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Effect of Silane Coupling Agent on the Mechanical Properties of Clay-filled Polybutadiene Rubber

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Clays belong to an economic class of fillers, which are used extensively in rubber and plastics. Being non-reinforcing in nature, there are limitations in their use. If the properties of filler are modified, it may get higher value as a filler. To achieve this modification of surface properties is one of the avenues. In the present work, the effect of treatment of coupling agent on clay has been studied with polybutadiene as a matrix. Composites were made with varying proportion of untreated and treated clay. A two-roll mill was used for dispersing the filler in the rubber and compression moulding technique was used to cure the compound in sheet forms. Tensile properties were measured on a computerised Universal Testing Machine according to ASTM *procedure. Comparison of properties of composites filled with treated and untreated clay showed that treatment of clay imparted better reinforcing properties. The properties under consideration were tensile strength, modulus at 100%, and 400%, Young's modulus, hardness, etc. Tensile strength improved by 54% whilst modulus at 400% was improved by 331%. Similarly Young's modulus also improved by 297% at 90 p.h.r.*

Key words: polybutadiene rubber; silane; coupling agent; clay; composites; mechanical properties; fillers; reinforcement

Clay is a low cost inorganic filler used extensively in rubber and plastics. Although it is economic, it does not reinforce the composites and there are several limitations on its use. In our efforts to find out an economical and yet a reinforcing filler, a study was undertaken on flyash earlier. Flyash was treated with various percentage of coupling agents and was incorporated in polybutadiene rubber[1,4]. Since coupling agents work as molecular bridges at the interface between two dissimilar substrates, it was reasoned that the treatment of coupling agents would convert an ordinary filler into a value-added one. The results were quite encouraging and hence the study has been extended to clay. In the present work, clay was treated with silane coupling agent (1.0% solution)[2,8]. The treated filler (in various percentages) was incorporated in polybutadiene rubber using a two-roll mill. Finally, the composites were moulded in sheet form using compression moulding technique at 150ºC. Properties under consideration were tensile strength, Young's modulus, modulus at various

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elongations, hardness *etc*. Comparison of the magnitudes of property reveal that the treatment had a favourable effect on properties of composites.

EXPERIMENTAL

Materials

Titanate coupling agent [(LICA 01®): Neopentyl (diallyl) oxy, trineodecanonyl titanate] was imported from Ken-React Petrochemical, Inc. USA. China-clay was procured from a local supplier. PBR, a *cis*-1,4-polybutadiene rubber was manufactured by Indian Petrochemical Corporation Limited, Baroda India. Other chemicals 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 used were manufactured by Bayer India Limited.

Physical parameters of polybutadiene, titanate coupling agent and constituents of clay are reported in *Tables 1*, *2* and *3*, respectively.

Particle Size Analysis

Surface area is a major parameter with respect to filler-matrix interaction for reinforcing purposes. The finer the particle size, the higher is the surface area and higher the reinforcement. The particle size distribution of the clay used in the study are given in *Figure 1*. This clearly indicates that about 60% particles had a diameter of 2 µm or less, while 90% of the filler had a particle diameter of below 6 µm. The analysis was done on a Shimadzu SALD–2001 instrument by Shimadzu (Asia Pacific) Pvt. Ltd. Singapore.

Treatment of Clay by Silane Coupling Agent

As per the recommendations of the manufacturer of the coupling agent, a 1.0% solution of coupling agent was prepared in ethanol[1,6] and applied to 100 g of clay. The solution was stirred for 30 min with the filler to ensure uniform distribution. The treated filler (clay) was then dried at 100ºC in an oven for about 5 h to allow complete evaporation of the alcohol.

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. The additives were then added sequentially as shown in the *Table 4*. After the incorporation of all of the additives, the compounding was continued for 30 min for homogeneous mixing. This compounded mix was then vulcanised using a sulphur cure system by press-curing (compression moulding machine) at 150ºC for 30 min in a chrome-plated mould having cavity dimensions of 15 cm × 15 cm × 0.3 cm. 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[4,11].

Scanning Electron Microscopy (SEM)

SEM was carried out on a 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 1000 × magnification.

