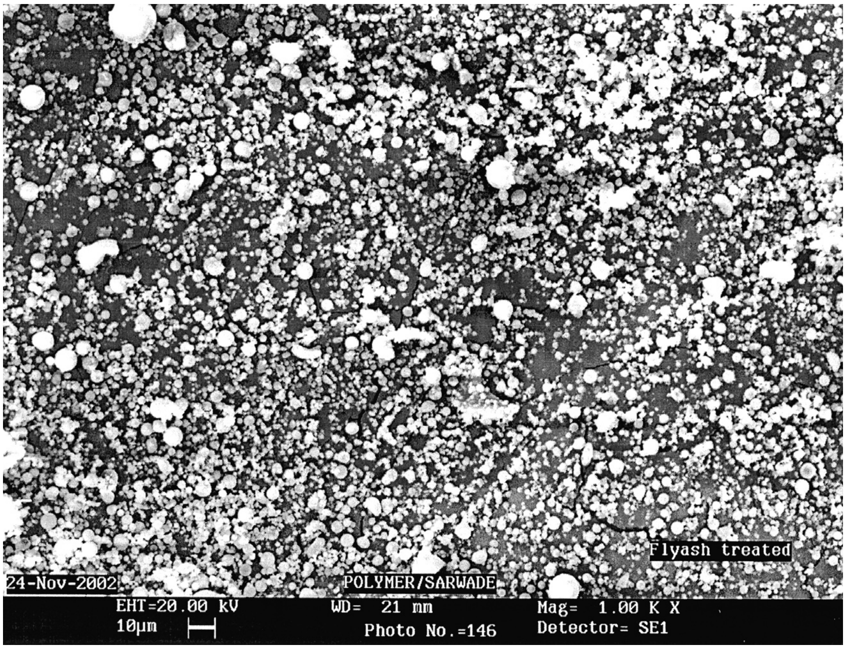


Figure 10. SEM of treated (Si-69®) flyash (75 µ).

Young's modulus

Young's modulus as a function of volume fraction of filler for treated and untreated flyash-filled PBR composites is shown in *Figure 8*. The peak value for treated flyash composites was 2.50 MPa at 0.50 volume fraction, and that for untreated was 0.46 MPa at 0.45 volume fraction, *i.e.* it exhibited about 5 times the strength of the untreated-flyash composite.

SEM of Composites

SEM photomicrographs of untreated and treated flyash filler are shown in *Figures 9* and *10*. It is evident from these photographs that treated flyash exhibited a uniform, spherical shape with a fine discrete particulate nature, while the untreated flyash showed a tendency to form agglomerates. Thus Si69® influenced the orientation of flyash particles and was thus responsible for the higher strength. SEM of fractured surfaces of untreated and treated flyash–filled vulcanisates are shown in *Figures 2* and *3*. The fractured surface of the composites filled with untreated flyash showed non-adhesive appearance and formation of agglomerates, while that filled with treated flyash showed a very uniform distribution, with a regular, adhesive appearance of the fractured surface indicating further enhancement in polymer-filler attachment.

CONCLUSIONS

The treatment of flyash with coupling agent [Bis (3-triethoxy-silyl propyl) tetrasulphide] has effected enhancement of tensile strength, modulus at 100%, and 400% elongation, and Young's modulus. The enhancement was prominent in modulus at 400% and Young's modulus, which showed that matrix filler-adhesion was made improved as result of the treatment. Further the treatment of filler resulted in incorporating the filler to a high level without compromising for quality. This shall definitely be useful for cost reduction.

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