TABLE 1. PROPERTIES OF POLYBUTADIENE RUBBER

Item	Particulars
Trade name	Cisamer 1220®
Manufacturer	Indian Petrochemicals Corporation Ltd
Appearance	Light amber / Bale
Polymerisation system	Solution
Micro-structure	98% *cis*
Specific gravity	0.91
Mooney viscosity	43 ML_{1+4} 100ºC
Ash content	0.1%

TABLE 2. PHYSICAL CHARACTERISTICS OF TITANATE COUPLING AGENTS (LICA 01®)

Item	Particulars
Chemical name	Neopentyl (diallyl) oxy, trineodecanonyl titanate
Typical purity	99%
Physical form	Liquid
Colour	Brownish-orange
Specific gravity	1.02
Flash point	160
Boiling point	320ºC
Viscosity	850 (cP.)
pH	5
Solubility	Isopropyl alcohol, xylene, toluene, DOP, mineral oil, MEK

TABLE 3. CONSTITUENTS OF CHINA-CLAY

Compounds	Percentage
SiO_2	46.29
Al_2O_3	38.38
Fe_2O_3	0.30
TiO_2	0.02
CaO	0.161
MgO	0.59
Na_2O	0.15
K_2O	0.15

TABLE 4. COMPOUNDING RECIPE

Component	Proportion (p.h.r.)
PBR	100
Stearic acid	2.0
Zinc oxide	3.0
Antioxidant [N - (1,3-dimethyl butyl) -N'-phenyl-*p*-phenylene diamine]	1.0
Accelerator (1) TMTD®	0.5
Accelerator (II) ZDC®	0.5
Sulphur	1.5
Filler (Treated/Untreated)	Variable
Curing Time	30 min
Curing Temp.	150ºC

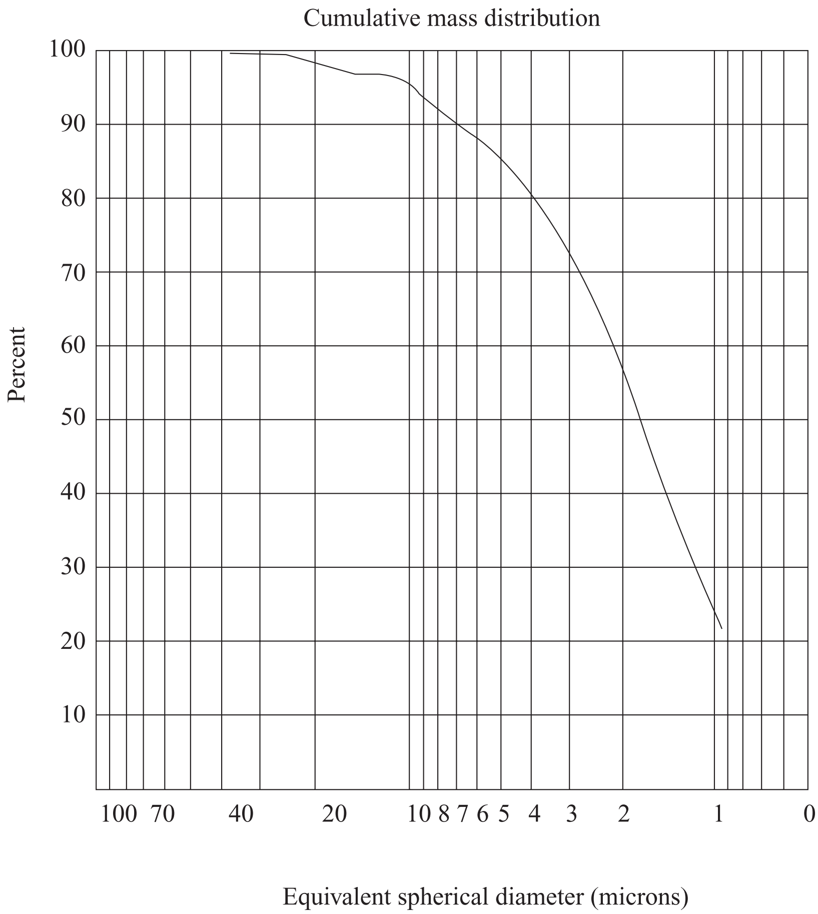


Figure 1. Particle size distribution of clay.

Measurement of Mechanical Properties

Mechanical properties such as tensile strength, modulus at 100%, 400% were determined by subjecting dumb-bell shaped specimens (in accordance 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 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

Treated clay composites showed improvement in mechanical properties and an adhesion mechanism to the clay due to the coupling agent is proposed for this.

Tensile Strength

The dependence of the tensile strength on concentration of clay is shown in *Figure 2*. It is seen that on increasing the p.h.r. of (both treated and untreated) clay, the tensile strength increases up to a certain value and then declines. The peak values of tensile strength of the composites correspond to 2.0 MPa and 1.30 MPa for treated and untreated clay composites, respectively. It is thus observed that the tensile strength of composites filled with treated clay (90 p.h.r.) is 52% higher than that of untreated clay composites.

Modulus at 100% and 400% Elongations

The dependence of modulus at 100% and 400% elongation with concentration of treated and untreated clay in PBR composites is depicted in *Figures 3* and *4* for 100% and 400% modulus, respectively. In both the cases moduli increased initially, attained a maximum value for a particular value of concentration of fillers and then decreased. The peak values of moduli of both the composites lie at 90 p.h.r. of clay (treated and untreated). The 400% modulus of treated clay is about 4.3 times higher than that of untreated clay. The rate of increment in the property with increasing concentration of filler was similar initially in both cases. However, after 30 p.h.r., the rate of increment for composites filled with treated clay was found to be substantially greater.

Young's Modulus

Young's modulus as a function of concentration of filler for treated and untreated clay filled PBR composites is shown in *Figure 5*. The peak value for treated clay composites was found to be 2.30 MPa at 90 p.h.r. and that for untreated clay is 0.58 MPa at 80 p.h.r., *i.e.* the Young's modulus of treated clay is about 4 times higher than that of untreated clay composites.

PBR-Clay Interaction

A mechanism[1–14], of PBR-clay interaction due to the incorporation of Si-69® into clay-filled PBR is proposed in the following two steps. Step 1: the condensation of silane coupling agent (Si-69®) with the surface hydroxyl groups of the filler *via* its silanol groups; and Step 2: the reaction of this with the unsaturation backbone of the PBR as set out below (*Scheme 1* and *2*).

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

SEM of Composites

The micrographs of fractured surfaces of untreated and treated clay-filled vulcanisates at 1000 × magnification are shown in *Figures 6* and *7*. The fractured surface of the composites filled with untreated clay showed a non-adhesive appearance and the formation of agglomerates, while that filled with treated clay showed a uniform distribution, with an adhesive appearance of the fractured surface indicating the enhancement in polymer-filler attachment.

Hardness

Figure 8 shows the dependence of hardness on concentration of treated and untreated

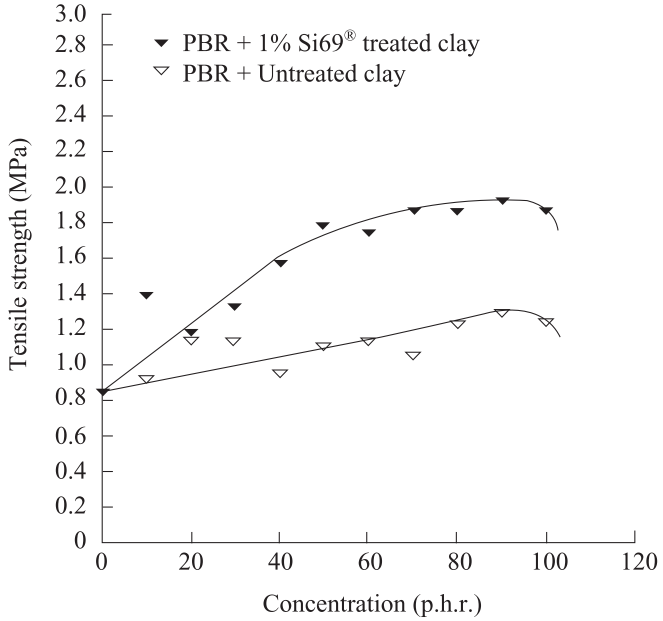


Figure 2. Tensile strength as a function of the volume fraction of treated and untreated clay-PBR composites.

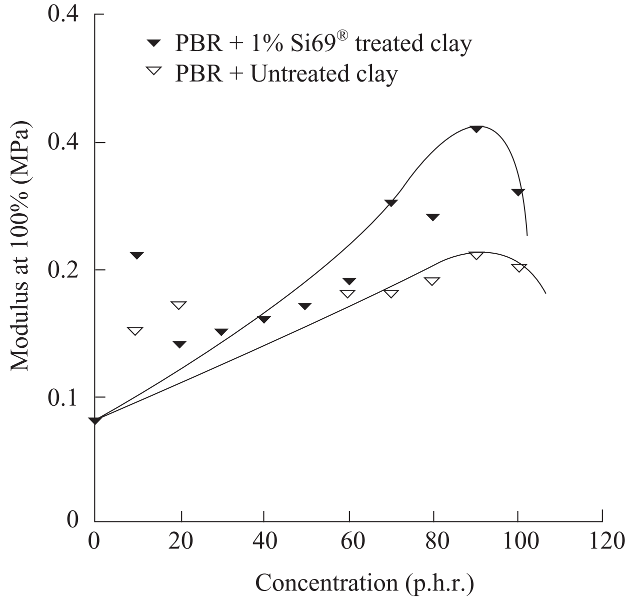


Figure 3. Modulus at 100% as a function of volume fraction of treated and untreated clay-PBR composites.

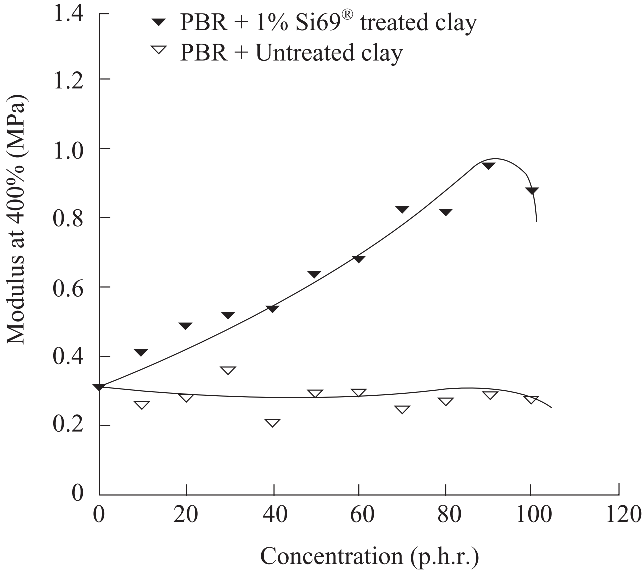


Figure 4. Modulus at 400% as a function of volume fraction of treated and untreated clay-PBR composites.

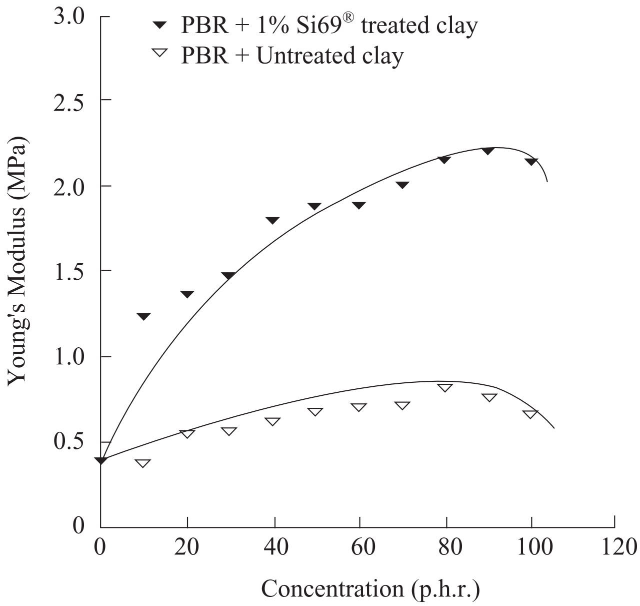
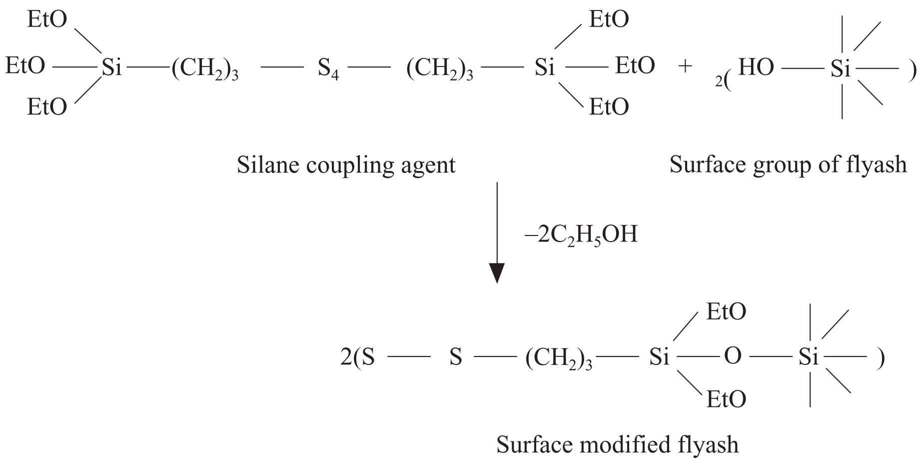
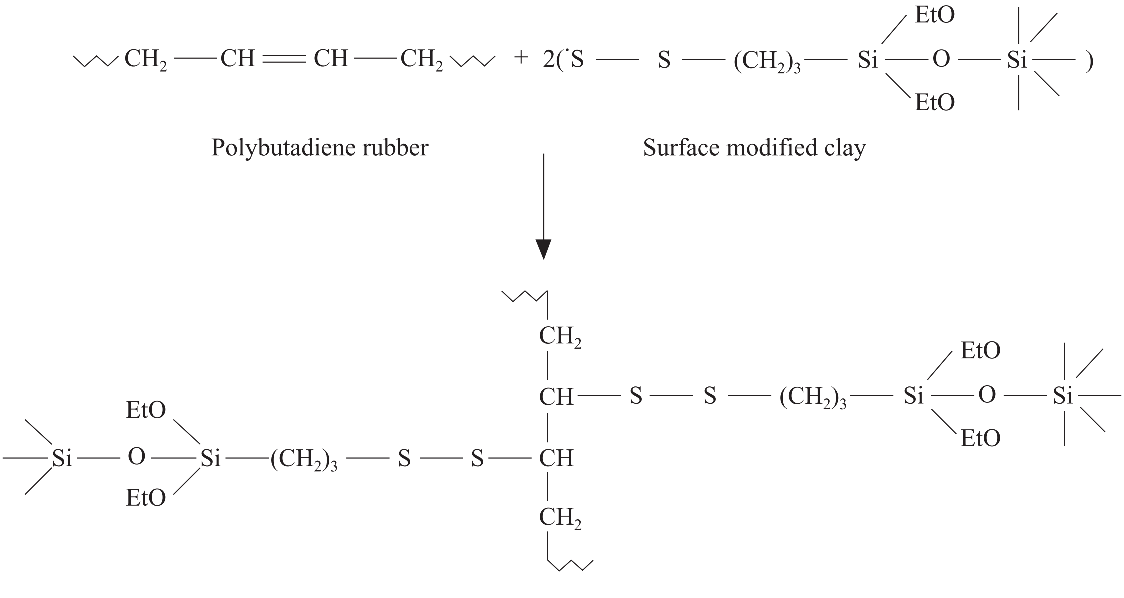


Figure 5. Young's Modulus as a function of volume fraction of treated and untreated clay-PBR composites



Reaction between coupling agent and clay surface.

Scheme 1



Reaction between surface modified clay and unsaturation in PBR.

Scheme 2

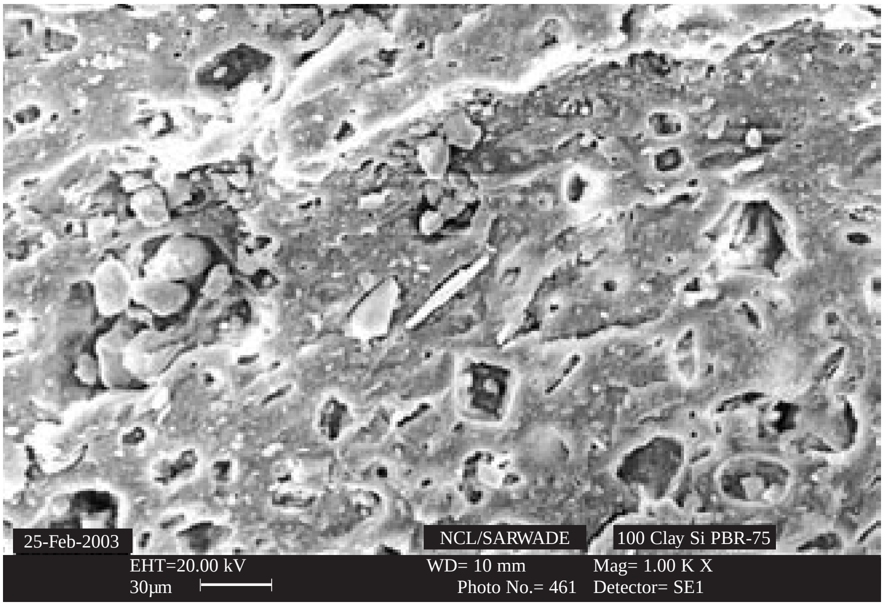


Figure 6. SEM (at 1000 × magnification) of untreated clay-PBR composite (at 100 p.h.r. filler).

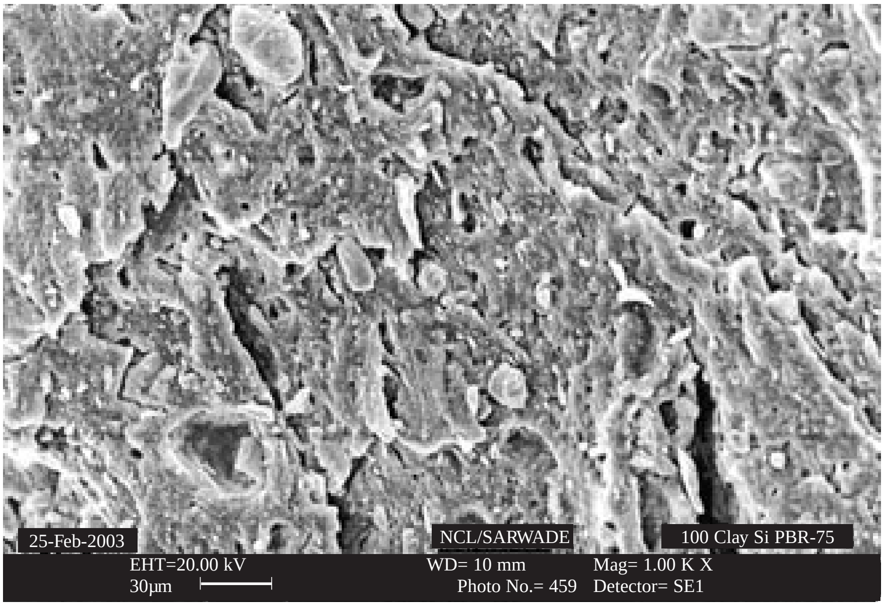


Figure 7. SEM (at 1000 × magnification) of silane treated clay-PBR composite (at 100 p.h.r. filler).

fillers in PBR. It is evident that, hardness of both treated and untreated clay-PBR composites increased linearly on increasing the concentrations of fillers, with a constant rate of increment for composites containing treated and untreated fillers (separately) as indicated by virtually identical slopes of the lines.

CONCLUSIONS

The treatment of clay with Si69® coupling agent [Bis (3-triethoxysilylpropyl) tetrasulphide] has significantly increased tensile strength, modulus at 400% elongation and Young's modulus in PBR. The filler treatment was shown by SEM study to be beneficial by enhancing polymer-filler adhesion. Considering the cost of the filler and the improvement in properties, the treatment is recommended.

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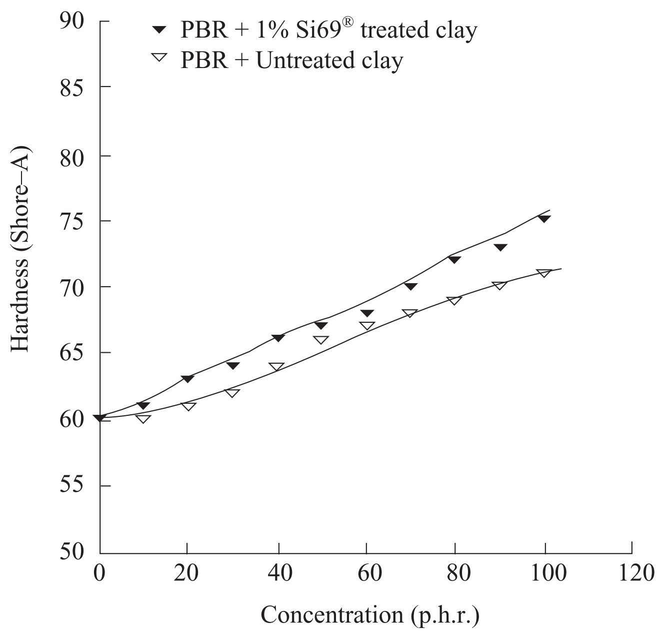

Figure 6. Hardness as a function of volume fraction of treated and untreated clay-PBR composites.

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